THE FRIEDEL CRAFTS REACTION OF SULFUR AND OXYSULFUR CHLORIDES WITH AROMATIC COMPOUNDS

Thesis for the Degree of Ph. D.
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THE FRIEDEL CRAFTS REACTION OF SULFUR AND OXYSULFUR CHLORIDES WITH AROMATIC COMPOUNDS

By

Charles Earl Villars

A THESIS

Submitted to the School for Advanced Graduate Studies
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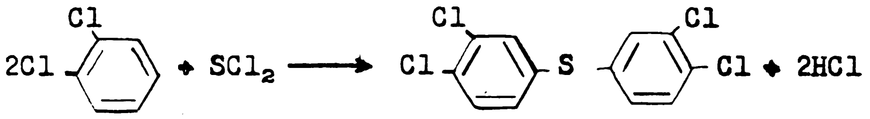
ABSTRACT

This study deals with an investigation of the Friedel Crafts reaction of the sulfur and oxysulfur chlorides with aromatic compounds. It was originally undertaken to investigate the potentialities of sulfur dichloride (SCl_2) as a coupling agent. When the initial investigation began to show good progress it was expanded to include analogous reactions with sulfur monochloride (S_2Cl_2), thionyl chloride ($SOCl_2$) and sulfuryl chloride (SO_2Cl_2). Chlorinated benzenes were selected for the majority of the coupling reactions and are illustrated by reaction (1) using o-dichlorobenzene and sulfur dichloride.



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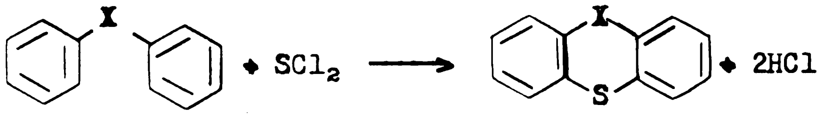
Ring closure reactions with diphenyl sulfide, diphenyl ether and diphenyl methane type compounds (reaction 2) were also investigated.



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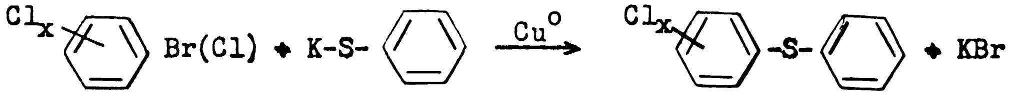
where X = O, S, or CH_2

The structures of the products obtained in these reactions were established by independent synthesis of the sulfides (reactions 3 and 4) and



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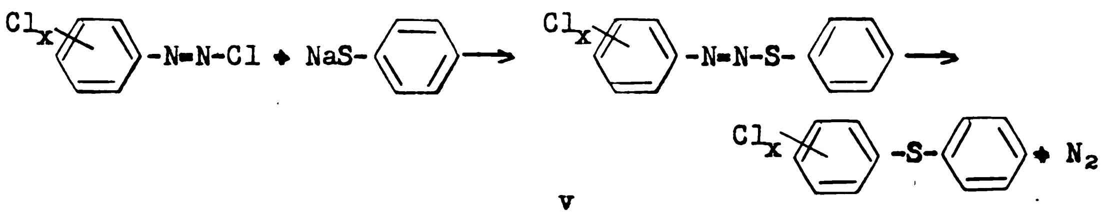

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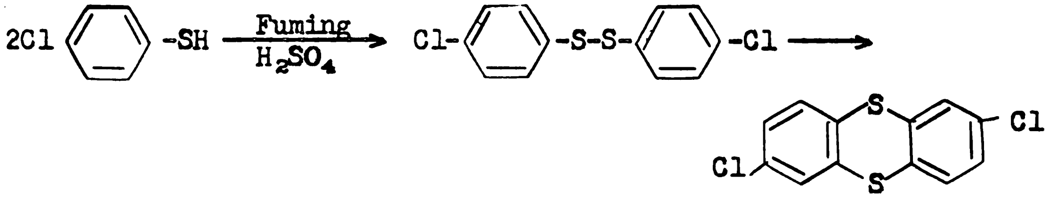
sulfones, and by ring closure reactions involving thiophenols with sulfuric acid (reaction 5).



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Structure proofs were further supplemented by interpretation of infrared spectra of the compounds. The oxidation state of the sulfur in such compounds was found to affect the hydrogen out of plane absorption peaks exhibited by the sulfide in a characteristic manner for each type of substitution. The synthesis of thiophenols by the lithium aluminum hydride reduction of xanthate esters and sulfonyl chlorides was also investigated.

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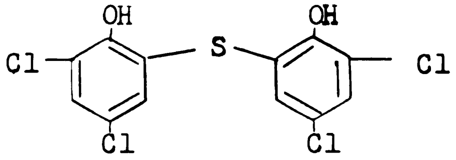
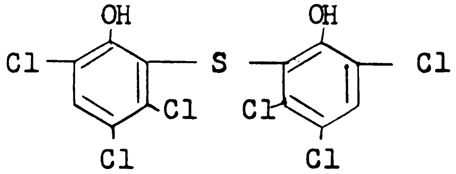
INTRODUCTION

The present investigation had its origin in a study of the preparation of 2,2'-thiobis(4,6-dichloro)phenol. This material



is an effective germicide[1,2,3] and has been offered commercially under the trade names of Actamer, Phenabis, Lorothiol and others in competition with Hexachlorophene, a chlorinated methylene



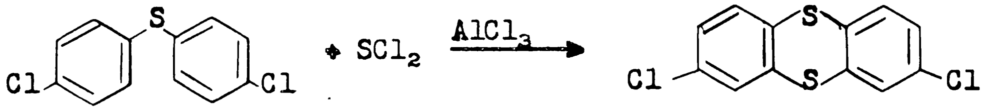
bisphenol, used in soaps, baby powders, hand lotions etc. Process studies on the condensation of 2,4-dichlorophenol with sulfur monochloride and sulfur dichloride to produce the thiobisphenol revealed a number of interesting facts concerning the two reagents. Namely, that when sulfur monochloride was used the product was heavily contaminated with elemental sulfur and that both sulfur chlorides were very reactive coupling agents in the presence of Friedel Crafts catalysts. It was found that normally non-reactive solvents such as chlorobenzene and o-dichlorobenzene reacted sufficiently in the presence of 2,4-dichlorophenol to make them unsatisfactory as solvents for the reaction. In reviewing the literature to determine the possible products resulting from these side reactions it was found that while some work had been done[4,5,6,7] there was considerable confusion in the literature concerning the products from chlorobenzene itself and the products from the higher chlorinated benzenes had not been studied. It was further discovered that very little use had been made of the reagent sulfur dichloride since it has generally been regarded, by most investigators, as a mixture since it is an unstable compound which dissociates into chlorine and sulfur monochloride and as a chlorinating agent since this is the basis for most of its industrial uses. In work with this material it was found that under suitable conditions it was a highly effective coupling agent with a minimum of interference from the side reaction of chlorination.

The reaction of the sulfur chlorides with benzene derivatives, primarily the chlorides, lead both to the formation of sulfides and thianthrenes. Both of these types of compounds immediately raised the question of isomer constitution which could not be evaded. The solution to those questions took various forms depending upon the particular structure involved. Many of the sulfone derivatives had been previously prepared by the condensation of benzene sulfonyl chlorides with benzene derivatives and were described in the literature[8,9] so that oxidation of the sulfides often gave a simple structure proof. A method was developed to prepare sulfides by the condensation of thiophenols with bromochlorobenzenes or higher chlorinated benzenes which was also useful for the preparation of intermediates required for ring closure reactions.

An effort was made to use the diazo condensation method[10,11,12,13] with thiophenols but in the initial experiment an inherent danger in the method from undecomposed intermediates prompted some effort in working out a more satisfactory technique for conducting this type of experiment in a safer manner. Some use was made of the sulfuric acid ring closure of thiophenols to thianthrenes[14,15,16,4,17] and the method was extended in one case to the ring closure of a disulfide to obtain specific thianthrene derivatives. However, it soon became apparent that the problem of structure proof by independent synthesis was going to be a major effort for which a simpler method would have to be found. Fortunately an interest in using infra-red spectra as an investigation tool led to the collection of spectra and identification of the simpler homologs using the hydrogen out of plane vibration peaks in the region of 11-15 microns. Spectra of the sulfoxides and sulfones were also collected as a matter of interest and when the spectra became complicated in cases of higher substitution it was discovered using the spectra catalog that conversion of the sulfide to the sulfoxide and the sulfone modified the substitution bands (hydrogen out of plane vibrations) in a characteristic manner so that it was possible to definitely characterize isomers by a comparison of the spectra of the sulfide and sulfone of a particular isomer. A discussion of this effect and a partial catalog of related spectra has been included in the appendix of this thesis.

Some effort was made to extend the condensation method (sulfur chloride coupling) to other benzene derivatives and heterocyclics with varying success. The use of thiophenols in a number of places prompted lithium aluminum hydride reductions of xanthate esters and benzene sulfonyl chlorides in an attempt to extend recent work[18] with that reagent.

The ring closure of diphenyl sulfides with sulfur dichloride to thianthrenes was studied with considerable emphasis on the ring closure of diphenyl sulfide to thianthrene in an attempt to outline



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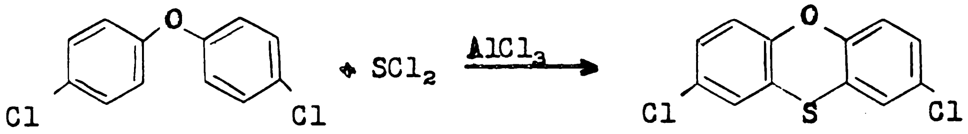
the proper conditions (i.e. mole ratios of reactants and catalyst) for effective ring closure. Phenoxathiin and 2,8-dichlorophenoxathiin



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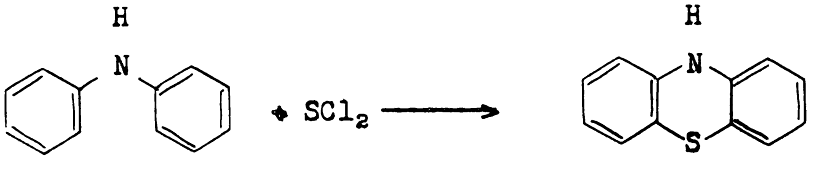
were likewise prepared from diphenyl oxide and bis(4-chlorophenyl) ether respectively. It had been planned originally to work with the ring closure of diphenyl amines with sulfur dichloride to phenothiazines



(3)

but the area under investigation proved to be so large that this had to be left to a future investigation.

During the course of this investigation it was realized that using thionyl chloride and sulfuryl chloride as the coupling agent would lead to new isomers and better preparative methods in some cases. Hence, related studies were carried out with these reagents. As a consequence the initial purpose of studying the sulfur chlorides in the Friedel Crafts reaction was enlarged to include the oxychlorides to some extent.

The nature of the problems encountered in the structure proof of the products necessitated the use and study of several synthetic methods as well as constant studies of the products by means of their infra-red spectra. Some of the problems involved in the use of these reagents have been well illustrated in some of the reactions studied and others have been pinpointed for future investigations.

In conclusion it is quite possible that a number of the compounds prepared, for the first time in these studies, may possess biological activity. Woodward and Mayer[19] reported that a number of aromatic sulfides were synergists for nicotine and nicotine compounds used as insecticides. March, Metcalf and Lewallen[20] reported that 2,4,2',4'-tetrachlorodiphenyl sulfide was a synergist for DDT. Deonier, Jones and Holler[21] reported effective destruction of mosquito larva with the bis(4-chlorophenyl) sulfide, sulfoxide and sulfone. The 4-chlorophenyl phenyl sulfide and sulfoxide as well as the analogous bromo derivatives were reported by Bender[22] to be active as insecticides. The bis(4-chlorophenyl) sulfone was reported by Langer, Martin and Muller[23] to be active as an insecticide. Olah and Pavloth[24] report that the fluorinated diphenyl sulfides, sulfoxides, and sulfones have a prompter but less durable effect than the chloro derivatives as insecticides. Huismann, Uhlenbroek and Meltzer[9] prepared a number of the higher chlorinated diphenyl sulfides, sulfoxides, and sulfones indirectly by the condensation of nitrochlorobenzenes with thiophenols and found a few of these possessed strong acaricidal properties with the total absence of phytocidal side effects and toxicity for warm blooded animals.

Utility of the chlorinated diphenyl sulfides has been claimed by Clark[25] as insulating and dielectric compositions (for transformers) and as additives for lubricants.

HISTORICAL

Friedel Crafts reactions of sulfur halides and oxyhalides are not particularly well-known. Krebaum[26] mentions about fifteen references using sulfur monochloride as a condensing agent with aromatics in his seminar on that reagent. A search of Chemical Abstracts for examples of coupling reactions using sulfur dichloride disclosed only six references. Machell in his review on thionyl chloride[27,28] includes condensations of that reagent under reactions with phenolic compounds and miscellaneous reactions giving in all seven references. The review on sulfuryl chloride by Brown[29] mentions the formation of sulfones only as a by-product of the sulfonation of aromatic compounds.

The chlorinated benzenes were chosen specifically for the majority of condensation reactions in this study. A supply, in research quantities, of all of the possible compounds of this family was available and a study of known coupling compounds indicated that they would have physical properties making them amenable to easy experimental handling. The choice of a single type of substitution would keep the number of possible isomers at a minimum and in addition very few of the products of these condensation reactions were known. A literature search on the chlorinated diphenyl sulfides revealed that of approximately 170 possible compounds of that series only nine had been prepared and characterized. Four of the analogous sulfoxides and fifteen of the sulfone compounds were found to have been previously recorded.

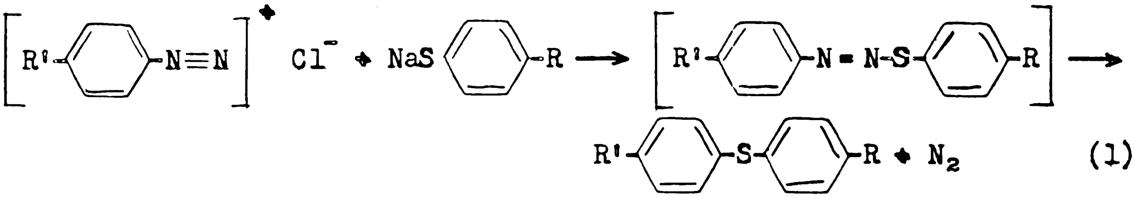
The formation of diphenyl sulfides by the condensation of a metal salt of a thiophenol with a halogenated benzene is not a new reaction.

The displacement of "activated" chlorines such as those found in the chlorinated nitrobenzenes has found widespread use in synthesis as attested by its frequent appearance in the literature.[30,31,32,33,34,35,18,36] The activity of the halogens in these compounds is such that the reaction will take place in refluxing alcohol without a copper catalyst. Other chlorines activated by electron withdrawing groups such as that found in chlorinated benzoic acids[25] or chlorinated acetophenones require a fusion procedure in the presence of a copper catalyst at approximately 200°C. to bring about the condensation reaction. The reaction of iodobenzenes with alkali thiophenates is well-known and occurs at relatively low fusion temperatures[37,38,39,40,41,42,43] but it has the disadvantage that the iodo compounds are not readily available nor are they inexpensive. The use of bromobenzenes for the condensation reaction has been only occasionally employed although their use with metal salts of phenols to form diphenyl oxides has been common practice.[44,37,45,35]

Graebe and Schultess[46] allowed the potassium salt of thiosalicylic acid methyl ester to react with bromobenzene to obtain a 50% yield of 2-phenyl mercaptomethyl benzoate. The lead salt of thiophenol was allowed to react with 4-bromophenyl phenyl sulfide, by Bourgeois and Fouassin,[47] to obtain 1,4-bis(phenylmercapto)benzene. These investigators also treated the lead salt of p-toluenethiol with p-dibromobenzene[48] to obtain the dimethyl derivative of that compound. Other studies with lead salts of mercaptans have been reported by Bourgeois[49] and Kraft and Bourgeois.[50] Robert and Smiles[41] allowed potassium thiophenoxide to react with 2-carboxy-3,4-dimethoxybromobenzene to obtain 2-carboxy-3,4-dimethoxyphenyl

phenyl sulfide but reported no specific yield for this reaction. There were no examples of this type of reaction found in the literature, except for the nitrochlorobenzenes, which did not require higher reaction temperatures and a copper catalyst for the condensation reaction to occur. A thorough search of the literature revealed no other examples for the condensation reaction with bromobenzene and no condensation reactions of a chlorobenzene where the chlorine was not activated by the presence of a nitro, carboxy or an ester group in the ortho or para position of the aryl ring.

The reaction of an alkali thiophenate with a diazotized aromatic amine (1) to form diphenyl sulfide derivatives has been employed by


(1)

Italian investigators[10,12,51,13] to prepare five of the possible chlorinated diphenyl sulfide isomers. An informative discussion of the reaction appears in the patents of Johnson[52,53] who employed this reaction to prepare phenylmercapto phenols. Wisner and Krollpfeiffer[11] used this same experimental procedure to prepare 4-tolyl-4'-chlorophenyl sulfide. Stadler[54] mentions the explosive nature of the diazointermediate involved in this reaction. Ziegler[55] found this difficulty in working with the analogous reaction using alkali phenates. Hodgson and Foster[56] condensed zinc complexes of diazonium salts with phenol and reports that the diazonium intermediate was so stabilized by a nitro group that it did not evolve nitrogen until temperatures of 130-140°C. were reached.

The use of sulfur chlorides and oxychlorides in thiophene chemistry has been relatively limited. The work described by Kroft[36,57,58] in three patents is notable. In the first[36] sulfur monochloride is condensed with an excess of thiophene in the absence of a catalyst to obtain a disulfide which is subsequently reduced to 2-thiophenethiol with zinc. The thiophenethiol was characterized by condensation with 2,4-dinitrochlorobenzene to form the solid 2-thienyl-2,4-dinitro phenyl sulfide. The second patent[58] deals with the destructive distillation of the disulfide, described above, to obtain bis(2-thienyl) sulfide. This was converted to bis(2-thienyl) sulfone by oxidation with hydrogen peroxide in glacial acetic acid. Finally Kroft[57] describes the condensation of sulfur monochloride with a large number of thiophene derivatives in the absence of a catalyst using equimolar quantities of the two reagents to obtain polysulfide resins.

Dann and Moller[59] describe the reaction of acetamidothiophene with sulfur mono- and dichloride to obtain bis(5-acetamido-2-thienyl) disulfide and bis(5-acetamido-2-thienyl) sulfide respectively.

The oxidation of sulfides to sulfoxides and sulfones has a widespread recordance in the literature. The most general procedure employed for the preparation of sulfoxides is the addition of the theoretical amount of 30% hydrogen peroxide to a solution of the sulfide in glacial acetic acid[60,61,62,63,64,9] or acetone[65] and isolation of the oxidation product after the reaction mixture has been set aside at room temperature for one to ten days. Bergmann and Tschudnowsky[64] prepared 4-chlorophenyl phenyl sulfoxide, bis(4-chlorophenyl) sulfoxide, and thianthrene disulfoxide in this manner with an oxidation period of one day. Shriner, Struck and Jorison[65] prepared dibenzyl sulfoxide (83% yield) in acetone using a two day oxidation period of dibenzyl sulfide. The 2,4,5-trichlorophenyl phenyl sulfoxide and 2,4,5-trichlorophenyl-4'-chlorophenyl sulfoxide were prepared[9] (76 and 67% yield respectively) by oxidation of the appropriate sulfide in acetic acid using a 10 day reaction period. Sulfoxides have also been prepared from sulfides using other oxidizing agents such as nitric acid,[66,67,68] chromic acid,[69] hot aqueous potassium permanganate[67,70] and perbenzoic acid.[71]

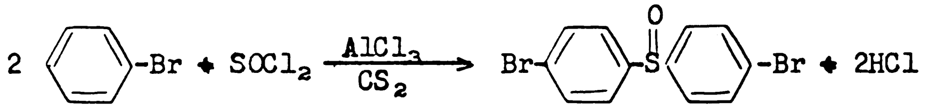
Sulfones have been obtained by the oxidation of sulfides and sulfoxides using excess peroxide. One of the better procedures is that of Michaels and Amstutz[72] (85-95% yield) who added all of the peroxide at once and warmed the reaction mixture to a temperature just below the point of bubble formation. Dibenzyl sulfide was oxidized to the sulfone, by this procedure, in an 83% yield after being set aside two days in acetone. Balasubramanian and Baliah[40] obtained a 60% yield of bis(5-acetamido-4-chloro-2-methylphenyl) sulfone from the sulfide after an oxidation period of two days at room temperature. Alkyl phenyl sulfides were oxidized to the sulfones by Ipatieff and Friedmann[73] using a large excess of peroxide in acetic and heating the oxidation mixture until all the water and acetic acid had evaporated and vapor of the distillate no longer bleached blue litmus when held over the reaction vessel. Many other examples of this type of oxidation abound in the literature.[30,33,65]

Szmant, Sedegi and Dudek[74] oxidized 10-thiaxanthenone to 10-thiaxanthenone-5,5-dioxide and 4,4'-(phenylmercapto) benzophenone to 4,4'-(benzenesulfonyl) benzophenone using peracetic acid.

Sulfides and sulfoxides have been oxidized to sulfones in acetic acid using potassium permanganate[40,34,78,42] or chromic acid.[76,75,65] Compounds containing aryl ring substituted alkyl groups are not attacked by potassium permanganate using the procedure of Bost, Turner and Norton[34] but alkyl side chains are oxidatively attacked by chromic acid.[76,77,75]

Similar oxidative procedures are applicable if the sulfide or sulfoxide link is part of a heterocyclic nucleus as in thianthrene[64,4] phenoxathiin[33] or phenothiazine.[72]

Condensation reactions with thionyl chloride are different from sulfur mono- and dichloride in the respect that they can give rise to the sulfoxide and frequently give the sulfide and chlorinated diphenyl sulfides. A variety of products[28] were obtained with phenols depending upon the reaction conditions employed. Benzene and toluene yielded the sulfoxide but further action of thionyl chloride on diphenyl sulfoxide at elevated temperatures yielded bis(4-chlorophenyl) sulfide.[78] Bromobenzene[79] (2) and fluorobenzene[37] (72% yield) gave



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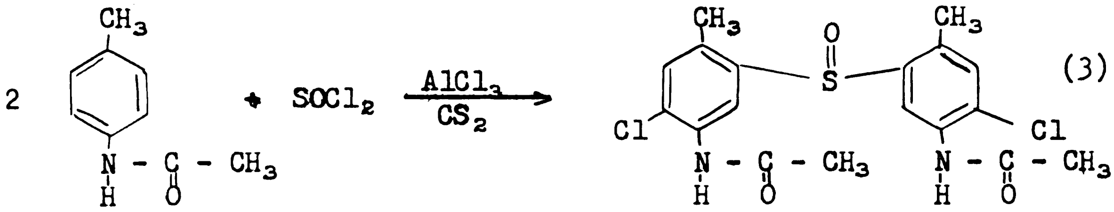
the respective sulfoxides but no record in the literature was found of the condensation of a chlorinated benzene compound with this reagent. The reaction of m-chlorotoluene with thionyl chloride gave a 57% yield of bis(4-chloro-2-methylphenyl) sulfoxide.[40] Acetanilide[80] gave bis(4-acetamidophenyl)sulfoxide and aceto-m-toluidide[40] gave an 81% yield of bis(4-acetamido-2-methylphenyl) sulfoxide. Aceto-p-toluidide, however, gave the chlorination product bis(5-acetamido-4-chloro-2-methylphenyl) sulfoxide[40] (3) in a 44% yield without



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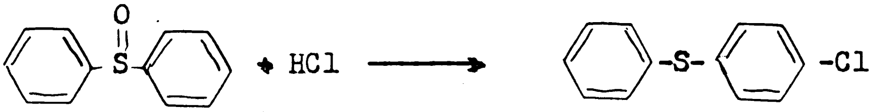
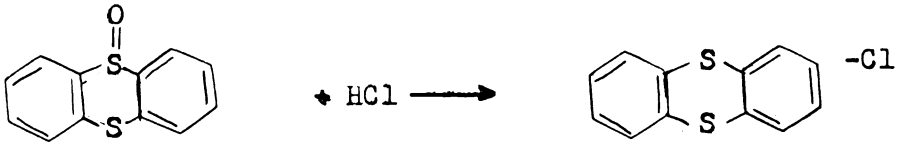
the further conversion of the product to the sulfide. The ring closure reaction of diphenyl amine[81,82,83] with thionyl chloride (under reflux) yielded 1,3,7,9-tetrachlorophenothiazine.

The citation reactions of sulfoxides with excess thionyl chloride or with hydrogen halides to obtain halogenated products are common in the literature. Loth and Michaelis[78] allowed diphenyl sulfoxide to react (4) with thionyl chloride to obtain 4-chlorophenyl phenyl sulfide.



(4)

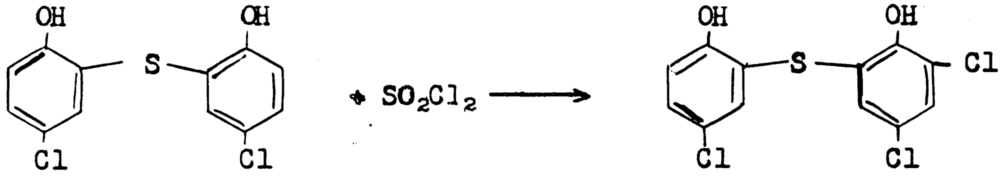
Gilman and Swayampati[84] found that hydrogen bromide converted thianthrene-5-oxide to 2-bromothianthrene but that thianthrene-5,5-10-trioxide was only converted to thianthrene-5,5-dioxide. Fries and Vogt[85] converted thianthrene-5-oxide to 2-chlorothianthrene by reaction with hydrogen chloride. (5) N-alkyl phenothiazine monoxides[86,87] have also been shown



(5)

to undergo a similar reaction. Massie discusses the halogenation of phenothiazine by this method in his review[88] and states that the best results are obtained with hydrogen chloride, while hydrogen bromide gives poorer results and hydrogen iodide fails to react. These general conclusions also depends somewhat on the nature and number of the substituents present in the phenothiazine molecule. The process of converting a sulfoxide to a sulfide with subsequent ring halogenation has been termed "reductive halogenation" by Paige and Smiles[89] and also by Gilman and Eisch.[87] Some insight into these various reactions may be obtained by studying the work of Bordwell and Pitt,[90] Fries and Vogt,[85] Schmalz and Burger,[86] Paige and Smiles,[89] and Gilman and Eisch.[87] These investigators studied various reactions of this general type and have proposed some possible mechanisms to explain the various courses taken by these reactions. These will be considered in more detail in the discussion part of this thesis.

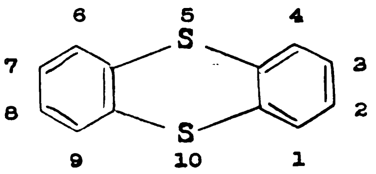
Sulfuryl chloride is relatively unknown as a sulfonating and coupling agent for aromatic compounds. The review by Brown[29] mentions only the work of Tohl and Eberhard[91] who recommended the addition of small quantities of aluminum chloride to a cooled reaction mixture of sulfuryl chloride and the hydrocarbon to effect sulfonation. They also obtained small quantities of sulfones as by-products in the sulfonation with sulfuryl chloride. With molar quantities of aluminum chloride as catalyst Boeseken[92] obtained a mixture of the sulfonyl chloride, sulfonic acid and large quantities of chlorinated material from the interaction of sulfuryl chloride with hydrocarbons. The work of Silberrad is instructive since he found that halogen carriers such as sulfur, iodine and aluminum chloride when used with sulfuryl chloride bring about chlorination of the benzene ring at relatively low temperatures[93] and that a catalyst mixture of aluminum chloride and sulfur monochloride effects chlorination rapidly and smoothly in the cold.[94] Cutler[95] found that sulfuryl chloride chlorinated 2,2'-thiobis(4-chloro) phenol at 15°C. in the absence of a catalyst to obtain an unsymmetrical product (6).



(6)

Kharasch and Read[96] found that it was possible to obtain sulfonation of aromatics, in low yields without sulfone formation, by the use of sulfuryl chloride, in a reaction occurring by a free radical mechanism.

In the thianthrene series only four of the structures of the chlorinated isomers had been definitely established. Thianthrene is the name currently used for the ring system, (I), by Chemical Abstracts. The older nomenclature employs such names as di-o-phenylene disulfide, diphenylene disulfide, and benzo-1,4-thiin. The alternate numbering system, (II), is found in the early literature. Gilman and Swayampati[97]



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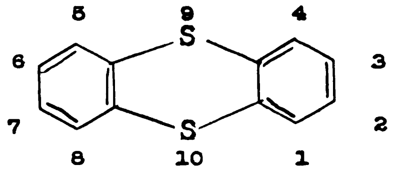


(II)

prepared 1-chlorothianthrene (m.p. 85-85.5°C.) from the corresponding amino analog and its tetroxide was reported to melt at 242°C. Fries and Vogt[85] prepared 2-chlorothianthrene (m.p. 84°C.) by heating thianthrene-5,5-dichloride. Preparation of 2-chlorothianthrene tetroxide is claimed by Kozlov, Fruktova and Shemyakima[98] who sulfonated thianthrene tetroxide, heated the potassium sulfonate with phosphorus pentachloride and oxychloride to obtain a 78% yield of a chlorothianthrenedisulfone which melted at 120°C. This product was claimed to be identical with that prepared from β-chlorothianthrene. The melting point is completely out of order, however, with other similar isomers.

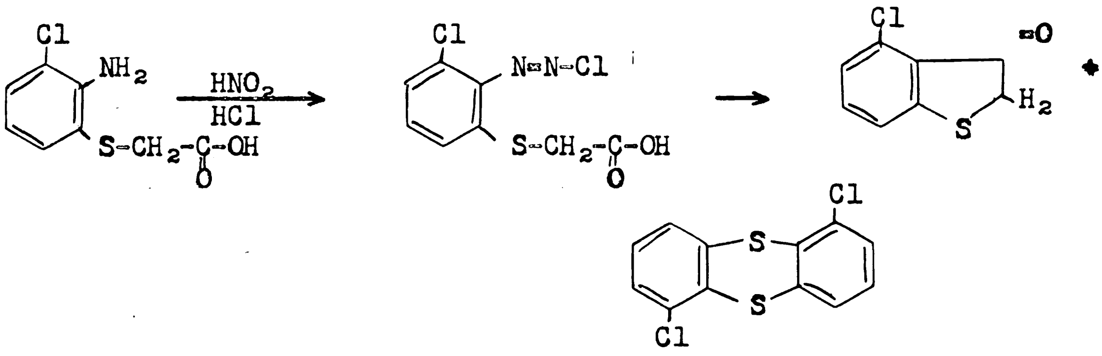
Fries and Vogt[85] prepared a dichlorothianthrene, which melted at 171°C., by the chlorination of 2-chlorothianthrene, or by treatment of the monosulfoxide of chlorothianthrene with hydrogen chloride and also by the condensation of chlorobenzene with sulfur monochloride. Although these investigators mentioned the monoxide of this material it was not characterized by them. Thus, the 1-chlorothianthrene-5,5,10,10-tetroxide of Gilman and Swayampati[97] is the only definitely characterized oxide of the monochlorothianthrenes.

Ray[5] condensed chlorobenzene with sulfur monochloride in the presence of an aluminum-mercury couple to obtain what he termed an isomeride melting at 147°C. The tetroxide of this material had a melting point above 225°C. He further claimed the isolation of an intermediate condensation product which was moisture sensitive.

Baw, Bennet and Dearns[4] prepared the 2,7-dichlorothianthrene (m.p. 181.5°C.) by a ring closure reaction of 4-chlorobenzenethiol with sulfuric acid. The tetroxide of this material melted at 293°C. (305°C. corr.).

They also repeated the condensation of chlorobenzene with sulfur monochloride (originally performed by Fries and Vogt[85]) to obtain a material heavily contaminated with sulfur. They submitted the material to several purification treatments and finally obtained a crystalline material melting at 180-181°C. which was not depressed on admixture with the 2,7-dichlorothianthrene obtained from 4-chlorobenzenethiol as a starting material. They stated that it was doubtful that Fries and Vogt[85] had isolated the 2,8-dichlorothianthrene since the other product isolated was the bis(4-chlorophenyl) sulfide. In connection with their stereoisomerism studies Baw, Bennet and Dearns[4] also prepared all of the possible oxide isomers of the 2,7-dichlorothianthrene.

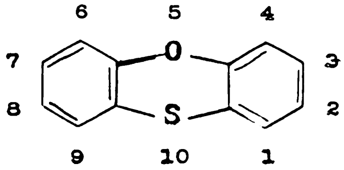
Dalgish and Mann[99] prepared 1,6-dichlorothianthrene (m.p. 174-5°C.) as a by-product in the preparation (7) of 7-chlorothiondoxyl from 5-chloro-3-keto-3,4-dihydro-1,4-benzothiazine.



(7)

They did not prepare any of the oxides of this compound.

The chemistry of phenoxathiin has been reviewed by Deasy.[100] The compound has also appeared under such names as penoxthiin, phenothioxin, dibenzothioxin and dibenzo-1,4-dioxathiin. The numbering system, I, is currently used by Chemical Abstracts but other systems (II and III) are also found in the early literature.



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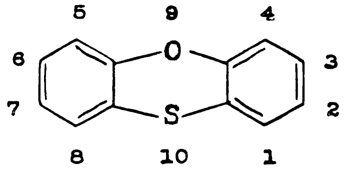

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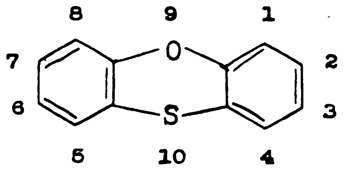
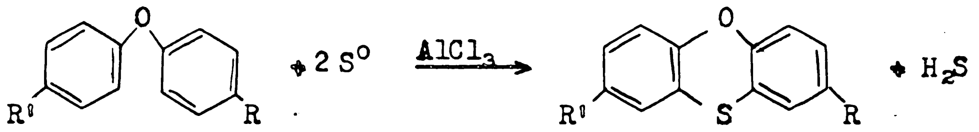


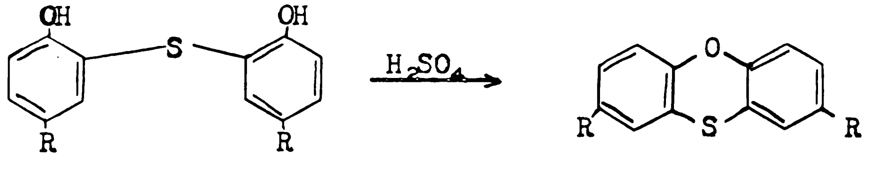
(III)

The ring closure of diphenyl ethers with sulfur (8) to obtain phenoxathiins



(8)

has been named the "Ferrario" reaction and it has been studied by several investigators.[101,44,33,102] Suter and Green[44] used a ratio of 1.3 moles of the ether to 1.0 mole of sulfur and 0.5 mole of aluminum chloride. They stated that the yield of phenoxathiin was higher when the directive influence of the ether oxygen and the substituent group coincided. Hilditch and Smiles[103] prepared substituted phenoxathiins by the ring closure (9) of substituted thiobisphenols to phenoxathiins using

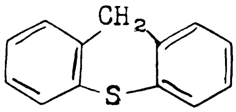


(9)

concentrated sulfuric acid as the dehydrating agent. The literature contains no record of the ring closure of a diphenyl ether with a sulfur chloride or oxychloride.

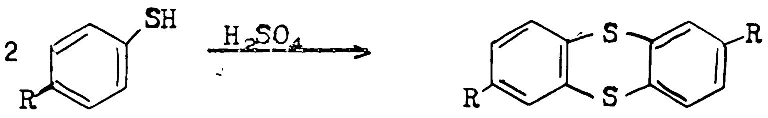
The ring closure reaction of diphenyl amine with sulfur dichloride to yield phenothiazine as studied by Holzmann[104] is rather unique in that no Friedel Crafts catalyst was used by the author to effect the condensation. Instead excess amine was used as the acid acceptor. Zerbe[105] claimed coupling between two phenothiazine molecules to obtain a nitrogen-sulfur-nitrogen cross link molecule using sulfur mono- and dichloride. These were the only references concerning this ring closure reaction until recently when three articles by Fujimo[81,82,106] appeared in the literature describing the reaction of diphenyl amine with thionyl chloride to obtain a ring closure product and chlorination simultaneously.

The heterocylic, thiaxanthene, is a comparatively rare nucleus.



Although a rather considerable amount of information dealing with the chemistry of its derivatives appears in the literature there are no review articles on thiaxanthene at the present time and no mention of it was found in heterocylic texts. The most general preparation of the molecule is made through 5-thiaxanthenone. This can be prepared by the condensation of thiosalicylic acid with benzene using concentrated sulfuric acid as the condensing agent (85% yield)[107] or from diphenyl sulfide by ring closure with phosgene in the presence of aluminum chloride.[74] The 5-oxide has been reduced to thiaxanthene using phosphorus and hydrogen iodide,[46] or with lithium aluminum hydride[108] in yields of 78%. The high temperature treatment of 2-methylphenyl phenyl sulfide in a hot tube gave thiaxanthene.[46] No record of a direct ring closure of diphenyl methane with sulfur or any sulfur compound was found in the literature. The dismutation of thiaxanthydrol to give thiaxanthene and 5-thiaxanthenene upon heating has, however, been recorded.[109]

The ring closure of thiophenols to thianthrenes (10) using sulfuric



(10)

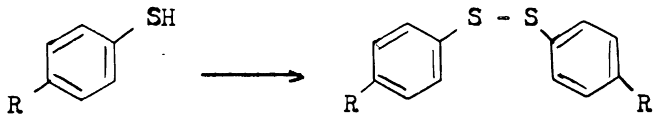
acid has not been employed extensively in the literature. The following table presents a summary of its use.

TABLE I

SULFURIC ACID RING CLOSURES OF THIOPHENOLS TO THIANTHRENES

Thiol Used	Moles of Thiol Used	H_2SO_4 Used (ml.)	Oleum Used (ml.)	Contact Time (hrs.)	Temp. (°C.)	Per- cent Yield	Refer- ence
m-Methoxybenzene	0.71	270	none	12	25	30	14
p-Methylbenzene	0.32	200	none	20	25	15	15
p-Methylbenzene	0.08	50	none	20	--	approx. 50	16
p-Chlorobenzene	0.18	185	100 (60%)	18	25	49	4
Benzene	0.045	--	none	24	25	approx. 20	17
Benzene	0.045	50 (mono- hydrate)	7.5 (40%)	--	--	10-20	16
3,5-Dichloro- 4-hydroxybenzene	--	--	--	--	--	10-20	16
2-Napthalene	0.03	50 (mono- hydrate)	7.5 (40%)	--	--	19	16

In addition to the ring closure of thiophenols Fries and Volk[16] mention the use of a disulfide and a disulfoxide for the ring closure reaction as well. They suggest that the ring closure proceeds from the thiophenol to the disulfide (11), disulfide to disulfoxide (12), disulfoxide to a hypothetical compound (13), hypothetical compound to thianthrenemonoxide (14) and finally to the thianthrene (15).



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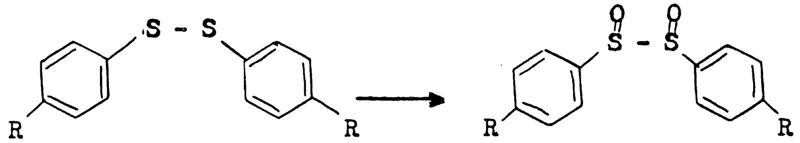

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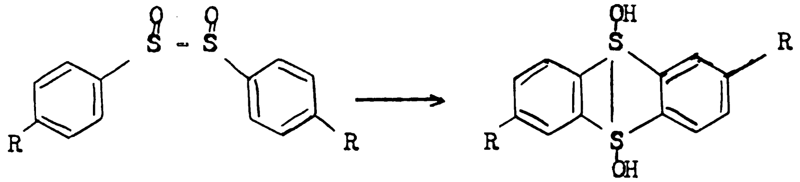

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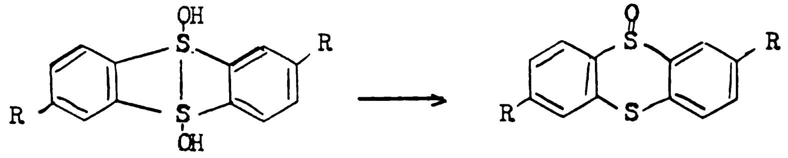

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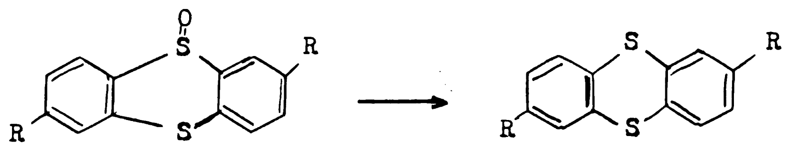
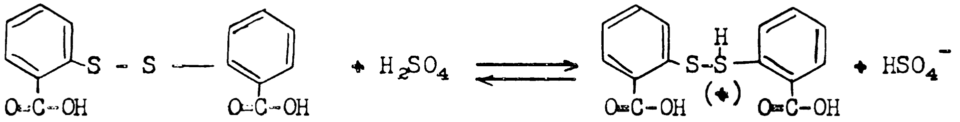


(15)

However the mechanism is not consistent with that of the more recent work by Suter and Archer[32] for the analogous condensations of thiosalicylic acid with benzene derivatives such as p-chlorotoluene and p-chloroanisole to form thiaxanthenones. The mechanism of these investigators also involves the disulfide but differs from there on in that it postulates protonation of the disulfide to obtain a reactive species which then attacks the benzene nucleus in the usual fashion of an electrophilic reagent (16-19).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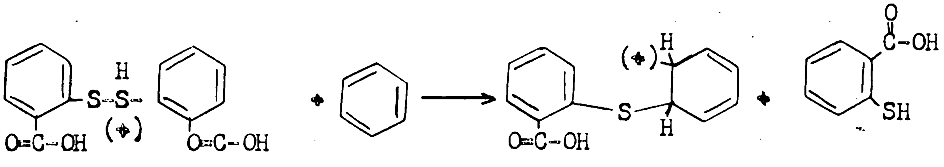
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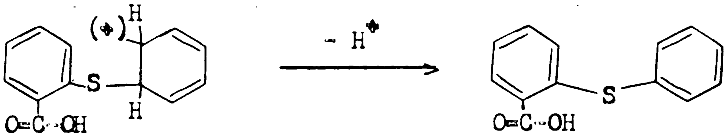
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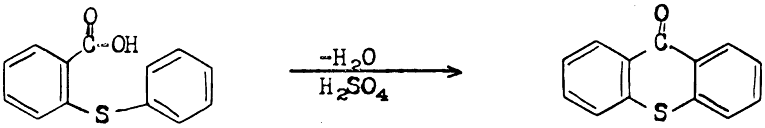
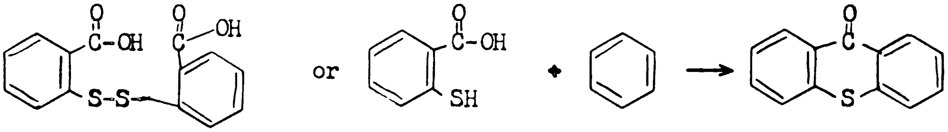
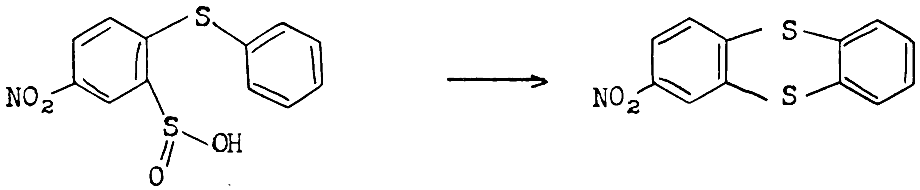

(19)

Related sulfuric acid condensations are found in the work of Prescott and Smiles[110] who studied the interaction of aromatic disulfides with benzene, toluene, anisole etc. Smiles and Marsden[111] synthesized thiaxanthenes from aromatic disulfides in this fashion while Smiles and Davis[112] studied the same ring closure using thiosalicylic acid (20).


(20)

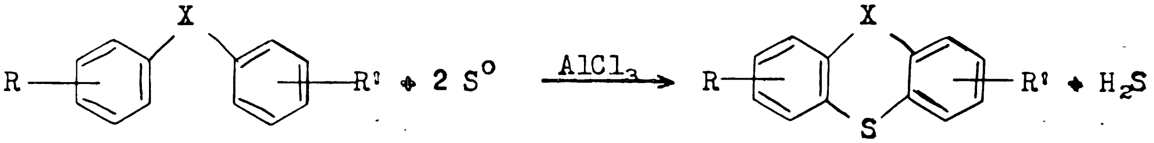
Hilditch[17] studied intermolecular condensations of aromatic sulfinic acids and aromatic disulfoxides in sulfuric acid. A ring closure[113] involving a diphenyl sulfide with an ortho sulfenic acid group to the thianthrene nucleus has been studied (21).



(21)

Recent work[114,115,116] has shown that free radicals exist in this media with these compounds.

Ring closures have been discussed briefly under the paragraphs on thianthrene, phenoxathiin, phenothiazine, thiaxanthene and sulfuric acid ring closure reactions. The formation of a heterocyclic ring (22)



(22)

using elemental sulfur as the ring closure agent is quite well-known. The reaction is known as the "Ferrario" reaction for the ring closure reaction of diphenyl ethers. Table II summarizes the present scope of the reaction where X represents oxygen. An attempt by Suter and Green[44] to form a second ring in the same molecule using 2-phenoxyphenoxathiin failed due to decomposition. They concluded from their study that a ring closure is favored by an excess of the ether and that the directive influence of the oxygen and the ring substituent affect the yield of the

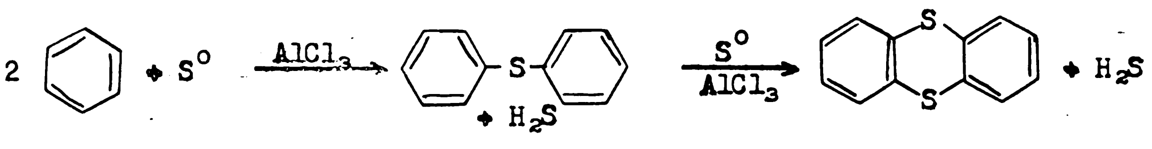
TABLE II

STATUS OF THE "FERRARIO" REACTION

Ether Composition		Product Obtained	Percent Yield	Reference
R	R'			
H	H	Phenoxathiin	74	33,44,101
H	2-Chloro	4-Chlorophenoxathiin	50	44
H	3-Chloro	3-Chlorophenoxathiin	71	44
H	4-Chloro	2-Chlorophenoxathiin	65	44,102
H	2-Methyl	4-Methylphenoxathiin	46	44
H	3-Methyl	3-Methylphenoxathiin	77	44
H	4-Methyl	2-Methylphenoxathiin	49	44
H	2-Methoxy	No reaction at 100°C.	0	44
H	4-Bromo	Tar	0	44,33
4-Bromo	4-Bromo	Tar	0	44,33

product. No examples of this ring closure reaction employing a sulfur halide or oxyhalide were found in the chemical literature.

In some cases where X is sulfur the ring closure reaction has been studied somewhat indirectly starting with benzene derivatives. Dougherty and Hammond[117] investigated the condensation of benzene with elemental sulfur (23) to obtain diphenyl sulfide and thianthrene.



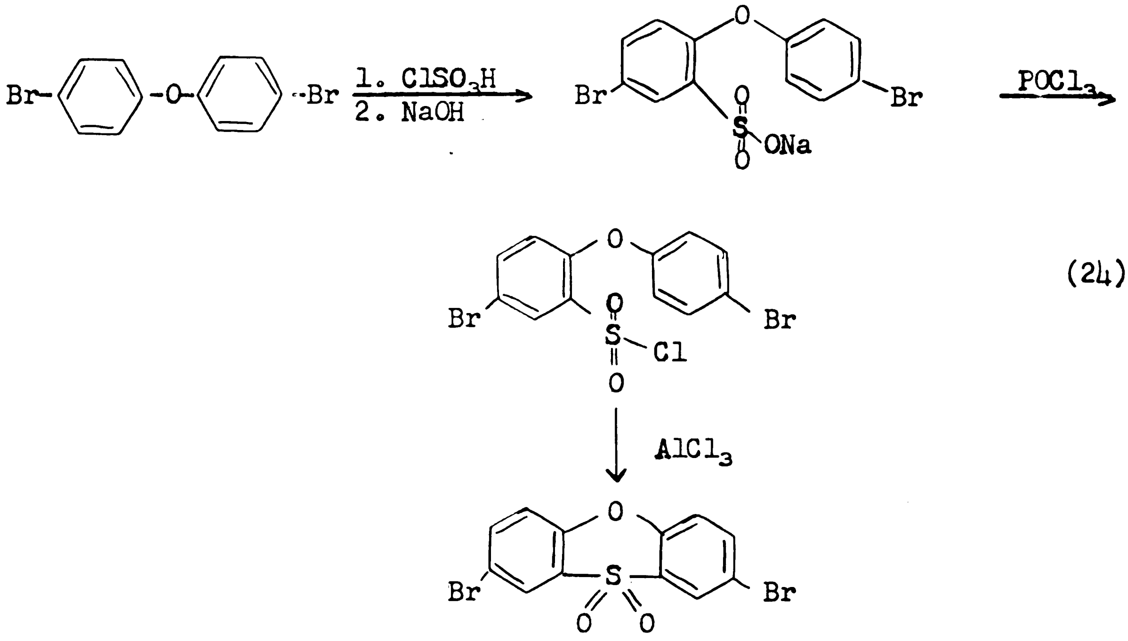
(23)

Using an excess of benzene they held the amounts of benzene and sulfur constant and varied the amount of aluminum chloride catalyst and found the optimum yield of thianthrene was formed when the ratio of sulfur to catalyst was 1.0/0.25 moles. They claimed stoichemetric yields of thianthrene at 80°C. from diphenyl sulfide and sulfur or from diphenyl disulfide in the presence of aluminum chloride using ligroin as a solvent. Gilman and Stuckwisch[38] carried out the ring closure of 2-bromophenyl phenyl sulfide by catalysis with aluminum chloride in carbon disulfide as a reaction medium with elemental sulfur to obtain a 20% yield of 1-bromothianthrene. No additional examples of ring closure reactions, with elemental sulfur, leading to thianthrenes were found recorded in the literature but a number of examples of ring closure reactions with sulfur monochloride were reported by Ray.[5] He condensed chlorobenzene, o-chlorotoluene, p-chlorotoluene, chloronapthalene, acetanilide, anisole, phenetole, acetophenone, diphenyl methane, iodobenzene, and benzoyl chloride with sulfur monochloride in the presence of an aluminum/mercury couple in a carbon disulfide media to obtain materials which analyzed correctly for the emphirical formula of the anticipated disubstituted thianthrene. He apparently made no attempt to isolate the intermediate sulfides and offered little evidence for the structure of the products he claims to have obtained. He carried out oxidations of the sulfide links of his assumed products but gave indefinite melting points for the sulfones obtained. Thianthrene has been prepared by Fleischer and Stemmer,[118] Bergmann and Tschudnowsky,[64] and Fries and Vogt[65] in 25-36% yield using sulfur monochloride as a ring closure reagent. Gilman and Swayampati[119] claimed improvements in the experimental procedure with sulfur monochloride to obtain a

70% yield of thianthrene and Kozlov, Fruktova and Shemyakima[98] claimed 78% yield of the identical product for the same reaction. Benzene and toluene have been found to react with sulfur dichloride[118] to give thianthrenes in low yields. Damanski and Kostic[120] claimed thianthrenes could be obtained from the condensation of toluene, xylene, napthalene, anthracene and phenanthrene with sulfur monochloride using aluminum foil as a catalyst. However their products took from three to five months to crystallize. Sen and Ray[121] obtained thianthrenes from paraxylene and 2-methoxyphenol and claimed ring closure reactions leading to additional thianthrenes from bromobenzene, p-chlorophenol, 4-methoxy toluene, 1,3-dimethoxybenzene, p-cresol, and guiacol dimethyl ether but they failed to obtain sulfur free products. Damanski[122] has written a review article entitled "Sulfur compounds of the Thianthrene Series." Some of the compounds mentioned above have had their structures verified by the sulfuric acid ring closure reactions of thiophenols, but the majority of thianthrene compounds prepared by sulfur mono- and dichloride condensation reaction are isomers of unknown constitution.

The ring closure reaction of diphenyl amines using elemental sulfur, and catalyzed by iodine to obtain phenothiazines has been widely developed.[120,123,124,88,125] Roe, Montgomery, Yarnell and Hoyle[120] made unsuccessful attempts to effect ring closures of this nature with sulfur dichloride and thionyl chloride. Fujimoto[106,81,82] succeeded in carrying out a phenothiazine ring closure reaction using thionyl chloride but obtained extensive chlorination of the product as well.

There are a number of additional ring closure reactions of interest in connection with the present investigation. Suter, Maxwell and McKenzie[33] prepared 2,8-dibromophenoxathiin-10,10-dioxide by the following sequence of reactions (24).



(24)

Newell[75] obtained a small quantity of 5-thiaxanthenone-10,10-dioxide on treating benzophenone with fuming sulfuric acid. A by-product of thiaxanthene-10,10-dioxide was obtained as well as sulfonation when diphenyl methane was allowed to react with chlorosulfonic acid.[126]

The classical preparations of aromatic thiols are the alkaline hydrolysis of a xanthate ester[106,127,30,128,129] and the zinc reduction of benzene sulfonyl chlorides.[30,130b,131,132]

Recently Djerassi, et al.,[133] reported that xanthate esters could be reduced to thiols using lithium aluminum hydride. Campaigne and Osborn[18] extended the application of this method to aromatic thiols and found that it gave better yields of the thiol than the alkaline hydrolysis and that it was particularly well-suited for hindered compounds.

Marvel and Caeser[134] claim the first lithium aluminum hydride reduction of a benzenesulfonyl chloride to a thiol. Since then several investigators have reported similar reductions[135,136,137,138] with varying results. Strating and Backer,[137] Schlesinger and Finholt,[139] and Field and Grunwald[136] report the formation of disulfides as by-products of the synthesis of thiols by such reductive procedures. Field and Grunwald[136] postulate that the reduction may occur via two routes, one of which involves the reaction of the sulfinate salt with a sulfonyl chloride giving a disulfone, or with a metal mercaptide to give a thiosulfonate. These intermediates are then converted to the mercaptan via the disulfide. Field and Grunwald[136] proved that the sulfenic acid was present in the reduction and recently the first example of a thiosulfinate ester has been reported by Shirley and Lehto.[135]

The synthesis of thiols by the reduction of the condensation products of sulfur monochloride with aromatics is worthy of mention here since little work appears to have been done in this area. Lazier, Signaigo and Wise[140] condensed napthalene in the presence of a zinc chloride catalyst using sulfur monochloride and subsequently reduced the condensation product with hydrogen in the presence of cobalt sulfide to obtain thio-alpha-napthol. Signaigo[141] prepared polysulfides in a similar manner from benzene, toluene, biphenyl, anthracene, xylene and napthalene and reduced the polysulfides to the corresponding thiols. Kroft[5] coupled thiophene with sulfur monochloride in the absence of a catalyst and reduced the heterocylic disulfide with zinc to obtain 2-thiophenethiol. However, it should be noted that it has not been shown that the structure of these disulfides is linear as is indicated by these reductions.

DISCUSSION

INTRODUCTION

COUPLING REACTIONS OF SULFUR CHLORIDES AND OXYCHLORIDES

- Sulfur Dichloride
  - General
  - Mechanism
  - Chlorotoluene Coupling Reactions
  - The Coupling of 1,2,4,5 Tetrachlorobenzene
  - Condensation of Bromo Benzene Derivatives
  - Condensation of Thiophene Derivatives

- Sulfur Mono Chloride
  - General
  - Thianthrene Ring Closure Mechanism

- Thionyl Chloride
  - General
  - Chlorination and Deoxygenation

- Sulfuryl Chloride

- Reaction Solvents

RING CLOSURE REACTIONS

- Thianthrene
  - Ring Closures with Sulfur Chlorides and Oxychlorides
  - Sulfuric Acid Ring Closures

- Phenoxathiin

- Thiaxanthene

METHODS FOR THE PREPARATION OF SULFIDES, SULFOXIDES AND SULFONES FOR STRUCTURE PROOF

- Diphenyl Sulfides by Fusion

- Diphenyl Sulfides by Diazo Condensation

- Oxidation Procedures

- Sulfones by Benzene Sulfonyl Chloride Condensations

THIOL PREPARATION

Lithium Aluminum Hydride Reduction of Xanthate **Esters**

Lithium Aluminum Hydride Reduction of Benzene Sulfonyl Chlorides

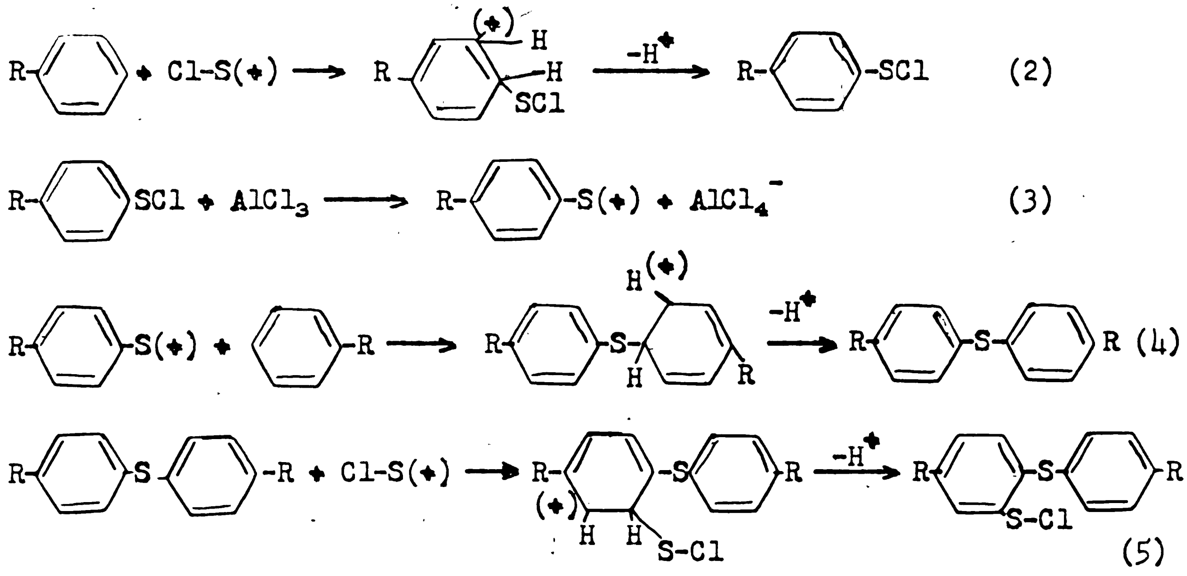
DISCUSSION

Although the sulfur chlorides and oxychlorides have been reported in the literature since the eighteen hundreds, information regarding their reactions in the presence of Friedel Crafts catalyst as coupling reagents is widely scattered throughout the literature. Many of the structures of the condensation products that are known have not been worked out nor have the conditions for the use of the reagents been well understood. In the older literature it is difficult to determine exactly which reagent investigators have used when they speak of using sulfur chloride although it is usually a reasonable assumption that they have worked with sulfur monochloride (S_2Cl_2) if they are not specific. Although coupling reactions of thionyl chloride have been known since early 1900[99] the reaction has been used little. This investigation has shown that it is a superior coupling agent but that it has its limitations when used with deactivated nuclei. Studies with sulfuryl chloride, in the present investigation, did not progress far enough to make an evaluation with that reagent but it was shown to be an effective chlorinating agent for the diphenyl sulfide nucleus under vigorous reaction conditions.

Sulfur dichloride was shown to be an effective coupling agent accompanied by a minimum of chlorination as a side reaction. For direct sulfide coupling it has the advantage over sulfur monochloride in that it gives a cleaner product uncontaminated by elemental sulfur. Both sulfur chlorides, however, react at relatively low temperatures compared to thionyl chloride so that they are both more effective for coupling deactivated nuclei. Although sulfur dichloride gives mixtures of isomers with the simpler substituted rings and therefore is a less desirable coupling agent for those nuclei than thionyl chloride it is particularly useful for 1,2,4 and 1,2,3 substituted benzenes. The high level of substitution eliminates undesirable isomer formation and multiple substitution. A summary of the coupling carried out with this reagent appears in Table III.

In accordance with the presently accepted mechanisms of Friedel Crafts reactions the following steps would reasonably appear to be operative in sulfur dichloride coupling reactions.

$$SCl_2 + AlCl_3 \rightleftharpoons Cl\text{-}S(+) + AlCl_4^- \qquad (1)$$

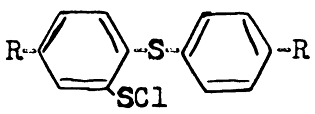


It was found necessary in using sulphur dichloride, to decompose unstable intermediate during the isolation procedure. These are believed to be the multiple substitution products I and II in which the sulfenyl chloride

TABLE III

SULFIDES AND SULFONES PREPARED VIA COUPLING REACTIONS OF SULFUR DICHLORIDE

Nucleus Coupled	Sulfide Formed	Sulfide B.p. or M.p.	Literature Reference	M.p. (°C.) Sulfone
Benzene	Diphenyl	140°C./5mm.	27	121-2
Chlorobenzene	Bis(4-Chlorophenyl)	95-6°C.	94,20,99, 104	147-8
o-Dichlorobenzene	Bis(3,4-Dichlorophenyl) 3,4-Dichlorophenyl-2',3'-Dichlorophenyl	74-5°C. 44.5-45°C.	---- ----	174-5 167.5-169
m-Dichlorobenzene	Bis(2,4-Dichlorophenyl)	58.5-59.5°C.	----	190.5-191
p-Dichlorobenzene	Bis(2,5-Dichlorophenyl)	114-115°C.	----	178.5-179
1,2,3-Trichlorobenzene	Bis(2,3,4-Trichlorophenyl)	139.5-141°C.	----	205.5-206
1,2,4-Trichlorobenzene	Bis(2,4,5-Trichlorophenyl)	149-150°C.	----	175-175.5
1,2,4,5-Tetrachlorobenzene	Bis(2,3,5,6-Tetrachlorophenyl) (?)	72-3°C. (?)	----	----
o-Chlorotoluene	Bis(4-Chloro-2-Methylphenyl)	217-19°C./2mm.	53	139-140
2,6-Dichlorotoluene	Bis(2,4-Dichloro-3-Methylphenyl)	111-112°C.	----	----
3,4-Dichlorotoluene	Bis(2-Methyl-4,5-Dichlorophenyl)	128.5-129.5°C.	----	----
2,4-Dichlorotoluene	Bis(2,4-Dichloro-5-Methylphenyl)	130-131°C.	----	----
Bromobenzene	Bis(4-Bromophenyl)	112-113°C.	98	----
1-Bromo-2,5-Dichlorobenzene	Tar	----	----	----
Thianthrene	Did not couple	----	----	----
Thiophene	Bis(2-Thienyl)	128°C./6 mm.	131	130.5-131
2-Chlorothiophene	Not isolated	----	----	----
2,5-Dichlorothiophene	Not characterized	190-230°C./ 15 mm.	----	----
Diphenyl Sulfide	4,4'-Bis(Phenylmercapto) Diphenyl Sulfide	110.5-111°C.	----	303.5-304



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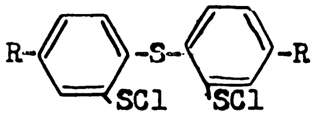


(II)

is deactivated sufficiently by the phenyl mercapto group that it does not react readily. These materials are not removed by caustic washing. Refluxing such products with alkali might destroy them but this was not investigated. It was found that long reaction periods employing large excesses of the compound being coupled reduced considerably the amounts of these multiple substitution products. It is believed that the longer reaction period allows the thianthrene ring closure of I. In the coupling of molecules with a high degree of substitution such as 1,2,3 and 1,2,4 trichloro benzene these decomposible materials are found to be almost completely absent indicating that molecules of type I and II are not able to form. The products of these decompositions are hydrogen chloride, hydrogen sulfide, aromatic thiols and tar. The crude distillate always has an odor of thiol and two thiols (2,5-dichlorobenzene thiol and 2-thiophenethiol) were isolated and identified in the distillable material. It might be possible to trap these sulfenyl chlorides using a highly reactive nucleus like phenol as an additive after the initial coupling has taken place.

The reaction of monochlorotoluenes with sulfur halides and oxyhalides in the presence of Friedel Crafts catalysts had been contemplated since the initiation of this investigation but since a thorough literature search for compounds related to the possible products revealed that only one sulfide,[145] none of the sulfoxides, and only three sulfones[145,146,147] (two of which[146,147] were questionable) had been reported previously. Thus, a study of their condensation reactions was delayed as there appeared to be no method to determine the structure of the products since it did not appear that infra-red examination could be applied in questionable cases because the same benzene substitution would be given by different isomers. However, near the close of the present investigation an article by Balasubramanian and Baliah[40] became available which established the structure of the bis(2-methyl-4-chlorophenyl) sulfoxide formed from the condensation of meta-chlorotoluene with thionyl chloride by independent synthesis. The bis(2-methyl-4-chlorophenyl)sulfoxide was prepared by the condensation of m-chlorotoluene and thionyl chloride and the product carefully purified by recrystallization. The sulfoxide was reduced to the sulfide using zinc and acetic acid to obtain an oil which crystallized with difficulty upon cooling. A small sample of that solid was recrystallized to obtain a pure sample melting at 30.5-31°C. The infra-red spectrum of this material was determined and a small sample was melted and the refractive index was taken on the super cooled liquid. The m-chlorotoluene was then coupled with sulfur dichloride and the product was found to be predominately the bis(2-methyl-4-chlorophenyl) sulfide by a comparison of the above data and conversion of the sulfide to the sulfone. However, it was slightly contaminated by other isomer products. The merit of using the sulfoxide route to prepare pure isomers became apparent at this juncture, since it had two advantages. First the sulfoxides have higher melting points than the sulfides, facilitating their purification by recrystallization. Secondly, the thionyl chloride is less reactive than sulfur dichloride and therefore it gives more specific orientation than is possible with sulfur dichloride. (It must be kept in mind, however, that in the case of highly deactivated nuclei side reactions may occur with thionyl chloride.) This synthetic route was immediately attempted in the preparation of bis(4-chlorophenyl) sulfide from chlorobenzene and thionyl chloride and found to be an excellent experimental procedure compared to direct coupling reaction with sulfur dichloride.

No experimental attempt was made to carry out condensation reactions with o-, or p- chlorotoluene since the reference compounds necessary to determine the structures of the products were not available.

The coupling reactions of the dichlorotoluenes were achieved and the identification of the resulting products posed little difficulty since the possible isomers gave different benzene ring substitution which allowed them to be easily characterized by the infra-red technique.

The reaction of sulfur dichloride with 1,2,4,5-tetrachlorobenzene presented two aspects which had not been present in condensations with other chlorinated benzenes. First, the 1,2,4,5-tetrachlorobenzene has a relatively high melting point (138°C.) compared to other chlorinated benzene derivatives and is insoluble in most solvents. Second, it was the first case in which the potentially reactive position on the ring was comparatively sterically hindered[148] since the two adjoining positions were occupied by chlorine atoms. In addition, if it were possible to form the condensation product, all four of the positions adjacent to the connecting sulfur atom would be occupied by chlorine atoms which it was anticipated should make the condensation reaction difficult to accomplish. The latter point was checked by constructing the Fisher-Hirshfelder model of bis(2,3,5,6-tetrachlorophenyl) sulfide and the spatial allowances seemed to support the possibility of its formation and accordingly an attempt was made to carry out a condensation reaction with this molecule. Hydrogen chloride evolution was not vigorous indicating a slow reaction rate. After a tedious isolation procedure a small amount of material was isolated which melted at 72-3°C. and which had an infra-red spectrum expected from a penta substituted benzene derivative. Unfortunately during the final purification procedure the material was lost as the result of an accident so that it could not be completely characterized. Since the condensation of the other two sterically hindered compounds (1,2,3,5-tetrachlorobenzene and pentachlorobenzene) was not tried, the reactivity of hindered compounds is still open to question.

The condensation reactions of bromobenzenes with sulfur dichloride were not studied as thoroughly as it was desired. Condensations were run with bromobenzene, 1-bromo-2,5-dichlorobenzene and bis(4-bromophenyl) sulfide. A moderate yield (28% based on the sulfur dichloride) of the bis(4-bromophenyl) sulfide and a small amount of some very impure dibromothianthrene was obtained from the condensation of bromobenzene in one instance but the primary product from these condensations was rather large amounts of insoluble tarry residues. The original clue as to what was happening in these condensations was overlooked when it was unfortunately assumed that a low melting crystalline solid which distilled over as an intermediate fraction following the recovered bromobenzene was 1-bromo-4-chlorobenzene (which would be formed by chlorination). Later a more thorough investigation, following the isolation of 1,4-dibromo-2,5-dichloro benzene from the condensation reaction of 1-bromo-2,5-dichlorobenzene showed that the low melting solid material was 1,4-dibromobenzene. Obviously there had been ring bromine displacement resulting in polymer formation and bromination of the starting material, bromobenzene. Thomas[149] reports that bromine displacement in the presence of aluminum chloride is well-known.

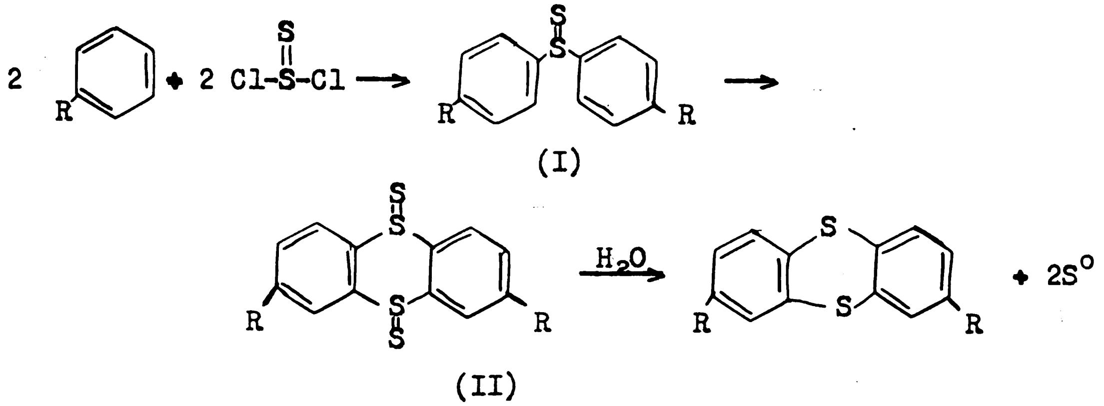
Suter and Green[44] and Suter, McKenzie and Maxwell[33] obtained only tar formation when they attempted a ring closure reaction with bromo diphenyl ethers with elemental sulfur catalyzed by aluminum chloride. The bromine displacement reaction is also suggested by the work of Gilman and Stuckwisch[38] who were able to obtain a 20% yield in the ring closure of 2-bromophenyl phenyl sulfide to 1-bromothianthrene using carbon disulfide as a solvent. The catalyst moderating effect of this solvent on aluminum chloride is well-known. The work of Tarbell and Wilson[150] also suggests that unusual effects occur with bromine compounds of this type in the presence of aluminum chloride. This evidence suggests that the application of weaker catalysts should be the next approach in the investigation of bromo benzene derivatives. In addition Billman and Dougherty[151] report that bromine displacement of this type occur with bis(4-bromophenyl) sulfide under high temperature. This might well be a contributing factor in the present work since these compounds are very high boiling (210°C./2mm.) materials due to their high molecular weight.

It had been anticipated to be able to prepare 2,7- and 2,8-dibromothianthrene as a result of these studies since although dibromothianthrenes have been reported[84,152] neither isomer has been fully characterized. However, further work with the bromine compounds was set aside in favor of the more promising chloro derivatives and also to await further development work with catalyst activity. This work was never done, however, as other fields investigated in the course of this work proved more fruitful and time did not permit a return to this particular phase of the problem discussed above.

Condensation reactions with thiophene derivatives were hardly successful. The well-known acid sensitivity of the thiophene nucleus is well demonstrated in these reactions. These condensations liberate two moles of hydrogen chloride whereas the usual acyl halides which are known to give poor reactions due to the polymerization side reaction liberate only one mole. The combination of a Friedel Crafts catalyst with all the hydrogen chloride liberated make short contact time a necessity. If a weak catalyst can be found and combined with short contact time and low catalyst ratio then it may be possible to achieve satisfactory yields of the condensation products. It was planned to continue this work using less acid sensitive molecules such as thianapthene and esters of 2-thenoic acid but time did not permit. The technique of Kroft[128,131] using sulfur monochloride in the absence of a catalyst at the thiophene reflux temperature to obtain the disulfide which he pyrolyzed to the sulfide may be the best method for acid sensitive thiophenes. This method should also provide easy access to the thiophene thiols through reduction of the disulfide.

Plans to extend this condensation to furan derivatives were put aside when conditions for good thiophene reactions failed to materialize. The esters of furoic acid should be good candidates for an attempt to enter this area.

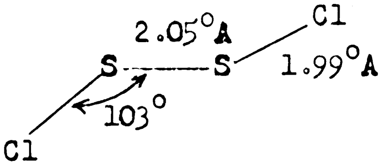
Condensation reactions with sulfur monochloride (S_2Cl_2) leave many questions about this reagent to be answered. It was not used extensively in this work since one of the initial premises was to show that sulfur dichloride (SCl_2) although an unstable compound in contrast to sulfur monochloride was a good condensing agent. However in comparing the two reagents some light has been cast on the nature of the monochloride. It was known from previous work[207,27] that coupling reactions with sulfur monochloride produced elemental sulfur which could be isolated after quenching the reaction mixture in water. This fact suggests that the intermediate structure I and II suggested by Ray[28] may be operative.



(I)

(II)

He claims to have isolated such intermediates and found them to be unstable and suffer decomposition with moisture liberating free sulfur. However, there has been considerable controversy in the literature[216, 217, 218, 219, 220] regarding the exact structure of the monochloride. The two possible structures are III and IV.



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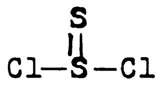
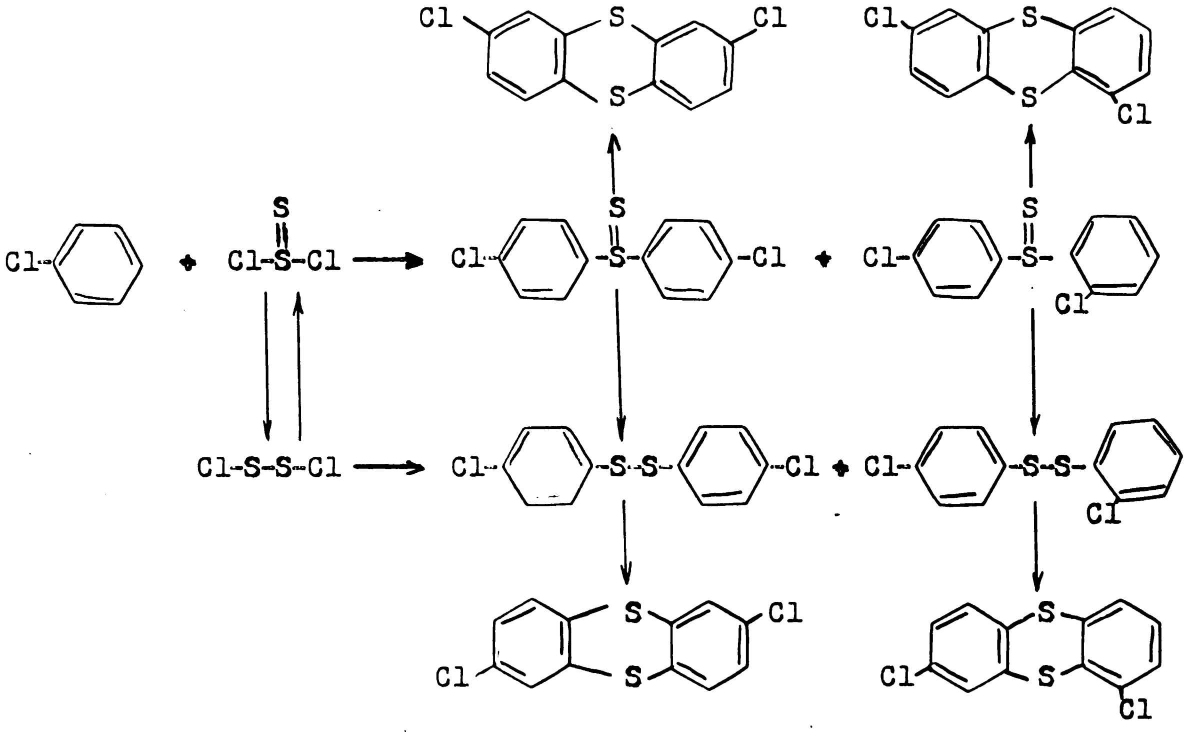


$$Cl-\overset{\overset{S}{\|}}{S}-Cl$$

(IV)

Krebaum in his seminar (a review with 137 references) on this reagent[86] states that it is currently regarded on the basis of electron diffraction studies[215] to have the structure and dimensions shown in III. The linear structure is also suggested by the work of Lazier, Signaigo and Wise,[206] Signaigo[205] and Kroft[128] who formed linear disulfides when reacting aromatics with sulfur monochloride which they subsequently hydrogenated to form the thiol. However these reactions were carried out at temperatures of 80-100°C. and under such conditions structure I could easily shift to the linear disulfide. Thus the many and varied reactions of sulfur monochloride in organic chemistry suggest that its structure could well be a hybrid or change with environment.

The initial interest in studying this reagent more fully came about when it was observed that thianthrene was formed in the reaction of benzene and sulfur monochloride to form diphenyl sulfide[27] whereas it was not found in condensations of sulfur dichloride under the same conditions. The liberation of hydrogen sulfide in the sulfur monochloride reaction even at temperatures as low as 20°C. seemed to indicate that the intermediate I might be present since elemental sulfur does not effect ring closure of diphenyl sulfide at that temperature[30] nor does diphenyl disulfide[30] form thianthrene under such conditions. Following this reasoning the condensation was carried out using a prolonged contact time followed by a heating period to drive the reaction to completion. It was found that equal amounts of diphenyl sulfide and thianthrene were found as predicted by the series of equations given in the introduction to that condensation in the experimental section of this thesis. The diphenyl sulfide must be formed by virtue of the fact that half of the excess sulfur is oxidized to hydrogen sulfide in the ring closure. It was found, however, that the same sequence of reactions would not explain the formation of the mixture of dichlorothianthrenes when chlorobenzene was condensed under these same conditions but that this required additional equations involving the linear disulfides as follows:



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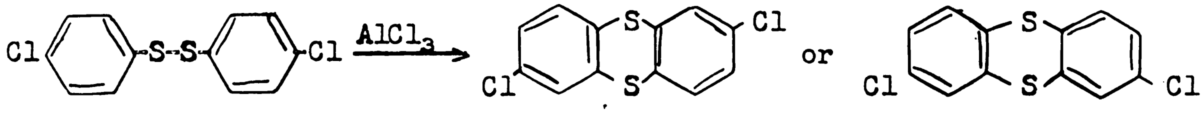
When it became known that this reaction was behaving differently it seemed that the identification of the product from the ring closure of bis(4-chlorophenyl) disulfide (reaction 7) might yield additional information as to the mechanism of these ring closures.



(7)

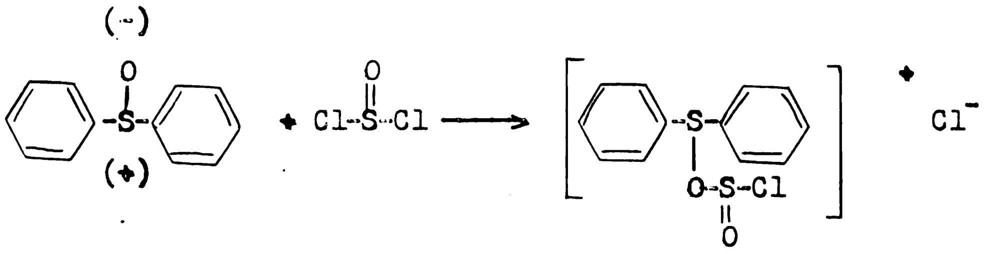
Time limitations, however, prevented further investigations in this area. It seems highly probable that this mode of ring closure might prove to be of advantage in the ring closure of such compounds as p-dichlorobenzene where sulfur dichloride gave predominately polymeric material. The difference in ring closure mechanism in addition to the fact that sulfur

monochloride appears to be of a lower order of reactivity than sulfur dichloride could favor the desired reaction.

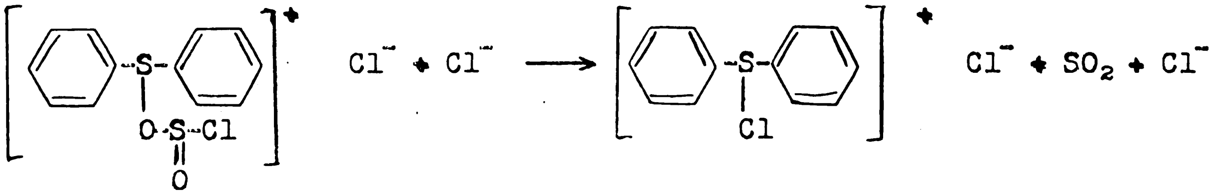
Thionyl chloride proved to be a good condensing agent. It was found that it condenses readily with benzene and its derivatives such as chlorobenzene, o-chlorotoluene, o-dichlorobenzene and p-dichlorobenzene to form the diphenyl sulfoxides. The ring closure of bis(4-chlorophenyl) sulfide to 2,8-dichlorothianthrene-10-oxide was also effected with this reagent. It was found to be a more specific substitution agent than sulfur dichloride due to its lower order of reactivity and since sulfoxides are in general higher melting than the corresponding sulfide the sulfoxide route to sulfides (via reduction) provided the best method of preparing pure sulfide isomers for ring closure experiments.

However, it was found that as negative substitution of the benzene ring increased side reactions began to enter the picture. In the condensation of o-dichlorobenzene chlorination and deoxygenation of the sulfoxide to the sulfide occurred in addition to the desired reaction making product isolation more difficult. Also in the attempted ring closure of diphenyl sulfide to thianthrene-5-oxide the only ring closure product isolated was thianthrene itself. As a result of these experiments a literature search was instigated and it was found that both thionyl chloride and hydrogen chloride cause such reactions. A survey of the literature references to such reactions appears in the historical section of this thesis.

Some insight into this type of reaction is furnished by the work of Bordwell and Pitt[151] who studied the formation of α-chlorosulfides from sulfides and sulfoxides. They propose that since sulfoxides are basic that they form salts (reaction 8) initially with thionyl chloride and


(8)

that the reactions are best interpreted as involving sulfonium salt intermediates. The $-O-\overset{O}{S}-Cl$ group may be displaced giving sulfur dioxide and chloride ion by the attack of chloride ion on sulfur (reaction 9). They formed the dichloride using diphenyl sulfoxide and then chlorinated


(9)

a more reactive species (methyl phenyl sulfide) with that intermediate. In the absence of other species chlorination of the diphenyl sulfide would occur.

Extension of their mechanism to the results of these condensations gives the following analysis of what happens in these reactions. If the nucleus being condensed is sufficiently reactive then the thionyl chloride reacts rapidly with that nucleus to form the sulfoxide and does not form the sulfonium salt. In this case a high yield of the sulfoxide would be obtained. For nuclei that do not react rapidly with thionyl chloride then the sulfoxide product forms the sulfonium salt with subsequent decomposition to the dichloride. According to Gilman[163] these dichlorides are not stable above 0°C. so that chlorination would occur rapidly at that point. The species that is chlorinated would make a great deal of difference in what the final product of the condensation would be. In the case of the ring closure of diphenyl sulfide with thionyl chloride the diphenyl sulfide is chlorinated in preference to the thianthrene which is formed by decomposition of the sulfonium salt. Both o-dichlorobenzene and the bis(3,4-dichlorophenyl)sulfide are chlorinated in the condensation of o-dichlorobenzene with thionyl chloride. The literature shows that acetanilide[180] and aceto-m-toluidide[53] give good yields of the sulfoxide which would be consistent with this mechanism. However, the formation of bis(5-acetamide-4-chloro-2-methylphenyl) sulfoxide from aceto-p-toluidide[53] would make that reaction questionable since the product should be bis(5-acetamide-4-chloro-2-methylphenyl) sulfide if this mechanism is correct. Since that is the only case found in which chlorination occurred without loss of the oxygen in the sulfoxide link it is highly probable that the product is in error. Chlorination can occur with thionyl chloride by decomposition of that reagent according to **reactions** 1,2,3 and 4 as listed in the section on reagent notes in the appendix of this thesis but it is not believed that this mechanism was operative here since the temperature was too low.

Mention must be made of the reductive halogenation process studied by Gilman and Swayampati,[16] Fries and Vogt,[4] and others.[152,150,179,181,15] In this mechanism sulfoxides are reduced to sulfides by hydrogen halides with attendant ring chlorination. The mechanism of this reaction has been studied by Gilman and Eisch[150] and it is discussed by Massie.[179]

Inasmuch as hydrogen chloride is present in all of these reactions and does not cause uniformity of reaction it is believed that it does not operate in condensation reactions of thionyl chloride and will not be discussed here.

Efforts to use sulfuryl chloride (SO_2Cl_2) as a condensing agent were restricted to attempted ring closures of substituted diphenyl sulfides since this reaction would have provided a route to thianthrenes with two oxygens on the same sulfur which are not readily obtainable by other methods.[14,16,20] The experiments led to a method for preparing chlorinated derivatives of diphenyl sulfides which are not available by direct condensation methods. Too little work was done with the reagent to evaluate its potential as a coupling agent. One material was obtained in the attempted ring closure of bis(4-chlorophenyl) sulfide which resisted efforts to characterize it. Proper identification of this material may open the door in this area. The results obtained definitely indicate that coupling reactions must be run as cold as possible in order to avoid the chlorination side reaction. The work with highly substituted benzene sulfonyl chlorides (which would be an intermediate in these coupling reactions) would seem to indicate that inverse addition may prove to be a helpful procedure in this area also. Inverse addition consists of adding the catalyst to the mixture of the other reactants at a controlled rate so that there is only a slight excess of catalyst present at any given instant which is not tied up in complex formation with the sulfone product. Negatively substituted benzenesulfonyl chlorides and deactivated substrate nuclei appear to promote a side reaction in which the benzene sulfonyl chloride acts as a chlorinating agent rather than the desired condensing reactant. The work of Suter, Maxwell and McKenzie[62] with chlorosulfonic acid in similar ring closure attempts of diphenyl oxides indicates also that substitution in both rings may be a side reaction to be avoided by the use of an excess of the sulfide.

Ethylene dichloride was employed for all studies of the coupling reactions in this investigation. It is particularly well suited for this purpose since it is non-reactive, dissolves most benzene derivatives readily, gives soluble aluminum chloride complexes and has a low boiling point which facilitates its removal from the reaction product. Other chlorinated solvents such as carbon tetrachloride, perchloroethylene, chloroform, tetrachloro ethane and methylene chloride can be used but they do not have some of the advantages of ethylene dichloride. Methylene chloride is a good second choice for reaction media. Carbon disulfide has been used and has a moderating effect on the activity of strong catalysts. Recently[152] fatty acid esters have been shown to be good solvents for coupling reactions with reactive nuclei which do not require any catalysis. It is obvious from this investigation that benzene or any of its derivatives do not make good solvents for coupling reactions since they themselves couple energetically.

Ring closures of diphenyl sulfides, diphenyl ethers and diphenyl methanes with sulfur chlorides and oxychlorides were studied in this investigation. In addition the ring closure of thiophenols with sulfuric acid was used as a method of preparing thianthrenes for structure study purposes.

A number of thianthrene isomers were isolated as by-products in the sulfide coupling reactions. Small amounts of these materials were present in practically all the condensations where sufficient contact time was allowed for ring closure of the sulfenyl chloride intermediate. Whenever it was convenient the thianthrenes were isolated and identified. Since these materials were extremely high boiling in many cases their separation from resinous tars in the distillation flask was impossible as the temperatures required to force their distillation were near the softening point of glass. A summary of all the ring closure products regardless of how they were prepared appears in Table IV.

A number of ring closure reactions were made starting with the sulfide. Most of these closures were made in the absence of any knowledge of good ring closure conditions. As better conditions became known the results were still affected by the fact that the starting materials were not available in large enough quantities to use the excesses of these materials required for good reaction. Catalyst ratios were never worked out satisfactorily since a lot depends upon the particular molecule which is being condensed. Most of the beginning work in ring closures was done using the 1-1 ratio of catalyst to sulfur dichloride. Nothing was known of the mechanism nor reaction rate of ring closure and the only clue was found in the work of Dougherty and Hammond[30] who studied the condensation of benzene to diphenyl sulfide and thianthrene with elemental sulfur. Their work indicated that better ring closure occurred as the

TABLE IV

RING CLOSURES WITH SULFUR CHLORIDES AND OXYCHLORIDES

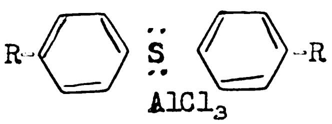
Starting Material	Ring Closure Product	M.p. (°C.)	Literature Reference	M.p. (°C.) Highest Oxide
Benzene	Thianthrene	154-5	29	325
Diphenyl Sulfide	Thianthrene	154-5	29	325
2-Chlorophenyl Phenyl Sulfide	1-Chlorothianthrene	84-5	170	242
3,4-Dichlorophenyl Phenyl Sulfide	2,3-Dichloro Thianthrene	Not Isolated	-----	-----
Bis(4-Chlorophenyl) Sulfide	2,8-Dichloro Thianthrene	172-172.5	20	288-9
Bis(4-Chlorophenyl) Sulfide	2,8-Dichloro Thianthrene-10-Oxide	166-7	-----	288-9
Bis(4-Chlorophenyl) Sulfide	2,8-Dichlorothianthrene-10,10-Dioxide	Attempted	-----	-----
o-Dichlorobenzene	2,3,7,8-Tetrachloro Thianthrene	272-3	-----	314-314.5
o-Dichlorobenzene	1,2,7,8-Tetrachloro Thianthrene	180-180.5	-----	191-191.5
4-Chlorophenyl-4'-Tolyl Sulfide	2-Methyl-8-Chloro Thianthrene	128-9	-----	-----
2,6-Dichlorotoluene	1,3,7,9-Tetrachloro-2,8-Dimethylthianthrene	227.5-228	-----	-----
Diphenyl Ether	Phenoxathiin	56-7	62	147-8
Bis(4-Chlorophenyl) Ether	2,8-Dichlorophenoxathiin	134-5	62,65	196-196.5
Diphenyl Methane	Thiaxanthene	128.5-129.5	77,78	184.5-185.5
Diphenyl Methane	Thiaxanthenone	213-15	41	184.5-185.5

ratio of catalyst to condensing agent decreased. Since diphenyl sulfide was the most easily prepared starting material it was selected for attempts to outline ring closure conditions. One preparation of diphenyl sulfide from benzene was slanted towards ring closure using a 0.65 mole ratio of aluminum chloride to sulfur dichloride and a prolonged contact time. The ratio of the thianthrene to diphenyl sulfide isolated was 0.54 compared to the isolation of no thianthrene for a 1-1 ratio of catalyst to condensing agent with a short contact time.

Ring closure of diphenyl sulfide (1.0 mole) with sulfur dichloride (0.5 mole) in the presence of aluminum chloride (0.25 mole) yielded approximately 0.30 mole of thianthrene, 0.21 mole of recovered diphenyl sulfide, some monochlorodiphenyl sulfide, a considerable amount of 1,4-bis(phenylmercapto) diphenyl sulfide (the linear coupling product) and evidence for 1,4-bis(phenylmercapto) benzene which would be formed by phenyl mercapto migration. Unfortunately this experiment was not repeated with a large excess of diphenyl sulfide. There are other indications in this work that the best ring closures are made in the presence of an excess of the original benzene derivative since it keeps polycondensation at a minimum.

It was found using sulfur monochloride that there is apparently a different mechanism of ring closure and this has been discussed in one of the preceding paragraphs covering that reagent. This mechanism may explain the thianthrene derivatives obtained by Ray.[28]

Ring closure in the presence of low catalyst to sulfur dichloride ratios may be attributed to the complexing (I) between the sulfide link and the aluminum chloride. There is always highly colored metal complex color formation in these condensations. Evidence that there is complexing comes from ring closure experiments. If a solid diphenyl sulfide is placed in ethylene dichloride and stirred it is found to be insoluble. However, upon the addition of aluminum chloride color formation takes place in a matter of minutes and the solid sulfide is solublized. This complex may be responsible for ring closure by attracting the sulfur dichloride into the vicinity of the ortho position where it can substitute the ring (II). However, considerable more study of such ring closures will be necessary to set a definite pattern as to what happens. The role of phenylmercapto migration is not understood although it may simply be another alkylation type reaction such as happened with diphenyl methane. The directive effect of substituting groups may play a considerable role as was found by Suter and Green in the Ferrario reactions.[61] The complete ring closure of II seems to be a slow step since short contact time leaves decomposible residues which are diminished by long contact time which is also accompanied by isolation of higher yields of the thianthrenes. There is a possibility that hydrochlorination of the ring takes place



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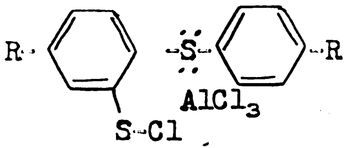
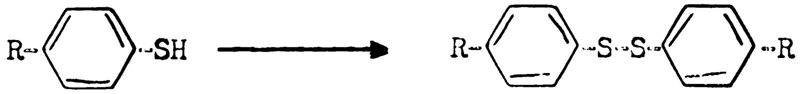


(II)

with subsequent breakdown although this would not explain the hydrogen sulfide which is usually given off in small quantities.

Ring closure reactions of thiophenols in sulfuric acid were undertaken to prepare chlorinated thianthrene isomers needed in some structure proof problems. It will be noted (see Historical) that a fair amount of work had been done previously in this area but experimental conditions were not well outlined. The ring closure reaction proved to be very intriguing so that some exploratory work was done with it. Concentrated sulfuric acid was found to oxidize thiophenols to their disulfides (10) and fuming sulfuric acid caused ring closure of the disulfide to thianthrene (11). Prolonged contact with fuming sulfuric acid was found to oxidize the thianthrene to its monoxide (12).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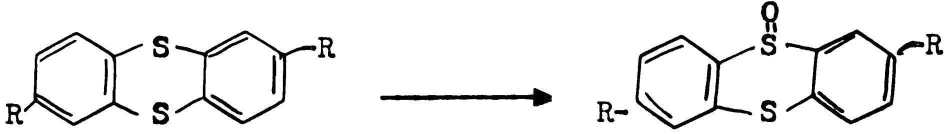

(12)

The experimental data obtained is summarized in Table V.

It is interesting to observe that yields greater than 50% have never been obtained by this method. Sulfonation or oxidation to give water soluble by-products would appear to be the main side reaction, causing low yields. It appears that a para substituent is necessary to obtain ring closure since several attempts to prepare 1,6-dichlorothianthrene

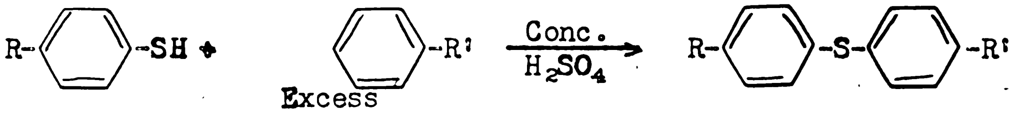
TABLE V

REACTIONS IN SULFURIC ACID MEDIA

Substrate	Acid Strength	Contact Time (Hrs.)	Product	M.p. °C.	Percent Yield
4-Chlorothiophenol	Conc.	48	Bis(4-chlorophenyl)disulfide	70-1	44.5
4-Chlorothiophenol	30% fuming	14	2,7-Dichlorothianthrene	181.5	31
4-Chlorothiophenol	30% fuming	48	2,7-Dichlorothianthrene and 2,7-Dichlorothianthrene Monoxide	181.5 228	Combined Yield 33
2-Chlorothiophenol	30% fuming	29	1,6-Dichlorothianthrene expected	------	0
2-Chlorothiophenol	30% fuming	19	1,6-Dichlorothianthrene expected	------	0
2-Chlorothiophenol	30% fuming	14	1,6-Dichlorothianthrene expected	------	0
2-Chlorothiophenol	Conc.	1	Bis(2-Chlorophenyl) Disulfide	------	Not Isolated
Bis(3,4-Dichlorophenyl) Disulfide	25% fuming	14	2,3,7,8-Tetrachlorothianthrene	272-3	30
Thiophenol in excess benzene	Conc.	9.5	Polymer	------	Major Product
			Diphenyl sulfide	oil	5
			1,4-Bis(phenylmercapto)benzene	81-2	1
			Thianthrene	154-5	0.5

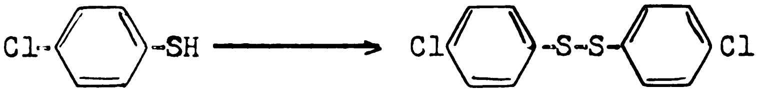
from 2-chlorothiophenol failed. Lower sulfur trioxide concentration may improve the performance of this reaction based on the observation that Suter and Archer[32] obtained good condensations of thiosalicylic acid with benzene derivatives using 1% fuming sulfuric.

The condensation of thiophenol with benzene suggests a useful potential route to substituted diphenyl sulfides. The presence of a substituent on each of the two condensing molecules should inhibit polymer formation and give practical yields of diphenyl sulfides (13).



(13)

In accordance with the mechanism proposed by Suter and Archer[32] for analogous condensations the following mechanism for the ring closure and condensation reaction could be postulated.



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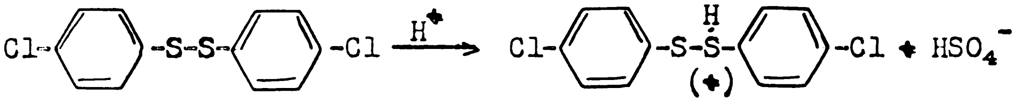

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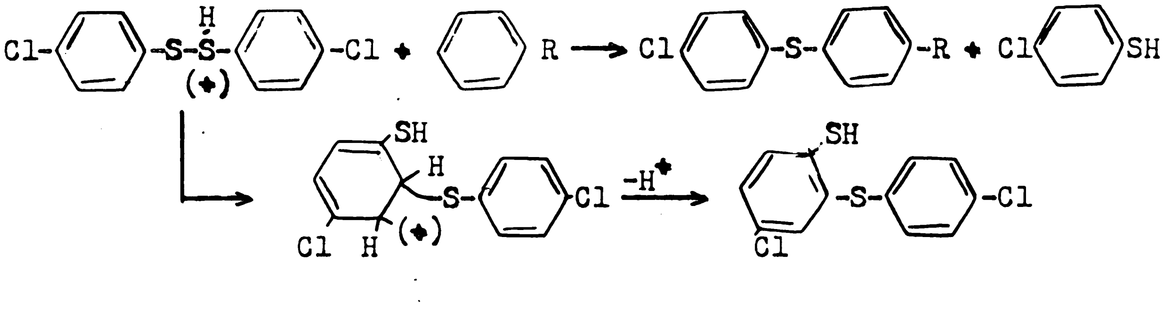

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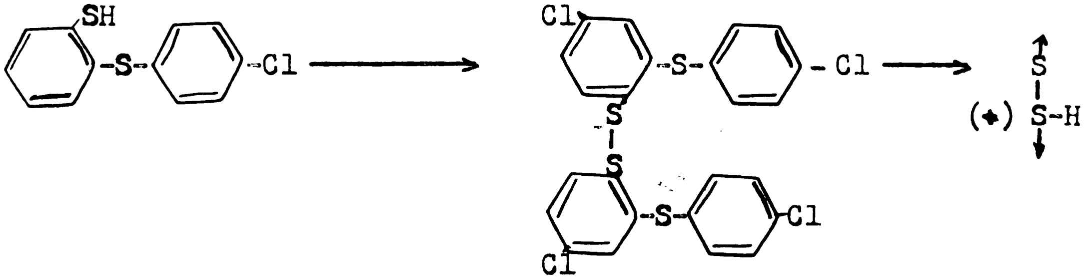

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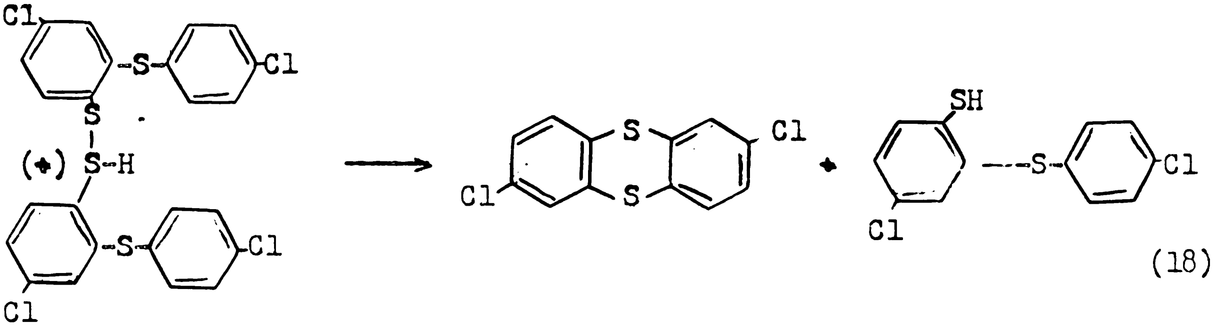
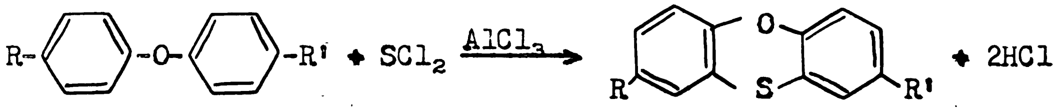


(18)

As Suter and Archer[32] state, polarization of the protonated disulfide with a charge separation gives a thiophenoxide ion which may well be the reactive intermediate. The situation may be more complex, however, since recent work[114,115,116] has shown the presence of free radicals in such solutions.

Two examples of the ring closure reactions of diphenyl ethers with sulfur dichloride (19) to phenoxathiin were studied. The two ethers were

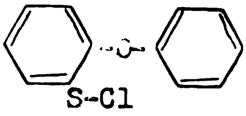


(19)

diphenyl ether and bis(4-chlorophenyl) ether. A high degree of chlorination (20) was found in the condensation of diphenyl ether.

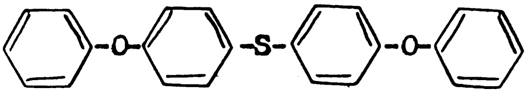
(20)

Although sulfur dichloride is well-known as a chlorinating agent no other case was found in this study where chlorination was a major side reaction. Since no attempt was made to purify the ether before use it is highly probable that peroxides were present and may have been responsible for the unusually large amount of this side reaction. Experience with the thianthrene ring closure reaction gained in some later work indicates that the reaction contact period used in the diphenyl ether experiments was not sufficient to obtain a good ring closure as the intermediate (IX)



(IX)

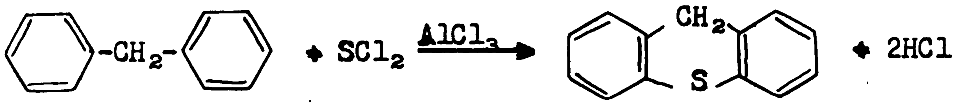
would (if analogous to thianthrene) probably not undergo ring closure at a rapid rate due to the electron withdrawing effect of the phenoxy radical which would be operative. The use of a large excess of the ether would undoubtably decrease the amount of tar formation with the net result of increasing the yields of the desireable products. Thianthrene experience and information available on ring closure reactions with elemental sulfur and aluminum chloride indicate that a catalyst ratio of about 0.5/1 of catalyst/sulfur dichloride is a great deal more effective in obtaining good ring closure than the ratios employed in this work. The isolation of only a small amount of higher boiling material in the present work was due to the formation of fairly large amounts of tarry residue with the result that the high boiling point of the linear condensation product (X) makes it difficult to separate it from the viscous



(I)

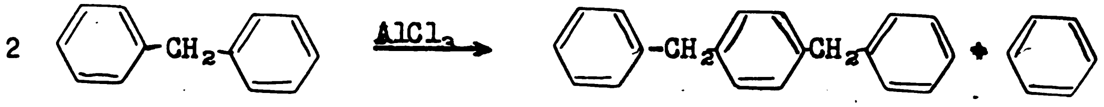
non-distillable material before the residues decomposed.

The ring closure reaction of diphenyl methanes was not studied in great detail. Early attempts to bring about ring closure of diphenyl methane and 1,1-bis(4-chlorophenyl) ethane resulted in intractable tars. Later, when the necessity of using excess material was realized two additional ring closure reactions with diphenyl methane were carried out. Small amounts of thiaxanthene, thiaxanthenone, and 1,4-(Dibenzyl) benzene were separated from the distillable oily fractions. Thiaxanthene was the desired ring closure product as indicated in reaction (21). No direct



(21)

evidence was obtained to explain the formation of thiaxanthenone. The presence of 1,4-(dibenzyl) benzene indicates that diphenyl methane is unstable in the presence of aluminum chloride and dismutates according to reaction (22). Fractionation of the products failed to give any distinct

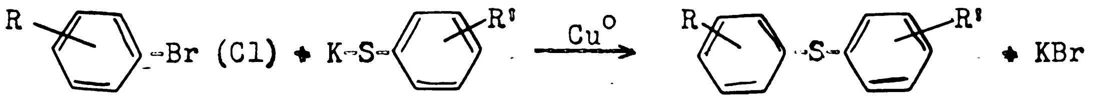


(22)

boiling fractions but merely a gradual raise in boiling point of the distillate as the distillation proceeded. These materials were isolated from the appropriate fractions by virtue of the fact that they are precipitated on being set aside at low temperature for long periods of time. The large volumes of the viscous oils from which these materials were isolated indicated they were crude products as evidenced by the overlapping of their boiling point ranges.

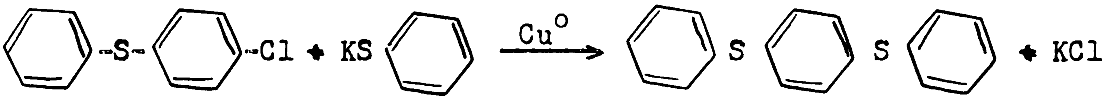
The data obtained in these preliminary studies indicates that future work in this area should be carried out with a weaker catalyst to prevent self alkylation by the diphenyl methane compounds. This change combined with the use of a large excess of the methane derivative should produce experimentally more workable reaction mixtures containing fewer by-products. This should be a fertile field for research once good ring closure reaction conditions have been determined. A literature survey revealed that ring closure reactions of this type have not been made even with elemental sulfur and that even the simple ring chlorinated derivatives are unknown.

The preparation of chlorinated or alkylated diphenyl sulfides by the fusion of an alkali metal thiophenoxide with "pseudoactivated" halobenzenes proved to be a useful synthetic method (**reaction** 23).



(23)

Halobenzenes in which the halogen is "activated" by a nitro group do not require a fusion technique to achieve this condensation. "Pseudoactivated" halobenzenes are considered to be those compounds in which one of the halogen is sufficiently activated so that the above condensation will proceed at a temperature below the atmospheric boiling point of the halobenzene employed. Chlorobenzene, bromobenzene and the dichlorobenzenes are excluded by this definition although it is highly probable that these compounds will also undergo this reaction in a pressure vessel where the necessary temperature for reaction could be achieved. The bromotoluenes, trichlorobenzenes, tetrachlorobenzenes, bromochlorobenzenes, polybromobenzenes etc. all fall in the "pseudoactivated" halobenzene class. As will be seen from the experimental results, phenoxy and thiophenoxy chlorobenzenes (reaction 24) are also "pseudoactivated" in that some higher



(24)

condensation also occurs although this latter reaction normally occurs at a slightly higher temperature than that required for the formation of the thiophenoxychlorobenzene (4-chlorophenyl phenyl sulfide). The results obtained using the fusion technique are summarized in Table VI.

It will be noted that a number of the compounds prepared have been described in the literature but none of these materials had been prepared previously by this type of reaction. The experimental procedure was investigated since prior work with the fusion technique using phenols[153] gave good results.

It was found that a copper catalyst was necessary for the reaction to proceed. The best results in yield and purity were obtained using an excess of the halobenzene since both the alkali thiophenate and the alkali halide formed proved to be relatively insoluble in the undiluted

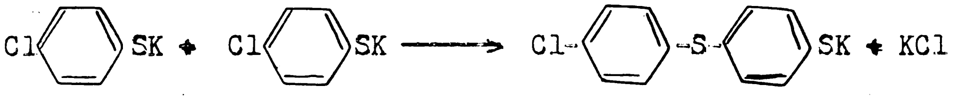
TABLE VI

DIPHENYL SULFIDES PREPARED BY FUSION CONDENSATION

	Starting Materials				Fusion Conditions			
Diphenyl Sulfide	Benzene Der.	Thiol Used	Yield Percent	B.p. or M.p. (°C.)	Temp. °C.	Time Hrs.	Lit. Ref.	M.p. Sulfone (°C.)
4-Chloro	4-Chloro-1-bromo	Benzene	75	167-8°C./9mm. n_D^{25} = 1.6354	200	4	162,78, 150,10	92.5-93.5
4-Phenylmercapto	4-Chloro-1-bromo	Benzene	By-product	81.5	200	4	47	230-231
4-Chloro-4'-methyl	4-Chloro-1-bromo	4-Toluene	57.5	73-4	200	8.5	11	128
4(4-Tolylmercapto)-	4-Chloro-1-bromo	4-Toluene	By-product	98.5-99.5	200	8.5	48	-----
2-Chloro	2-Chloro-1-bromo	Benzene	23.1	159°C./10mm. n_D^{25} = 1.6383	170	5	10,51	105-106.5
2-Phenylmercapto	2-Chloro-1-bromo	Benzene	By-product	149°C./5mm.	170	5	None	-----
2,4,5-Trichloro	1,2,4,5-Tetrachloro	Benzene	29.7	84.5-85	240	8	9	127-128
2,5-Dichloro-4-phenylmercapto	1,2,4,5-Tetrachloro	Benzene	By-product	185-6	240	8	None	236-237 (Di)
3,4-Dichloro	1,2-Dichloro-4-bromo	Benzene	55	152°C./5 mm. n_D^{25} = 1.6460	200	6	None	123.5-125

melt. Excess thiophenoxide could not be used as it was oxidized to the disulfide if it was not present as a salt. In addition most thiophenols are relatively more difficult to obtain at the present time and it is easier, experimentally, to recover a halobenzene than a thiophenol. Either the sodium or the potassium salt may be used but experience seems to favor the use of the potassium salt due to its greater solubility in the reaction melt.

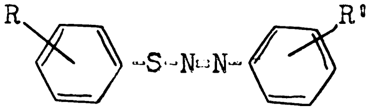
In addition to its function as a diluent the excess halobenzene serves to keep the primary side reaction (condensation of products containing a second halogen with a second mole of the thiophenol) at a minimum. Although all of the trichloro and tetrachlorobenzenes can be made to undergo this fusion reaction only symmetrical compounds in which any of the chlorines can react to give the same isomer can be used to obtain pure isomers. Experience in reacting 1,2,4-trichlorobenzene[153] with phenols showed preferential reaction of the most active halogen but in addition some of all the possible isomers were formed. No literature record was found of any previous reaction of a chlorobenzene compound with a thiophenoxide. Further, a thorough search of the literature revealed only a few cases of the reaction of a bromobenzene derivative undergoing this reaction. The ready availability of halogen compounds that will undergo this reaction and its adaptability to large scale laboratory work should make it a very useful synthetic route to diphenyl sulfide derivatives. The work with p-toluenethiol shows that it can be used with alkylated thiophenols and it is quite probable that it can be used with chlorobenzene thiols although the presence of an additional halogen in this molecule introduces the possibility of a second side reaction, namely, the reaction of two molecules of the chlorinated thiophenol as in **reaction** 25.



(25)

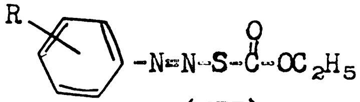
It should be emphasized that the experimental conditions given in Table VI for the fusion reaction are not optimum and that the conditions for the best yield should be worked out, in each case, according to the lability of the halogen being displaced.

The condensation of aromatic diazonium chlorides with alkali metal salts of thiophenols as a preparative route to diphenyl sulfides was tried in a single case. Lack of information on the temperature necessary to decompose the diazonium intermediate (XI) nearly resulted in an



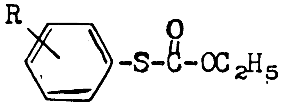
(XI)

accidental explosion. Some work had just been completed in preparing aromatic thioxanthate esters via the decomposition of diazo intermediates (XII) prior to undertaking the above experiment in which it was found



(XII)

that such intermediate materials decomposed spontaneously at 20-40°C. during the preparation of the thio esters (XIII).



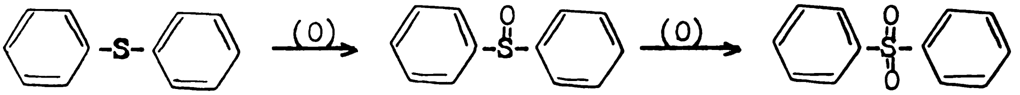
(XIII)

An erroneous assumption was made based on this background as well as the fact that the abstract covering the work of Rolla, Sanesi and Leandri[10] contained no warning as to the decomposition point of the diazo intermediate. The orange oil had been extracted from the reaction mixture with ether, the resulting ether solution was washed in the usual manner and the last of the ether was being removed on the steam bath when the oily material reached the necessary temperature (70°C.) for decomposition. The oil commenced to froth and then the flask was blown, fortunately intact, against the hood wall, smashing itself. If the flask had been placed in a partially closed system there would undoubtably have been a very serious explosion. Part of the oily material was recovered and decomposed by dropping it into hot dibutyl ether (140°C.). This procedure gave a small yield of 2-chlorophenyl phenyl sulfide. No further work was done with this reaction, however, the following comments may be of use to future investigators.

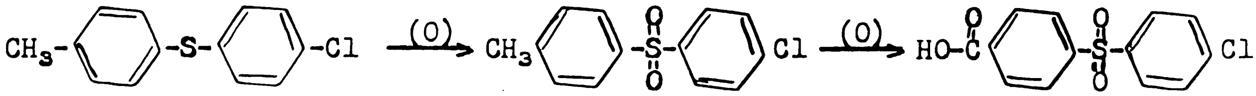
Increased negative or electron withdrawing substituents (i.e. multiple halogen, nitro, carboxy, acetyl etc.) should further stabilize the diazo intermediate against thermal decomposition. (Compare the work of Hodson and Foster[56] using phenols). Distillation of the products from this reaction should not be attempted without first subjecting them to a process which will thoroughly destroy any remaining diazo intermediate.

(For example dropping the oily product into boiling dibutyl ether.) Finally they should be run <u>only</u> on a small mole scale.

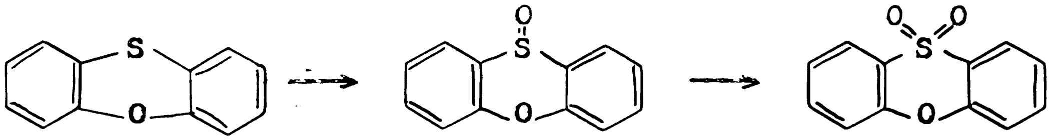
The preparation of sulfoxides and sulfones from sulfides as well as sulfones from sulfoxides by oxidation procedures (26) has taken many


(26)

variations in this investigation. The oxidation products have been very useful as solid derivatives and their infra-red spectra correlation with that of the sulfide derivatives was of invaluable aid in solving many of the more difficult structural problems. The original oxidations were carried out employing an excess of 30% hydrogen peroxide in acetic acid as a solvent and this reagent was successful in cases of simple halogen substitution products. However as the number of halogen substituents on the aromatic ring increased it was found that even repeated treatment with this same reagent was not sufficient to obtain a good conversion of the sulfides to the sulfones. Infra-red spectra of the impure oxidation products showed strong sulfoxide bands in the 9-10 micron region. In addition when methyl groups were present on the aromatic rings the sulfone products were found to be contaminated by small amounts of the carboxylic acids (27) which further complicated the purification of

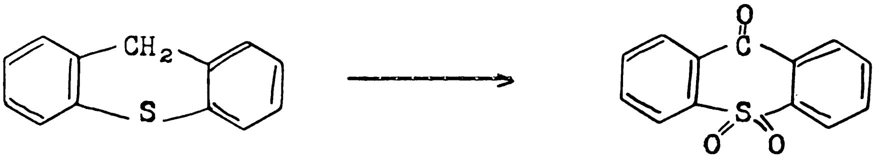

(27)

the oxidation products. Obtaining sulfoxides by oxidation with hydrogen peroxide in acetic acid proved to be quite a problem in cases where the solubility of the sulfide was low in this reagent. Any attempt to use reaction temperature above that of room temperature to increase the sulfide solubility resulted in some sulfone formation which must be avoided since the higher melting sulfone concentrates in the recrystallized product and cannot be completely removed. The use of chromic acid for the oxidation of sulfide and sulfoxide links to sulfones (28) proved to be a very satisfactory procedure for compounds which did not contain alkyl groups in the aryl rings.



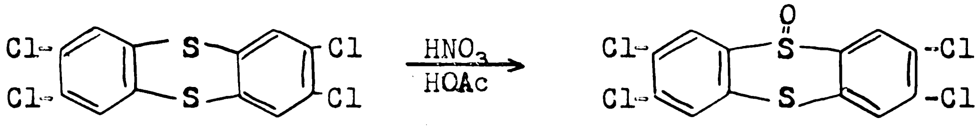
(28)

Three equivalents of chromic acid (CrO_3) per sulfide link and one and one-half equivalents per sulfoxide link were found to be satisfactory quantities of the oxidizing agent. This oxidizing reagent was also useful for the oxidation of the methylene link in thiaxanthene (29) to a carbonyl group using a total of 2 equivalents per methylene group. Oxidation of



(29)

ring substituted methyl groups can also be achieved with this reagent but the carboxy diphenyl sulfones were found to give unsatisfactory melting points as previously indicated by the work of Buehler and Masters.[76] The conversion of thianthrenes to thianthrene monoxides (30) by dropping



(30)

nitric acid into a glacial acetic acid solution of the compound to be oxidized was another good technique and undoubtably deserves more use than has up to the present been made of it.[66,67,68] Some experience was obtained using potassium permanganate in glacial acetic acid as an oxidizing reagent. The reactivity of this reagent seems to vary widely with the structure of the molecule being oxidized. Bost, Turner and Norton[34] recommend that the oxidation be carried out at room temperature with this reagent to obtain the sulfone. However, in actual practice it was found that many of the compounds obtained in the present study were insoluble even in large volumes of solvent at room temperature and that the more highly substituted compounds did not oxidize completely to the sulfone even at reaction temperatures of 70-90°C. Thus it would appear that in this series, at least, that permanganate oxidation may be more useful to obtain sulfoxides and for use in the oxidation of compounds containing ring substituted alkyl groups where oxidation of such groups is not desired.

The reaction of benzenesulfonyl chlorides with benzene derivatives to form sulfones (31)is a well-known reaction.[163] It was very useful

$$\text{R-C}_6\text{H}_5 + \text{R'-C}_6\text{H}_5\text{SO}_2\text{-Cl} \longrightarrow \text{R-C}_6\text{H}_4\text{-SO}_2\text{-C}_6\text{H}_4\text{-R'} + \text{HCl} \qquad (31)$$

in the present studies in characterizing sulfide and sulfoxide derivatives which could be readily oxidized to the sulfone using hydrogen peroxide, chromic acid or potassium permanganate and compared with the sulfone prepared by a direct condensation reaction. The latter method worked well for condensation reactions involving benzene, chlorobenzene and o-dichlorobenzene with benzenesulfonyl chloride, although o-dichlorobenzene showed a marked decrease in yield using standard techniques. Sulfone formation failed, however, when the usual technique (addition of the benzenesulfonyl chloride to a mixture of anhydrous aluminum chloride and an excess of the benzene derivative) was used for the higher chlorinated derivatives and instead only chlorination products were isolated. While chlorination was known to be a side reaction[163] in the condensation reaction no mention was found in the literature where it was reported as the predominate reaction. The mechanism of sulfone formation had been studied by Oliver[164] who found that benzenesulfonyl bromides formed a sulfinate complex (32) with anhydrous aluminum bromide in carbon disulfide.

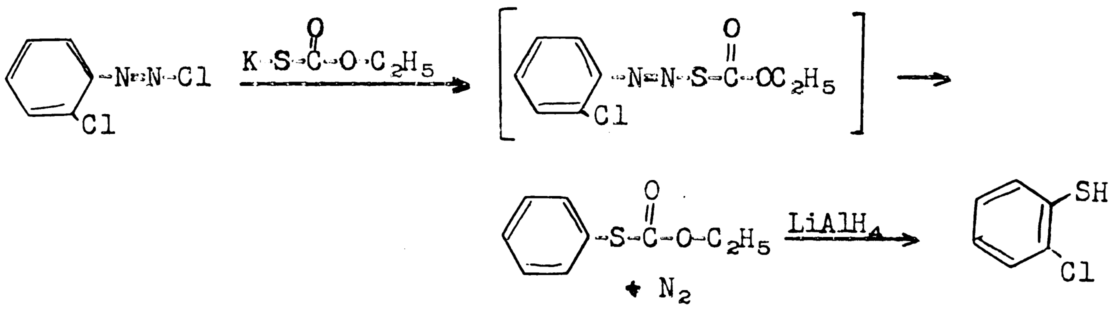
$$\text{p-Br-C}_6\text{H}_4\text{SO}_2\text{-Br} + \text{AlBr}_3 \longrightarrow \text{p-Br-C}_6\text{H}_4\text{-SO}_2\text{-AlBr}_2 + \text{Br}_2 \qquad (32)$$

Suter[163] states that by analogy the same reaction should take place with the chloride and that chlorination products had been isolated.

A very marked departure from the sulfone reaction was found in this work upon changing from o-dichlorobenzene to 1,2,4-trichlorobenzene and also upon using benzenesulfonyl chlorides with chlorine substituted in the ring. In these cases, chlorination proved to be the predominate reaction with only a trace of the sulfone being formed. After several failures to achieve sulfone formation with the higher chlorinated derivatives of benzene the reaction was abandoned until much later in the investigation when the work of Huismann, Uhlenbroek and Meltzer[9] using a modified procedure was found. A re-examination of the earlier failures employing their procedure of adding the aluminum chloride catalyst slowly to a mixture of the sulfonyl chloride dissolved in an excess of the benzene derivative at elevated temperature gave substantial yields of the desired compounds.

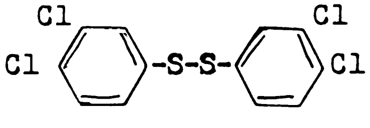
Apparently as the benzene derivative becomes less reactive (due to the negative chlorine substitution) and as the benzene sulfonyl chloride becomes less active[164] it is necessary to avoid an excess of the Friedel Crafts catalyst and add it only as fast as the sulfone is formed which then deactivates the catalyst by complex formation with the sulfone linkage.

The work of Djerrassi, *et al.*,[133] and Campaigne with Osborn[18] who reduced xanthate esters to thiols using lithium aluminum hydride was extended to the preparation of 2-chlorobenzenethiol (**reaction** 33).

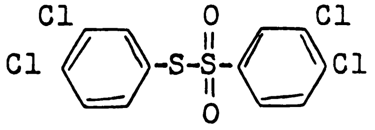


This is believed to be the first application of this reductive method to a chlorinated aryl xanthate. A 70% yield of the thiol was obtained and the method was found to be well suited to small scale synthetic preparation of aromatic thiols. The method also appears to be superior to the usual alkaline hydrolysis of the xanthate ester.

An attempt to prepare 3,4-dichlorobenzenethiol by the reduction of 3,4-dichlorobenzenesulfonyl chloride with lithium aluminum hydride resulted in an incomplete reduction. Bis(3,4-dichlorophenyl)disulfide (XIV) and bis(3,4-dichlorophenyl) thiosulfonate (XV) were isolated from the reduction mixture.

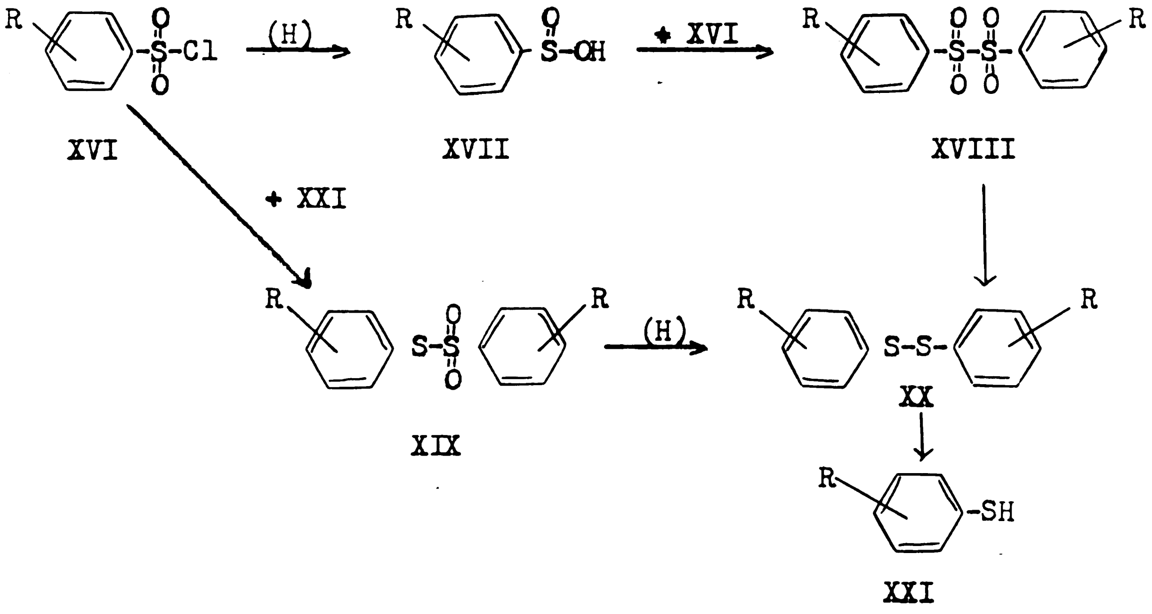


(XIV)



(XV)

These structures (Formulas XIX and XX) fit well into the reduction mechanism (34) for this reaction postulated by Field and Grunwald.[136] (See Historical)



(34)

Disulfides (XX) had been isolated[136,137,139] frequently and Field and Grunwald had shown that the sulfenic acid could be prepared by the use of the inverse addition procedure. However, until recently[135] the thiosulfonate link (XIX) in the reduction sequence had not been experimentally verified. The isolation of the thiosulfonate in the reduction of 3,4-dichlorobenzene sulfonyl chloride lends additional confirmation to this reductive reaction mechanism.

EXPERIMENTAL

Coupling Reactions with Sulfur Monochloride

The Preparation of Diphenyl Sulfide using Sulfur Monochloride

This preparation was carried out to obtain a comparative evaluation of the use of sulfur monochloride versus sulfur dichloride. In practice it parallels the preparation of Hartman, Smith and Dickey[142] in part.

The quantities, 790 g. (10.0 mole) of thiophene-free benzene and 464 g. (3.25 moles) of anhydrous aluminum chloride, were placed in a five-liter three-neck round-bottom flask equipped with a stirrer, thermometer, dropping funnel and a hydrogen chloride scrubbing tower. The mixture was cooled to 5°C. and 405 g. (3.05 mole) of sulfur monochloride dissolved in 450 ml. of ethylene dichloride was added to it during a two hour period. The reaction was quite spontaneous and hydrogen chloride evolution was vigorous during the addition of the sulfur monochloride. Following the addition of the latter reagent the ice bath was removed and the reaction mixture was stirred for four hours. The reaction flask was examined at this point for evidence of the presence of a yellow complex mentioned by the above authors.[142] Some insoluble complex was found to be present but the solution was definitely not viscous nor was it yellow. The reaction mixture was quenched by pouring it into ice water, stirred vigorously to hydrolyze the metal complex, placed in a separatory funnel to separate the oil layer and finally the oily layer was washed consecutively with dilute hydrochloric acid and water. The solvent was removed by vacuum distillation and the residue was cooled to 0°C. The precipitated sulfur was removed by vacuum filtration on a Buchner funnel. The filtrate was mixed with 500 ml. of absolute methanol, cooled to 0°C. in an ice-salt bath, stirred for three hours and the precipitated sulfur was again removed as before. The methanol was removed on a steam bath and the residual oil was distilled through a 10 cm. vigreux column to remove the decomposable and polymeric material. A caustic tower was placed in the vacuum line to absorb the acid fumes and a distillation fraction boiling in the range 51-200°C./ 5 mm. was collected. A 98 g. quantity of a tarry residue remained in the distillation flask. The distillate was refractionated through a 20 cm. vigreux column to obtain 370 g. (2.0 mole, 66.7% yield) of diphenyl sulfide (b.p. 140°C./5 mm., n_D^{20} = 1.6310). The product distilled over a narrow boiling range but had a distinct deep yellow coloration. Further refractionation of the higher boiling materials gave a fraction (b.p. 140-162°C./5 mm.) from which a solid precipitated. The solid was recovered by filtration and recrystallized from ethanol to obtain a material melting at 60-61°C. The solid was identified as diphenyl disulfide. (Literature[165] m.p. 60-61°C.) The filtrate was examined by infra-red technique and found to contain mono and para-substitution products which indicated that some chlorination of the product had taken place. The fraction boiling at 163-188°C./5 mm. likewise precipitated a solid material which distilled at 188-190°C./5 mm. This material was recrystallized from glacial acetic acid to obtain a solid with a melting point of 154.5°C. The material was identified as thianthrene. No attempt was made to obtain a quantitative evaluation of the amounts of these materials which were present since the quantities present were too small to make it practical.

Coupling Reactions with Sulfur Dichloride

The Preparation of Diphenyl Sulfide with Sulfur Dichloride

This preparation was carried out using the same molar basis of reactants as were employed in the synthesis of diphenyl sulfide using sulfur monochloride to obtain a comparative evaluation of the two reagents, sulfur mono- and dichloride.

The quantities, 790 g. (10.0 moles) of thiopene-free benzene and 494 g. (3.25 moles) of anhydrous aluminum chloride, were placed in a five-liter three-neck round-bottom flask. The mixture was cooled to 5°C. and 309 g. (3.0 mole) of sulfur dichloride dissolved in 450 ml. of ethylene dichloride was added during a two hour period. A copious evolution of hydrogen chloride accompanied the addition of sulfur dichloride after which the reaction mixture was stirred for four hours without external cooling. The product was isolated in a manner identical to that used in the sulfur monochloride experiment up to the point where the elemental sulfur was removed. Instead of cooling the oily residue after solvent removal it was immediately distilled through a 10 cm. vigreux column to remove the decomposable and polymeric material. It was necessary to place a caustic tower (sodium hydroxide with alternate layers of calcium chloride) in the vacuum line to absorb the hydrogen chloride fumes in order to maintain a vacuum. The internal flask temperature was raised to 250°C. to obtain a distillation fraction boiling in the range 50-160°C./5 mm. and 85 g. of a tarry residue. The distilled material was refractionated through a 20 cm. vigreux column to obtain 407 g. (2.19 moles, 73% yield) of diphenyl sulfide (b.p. 140°C./5 mm., $n_D^{20} = 1.6312$) and 12.0 g. (0.057 mole, 1.9% yield) of 4-chlorophenyl phenyl sulfide (b.p. 151°C./5 mm., $n_D^{25} = 1.6351$) as identified by its infra-red spectrum and its oxidation to 4-chlorophenyl phenyl sulfone, melting at 92-3°C. (Literature[150] m.p. 91-2°C.) The diphenyl sulfide prepared using sulfur dichloride as the coupling agent had a straw-yellow color in contrast to the reddish-yellow coloration found in the product from sulfur monochloride. The sulfur dichloride gave a higher yield of the desired diphenyl sulfide.

Bis(4-Chlorophenyl) Sulfide by Condensation

This material was prepared using a normal Friedel Crafts procedure by placing 900 g. (8.0 moles) of chlorobenzene and 266 g. (2.0 moles) of anhydrous aluminum chloride in a two-liter three-neck round-bottom flask suitably equipped and adding 206 g. (2.0 moles) of sulfur dichloride, while cooling the reaction mixture in an ice bath, during a two hour period. Copius hydrogen chloride evolution occurred during the addition of the dichloride and continued slowly during the one hour stirring period following its addition. The reaction mixture was warmed to 45°C. for twenty minutes, quenched by pouring it into ice water, and stirred vigorously to hydrolyze the metal complex. The oily layer was separated and washed consecutively with dilute hydrochloric acid and water. The excess chlorobenzene was removed by vacuum distillation and the residue fractionated through a 15 cm. vigreux column to obtain a sulfide fraction (b.p. 169°C./2 mm.) weighing 354 g. (69.5% yield) which gradually solidified in the receiver. Heavy decomposition occurred during the final stage of the distillation and a brittle tar formed in the distillation flask. Dichlorothianthrene was not isolated in this experiment since the reaction period was too short to permit a ring closure to occur. The sulfide fraction was taken up in a large volume of alcohol, treated with darco, filtered and allowed to cool slowly at room temperature. If the solution was too concentrated the sulfide would separate from the solution as an oil before it had cooled very much and then additional alcohol had to be added and the entire solution had to be reheated to its boiling point and the process repeated. Alcohol proved to be a rather poor recrystallization solvent for the impure material but the opportunity to select a better media did not present itself during the work. The first recrystallization gave material melting at 78-82°C., the second 84-7°C., the third 88-90°C., the fourth 93.5-95°C., and finally the fifth recrystallization gave 94-95.5°C. A 39% yield of purified material was obtained. The literature[12,85,79,143] lists melting points ranging from 88-98°C. for this compound indicating heavy contamination from impurities such as isomers. This material was prepared early in the present investigation before the infra-red technique for isomer identification and separation was evolved and as a result the impure oily residues left in the alcohol filtrates were not studied further. The sulfide was prepared later from purified bis(4-chlorophenyl) sulfoxide using a zinc reduction in acetic acid to obtain an 84% yield of beautiful plate crystals melting at 95-6°C.

Some of the bis(4-chlorophenyl) sulfide (m.p. 94-95.5°C.) was oxidized with chromic acid in galcial acetic acid to obtain an 88% yield of bis(4-chlorophenyl)sulfone melting at 147-8°C. Literature value[8] m.p. 147.5°C.

Bis(4-Bromophenyl) Sulfide

In a three-liter three-neck round-bottom flask fitted with a stirrer, thermometer, dropping funnel and gas scrubber were placed 2,240 g. (14.0 moles) of bromobenzene and 200 g. (1.5 moles) of anhydrous aluminum chloride. The reaction mixture was cooled to 10°C. and 155 g. (1.5 moles) of sulfur dichloride was added during a two hour period. The reaction occurred readily yielding a dark metal complex. After heating the reaction mixture to 45°C. for fifteen minutes it was poured into ice water and stirred vigorously to hydrolyze the metal complex. An orange viscous material which was insoluble in water and bromobenzene settled to the bottom of the flask. The water layer was decanted and the residual material was washed consecutively with dilute hydrochloric acid and water. The bromobenzene and water layers were decanted from the other material, placed in a separatory funnel and separated. The excess bromobenzene was removed by vacuum distillation and the viscous material was added to the distillation flask using the distilled bromobenzene to wash it into the flask. The bromobenzene was again removed by distillation carrying with it the residual moisture from the viscous material. A fractionation of the residue was made through a 15 cm. vigreux column The first fraction (b.p. 30-160°C./2 mm.) appeared to be a chlorination product of bromobenzene. However, after recrystallization from ethanol it melted at 87-8°C. and its infra-red spectrum exhibited para-substitution. (Absorption at 12.35 microns) Since 1-bromo-4-chlorobenzene melts at 67-8°C. this possibility was immediately eliminated and the compound was identified as 1,4-dibromobenzene (Literature value[166] m.p. 89°C.) by comparison with a known sample of the later material. Fraction II (b.p. 160-220°C./2 mm.) solidified in the receiver as an orange solid (weight 247 g.) and Fraction III (weight 5 g.) distilled in the boiling range 220-290°C./2 mm. Decomposition set in when the internal flask temperature reached 260°C. The non-distillable residue cooled to a hard brittle tar (weight 95 g.). Fraction II was redistilled (b.p. 205-10°C./2 mm.) to obtain a slight color improvement and a narrow boiling range material. This was recrystallized from a large volume of ethanol to obtain 144 g. (0.42 mole, 28% yield) of bis(4-bromophenyl) sulfide melting at 112-113°C. (Literature value[144] m.p. 112-113°C.) Fraction III was recrystallized twice from glacial acetic acid to obtain a product melting in the temperature range 125-140°C. which probably contained some dibromothianthrene but there was not enough of the material to attempt fractional crystallization of the possible isomers. A second preparation of bis(4-bromophenyl) sulfide which allowed 60 hours contact time gave only decomposable material and no product.

Although bromobenzene has been reported to interact with thionyl chloride[79] no previous record of its reaction with sulfur mono- or dichloride was found in the literature.

The Reaction of Sulfur Dichloride with o-Dichlorobenzene

This particular reaction was investigated in some detail since both the diphenyl sulfide and thianthrene isomers were produced and the isomer possibilities were relatively simple. In a three-liter three-neck round-bottom flask equipped with a stirrer, thermometer, dropping funnel, and hydrogen chloride scrubber were placed 1433 g. (9.75 moles) of o-dichlorobenzene (better than 99% pure), 266 g. (2.0 moles) of anhydrous aluminum chloride, and 250 ml. of ethylene dichloride as a reaction media. The reaction mixture was cooled to 10°C. and 258 g. (2.5 moles) of sulfur dichloride dissolved in 500 ml. of ethylene dichloride was added during a ten hour period. At the end of the addition of the sulfur dichloride the reaction flask was removed from the ice bath and the reaction mixture was stirred for 48 hours, warmed to 50°C. for a half hour and then quenched by pouring it into ice water. Some solid was precipitated upon hydrolysis of the metal complex and the addition of more ethylene dichloride to the hydrolysis mixture followed by warming it to 70°C. failed to dissolve the precipitate and it was necessary to remove the precipitate by filtration prior to attempting product isolation. The solid was recrystallized from ethylene dichloride to obtain 35 g. of a yellowish-white colored solid melting at 272-3°C.

Anal. Calc'd for $C_{12}H_4Cl_4S_2$: C, 40.70; H, 1.13; Cl, 40.05; S, 18.11

Found: C, 40.77; H, 1.37; Cl, 39.41; S, 17.77

The analysis suggested that the material was a tetrachlorothianthrene. Its infra-red spectrum in carbon disulfide (see Figure 57) had a single peak in the substitution region (11-14.5 microns) at 11.40 microns. The only tetrachlorothianthrene isomer derivable from o-dichlorobenzene which would give only a single hydrogen deformation peak that appears at this location would be 2,3,7,8-tetrachlorothianthrene. The material was oxidized to a tetroxide in 91% yield using chromium trioxide in glacial acetic acid by the usual procedure. The dried solid was recrystallized from acetone to obtain the 2,3,7,8-tetrachlorothianthrene-5,5,10,10-tetroxide melting at 314-314.5°C.

Anal. Calc'd for $C_{12}H_4Cl_4O_4S_2$: C, 34.46; H, 0.96; Cl, 33.86; S, 15.33

Found: C, 34.52; H, 1.00; Cl, 33.86; S, 15.21

Oxidation of the tetrachlorothianthrene with dilute nitric acid in glacial acetic acid as previously described in another experimental section of this thesis gave the 2,3,7,8-tetrachlorothianthrene-5-oxide melting at 278.5-279°C. The infra-red spectra of the two oxidation products gave additional confirmation to the assignment of structure since the single hydrogen deformation peak at 11.40 microns (for the parent structure) is very definitely modified in the spectra of the oxidation products as would be expected for the assigned structure (see discussion of single hydrogen interaction with adjacent sulfoxide and sulfone groups in the appendix).

After characterization of the solid recovered by filtration the oily layer was separated from the filtrate, added to the mother liquor from the recrystallization of the tetrachlorothianthrene and washed consecutively with 6N hydrochloric acid and water. The ethylene dichloride was removed by distillation under vacuum and a crude fractionation of the unreacted o-dichlorobenzene was made. Redistillation of the o-dichlorobenzene gave 709 g. (4.82 moles) of recovered starting material boiling at 60°C. (10 mm.). The crude product was then distilled through a 10 cm. vigreux volumn to remove tarry residues. Considerable hydrogen chloride was evolved at the beginning of the distillation and it was necessary to introduce a tower into the vacuum line filled with alternating layers of sodium hydroxide and anhydrous calcium chloride (which absorbed the moisture formed in the neutralization of the acid and prevented plugging of the tower). When the decomposable material had been broken down by heat the residue distilled normally to give a crude product distilling in the temperature range 150-280°C. (1 mm.). A brittle tar residue (weight 76 g.) remained in the distillation flask. The distillate was refractionated through a twenty cm. vigreux column to obtain 420 g. of crude tetrachlorodiphenyl sulfide [b.p. 200°C. (3 mm.)]. The column was then removed and the crude tetrachlorothianthrene [weight 71 g., b.p. 260°C. (1 mm.)] was distilled using a still head as a short path column. The crude tetrachlorothianthrene was recrystallized from chlorobenzene to obtain a fairly pure product melting at 267-70°C. This material was recrystallized twice from ethylene dichloride to obtain 38 g. of yellowish-white colored solid melting at 272-3°C. which was found to be identical to the 2,3,7,8-tetrachlorothianthrene which had been characterized earlier. The mother liquors from the recrystallizations were combined and the solvent was removed by vacuum distillation. The residue was recrystallized from ethanol and the crude material (m.p. 245-252°C.) obtained was examined by infra-red and found to exhibit peaks in the substitution region at 11.40, 12.00, 12.40 and 13.10 microns (see Figure 55). After comparison with the spectrum of the previously isolated thianthrene isomer (see Figure 57) it was clear that an additional isomer was present. The initial separation of this isomer proved to be very difficult but it was eventually found that extraction of the crude 2,3,7,8-tetrachlorothianthrene (m.p. 245-252°C.) with alcohol in a Soxhlet extractor concentrated the new isomer in the solvent and a simple series of crystallizations from alcohol isolated a pure material melting at 180-180.5°C.

Anal. Calc'd for $C_{12}H_4Cl_4S_2$: C, 40.70; H, 1.13; Cl, 40.05; S, 18.11

Found: C, 40.58; H, 1.36; Cl, 40.23; S, 18.16

Analysis of the infra-red spectrum of this material (Figure 54) indicated that it was 1,2,7,8-tetrachlorothianthrene since the peak at 11.40 microns could be attributed to the two single hydrogens in the 6 and 9 positions and the peak at 12.40 microns could be attributed to the two adjacent hydrogens in the 3 and 4 positions. The peak at 13.10 microns is undoubtably a carbon-chlorine absorption. This isomer would arise from the ring closure of the 2,3,3',4'-tetrachlorodiphenyl sulfide which was isolated later. Oxidation of the 1,2,7,8-tetrachlorothianthrene with chromic acid in glacial acetic acid by the usual procedure gave the tetroxide. This was recrystallized from ethanol to obtain a 89% yield of 1,2,7,8-tetrachlorothianthrene-5,5,10,10-tetroxide as a colorless crystalline solid melting at 191-191.5°C.

Anal. Calc'd for $C_{12}H_4Cl_4O_4S_2$: C, 34.46; H, 0.96; Cl, 33.86; S, 15.15

Found: C, 34.53; H, 1.20; Cl, 33.72; S, 15.15

The infra-red spectrum of this material (Figure 55) provided further support for the structure assignment since the single hydrogen deformation peak at 11.40 microns in the infra-red spectrum of the parent compound was depressed and broadened, the peak due to the two adjacent hydrogens at 12.40 microns was split to give peaks at 12.1 and 12.9 microns and the carbon-chlorine peak at 13.10 microns was displaced to 14.4 microns and strengthened as would be expected from sulfone interaction with the ring hydrogens (see infra-red spectrum discussion in the appendix).

A total of 5.1 g. (0.0143 mole) of the 1,2,7,8-tetrachlorothianthrene (m.p. 180-180.5°C.) was purified. Recrystallization of the material remaining in the Soxhlet thimble from ethylene dichloride yielded an additional 21 g. (0.059 mole) of the 2,3,7,8-tetrachloro isomer and there were in addition a number of mixed tetrachlorothianthrene fractions which had a combined weight of 22.1 g.

The tetrachlorodiphenyl sulfide fraction crystallized on being set aside and was recrystallized from ethanol to give 350 g. (1.08 moles) of impure bis(3,4-dichlorophenyl) sulfide melting at 68-70°C. Ethanol proved to be a very poor recrystallization solvent for the crude sulfide since the material oiled badly and excess solvent had to be used to make an effective isomer separation. The impure sulfide was recrystallized an additional three times from ethanol to obtain 275 g. (0.85 mole) of purified bis(3,4-dichlorophenyl) sulfide melting at 74-5°C.

Anal. Calc'd for $C_{12}H_6Cl_4S_1$: C, 44.47; H, 1.86; Cl, 43.76: S, 9.89

Found: C, 44.25; H, 2.00; Cl, 43.40; S, 9.81

The material exhibited an infra-red spectrum typical of 1,2,4 substitution with a single hydrogen deformation peak at 11.50 and that from the two adjacent ring hydrogens at 12.35 microns. The sulfide was oxidized in the usual manner with chromium trioxide to obtain a 90% yield of bis(3,4-dichlorophenyl) sulfone melting at 174-5°C. This material was identical with that obtained as a by-product in the chlorosulfonation of o-dichlorobenzene. Literature value,[8] m.p. 173-4°C.

The alcohol mother liquor from the recrystallization of the bis(3,4-dichlorophenyl) sulfide was evaporated on the steam bath and the residue was fractionated through a 25 cm. vigreux column to obtain nine fractions boiling in the temperature range 200-210°C. (5 mm.). The fractions were examined by infra-red and it was found that a new peak at 13.01 microns appeared that was not present in the spectrum of the bis(3,4-dichlorophenyl) sulfide. The higher boiling fractions solidified into a mush and the sulfide was slurried with alcohol, filtered and the solid was recrystallized from ethanol to obtain an additional amount of the bis(3,4-dichlorophenyl) sulfide. The filtrates and the lower boiling fractions were recombined, fractionally distilled, and the sulfide again isolated upon solidification. The third time this process was repeated solidification occurred in the lower fractions. This solid was filtered from the oil and recrystallized from ethanol to obtain a light yellow colored solid melting at 45-45.5°C. after two recrystallizations.

Anal. Calc'd for $C_{12}H_6Cl_4S_1$: C, 44.47; H, 1.86; Cl, 43.76; S, 9.89

Found: C, 44.58; H, 1.91; Cl, 44.03; S, 9.95

The infra-red spectrum of this material (Figure 30) exhibited peaks at 11.50, 12.35 and 13.01 microns. The first two peaks are characteristic of 1,2,4 type substitution as was found in the previous isomer isolated and the third is characteristic of 1,2,3 type substitution such as is found in the spectrum of 1,2,3-trichlorobenzene (Figure 7). Obviously the only unsymmetrical sulfide isomer obtainable from o-dichlorobenzene is the 2,3,4',4'-tetrachloro diphenyl sulfide which agrees with the spectral analysis. A total of 4.5 g. (0.0139 mole) of purified material was obtained and there was 45 g. of a mixture of sulfide isomers remaining as an oil which was not prufied further. An additional 36 g. (0.11 mole) of the symmetrical isomer was obtained as a result of the sweating process employed for the isolation of the unsymmetrical isomer. The sulfide was then oxidized in the usual manner with chromic acid in glacial acetic acid to obtain an 88% yield of the 2,3,4',4'-tetrachlorodiphenyl sulfone melting at 167.5-169°C. after recrystallization from alcohol.

Anal. Calc'd. for $C_{12}H_6Cl_4O_2S_1$: C, 40.57; H, 1.69; Cl, 39.83; S, 9.00

Found: C, 40.82; H, 1.89; Cl, 39.70; S, 9.00

Results for the over-all yields obtained were as follows:

Compound	Product Weight (g)	Moles	Moles of S Acct. For
bis(3,4-dichlorophenyl) sulfide	311	0.96	0.96
2,3,3',4'-tetrachlorodiphenyl sulfide	4.5	0.0139	0.0139
sulfide residues	45.0	0.139	0.139
2,3,7,8-tetrachlorothianthrene	94	0.264	0.528
1,2,7,8-tetrachlorothianthrene	5.1	0.0143	0.028
thianthrene residues	22.1	0.062	0.124
tarry residues	76		

Total moles of sulfur accounted for 1.77

This compared with 2.5 moles of sulfur in the initial sulfur dichloride. The large amount of thianthrene formed in this reaction was attributed to the low catalyst ratio (i.e., 2.00/2.50 mole ratio).

Eight of the nine compounds described in this section have not previously been described in the literature.

Bis(2,4-Dichlorophenyl) Sulfide

This condensation was run in the presence of 100 ml. of ethylene dichloride as a reaction medium and diluent since m-dichlorobenzene is a sufficiently difficult chemical to obtain that a large excess of the compound could not be used. The quantity, 203 g. (1.40 moles) of m-dichlorobenzene was placed in a 500 ml. flask with the solvent and 45 g. (0.30 mole) of anhydrous aluminum chloride. A red-brown complex color appeared prior to the addition of the sulfur dichloride. The careful addition of 25 g. (0.24 mole) of sulfur dichloride was started at 25°C. and a rapid temperature rise of the reaction mixture to 31°C. was observed, whereupon an ice water bath was placed under the reaction flask and the remainder of the sulfur dichloride was added. The complex coloration rapidly changed to a rust-brown color and hydrogen chloride evolution was rapid. The complete addition of sulfur dichloride at 10°C. required six hours, after which the reaction mixture was stirred at room temperature for 48 hours. The reaction was then quenched in dilute hydrochloric acid and the oil layer was separated and washed. The solvent was removed by distillation and the excess m-dichlorobenzene was recovered and redistilled (b.p. 76°C./4 mm.) to give 108 g. (0.735 mole) of pure m-dichlorobenzene. The initial distillation residue on vacuum distillation gave a yellow oil (b.p. 201-8°C./3 mm.). There were 5 g. of black tar in the distillation flask and no evidence of decomposition was observed during the fractionation. The yellow oil solidified after being set aside for twelve hours at room temperature and this solid on recrystallization from absolute ethanol gave 50 g. (0.154 mole, 64% based on the sulfur dichloride) of white needles melting at 58.5-59.5°C. An infra-red spectrum of this material in carbon disulfide gave substitution peaks at 12.30 and 11.55 microns which is characteristic of 1,2,4 substitution showing the compound to be bis(2,4-dichlorophenyl) sulfide.

Anal. Calc'd for $C_{12}H_6Cl_4S_1$: C, 44.47; H, 1.86; Cl, 43.76; S, 9.89

Found: C, 44.18; H, 1.95; Cl, 43.94; S, 9.82

A 3 g. quantity, (0.0093 moles) of the sulfide and 50 ml. of glacial acetic acid were placed in a 300 ml. round-bottom flask equipped with a reflux condenser and the mixture was brought to its boiling point. Solid chromic acid (2.8 g., 0.028 moles) was then added, portionwise, through the condenser using 25 ml. of acetic acid to wash it into the reaction mixture. The addition of chromic acid was complete in thirty minutes and the mixture was kept at its reflux temperature for an additional fifteen minutes before pouring it into ice water and stirring vigorously to effect crystallization. The solid was recovered by filtration and washed with water until the greenish coloration disappeared. It was then recrystallized from absolute ethanol to give 3.0 g. (0.0084 mole, 91%) of bis(2,4-dichlorophenyl) sulfone melting at 190.5-191.0°C.

Anal. Calc'd for $C_{12}H_6Cl_4O_2S_1$: C, 40.47; H, 1.69; Cl, 39.83; S, 9.00

Found: C, 40.75; H, 1.84; Cl, 39.61; S, 8.93

Neither the sulfide nor the sulfone have been described previously in the literature.

The Reaction of Sulfur Dichloride with p-Dichlorobenzene

Both condensations of sulfur dichloride with p-dichlorobenzene were very similar in their results, but only the latter one will be described here, except to point out that the distillable material obtained from the initial condensation was saved and later combined with the distillate from the second condensation for further work.

The quantity, 294 g. (2.0 moles) of p-dichlorobenzene was placed in a three-liter three-neck round-bottom flask with one liter of ethylene dichloride solvent and 133 g. (1.0 mole) of anhydrous aluminum chloride, catalyst. After the solid had dissolved the reaction mixture was cooled to 20°C. and 103 g. (1.0 mole) of sulfur dichloride was added to it during a period of two and a half hours. Hydrogen chloride evolution was spontaneous and the reaction mixture was stirred for an additional two hours at room temperature following the addition of the sulfur dichloride. It was then warmed to 50°C. for 30 minutes, and quenched by pouring it into cold dilute hydrochloric acid. The metal complex was readily hydrolyzed and a brown colored solid precipitated. The quenched reaction mixture was stirred vigorously for two hours to complete the hydrolysis of any complex in the solid after which it was set aside overnight. After removal of the solid by filtration it was slurried with acetone to remove moisture, filtered and dried to obtain 143 g. of a tan colored solid. The solid did not melt or decompose at temperatures up to 320°C. When it was subjected to a direct flame it burned poorly and formed a black carbonaceous residue. An infra-red examination (KBr pellet technique) indicated a probable 1,2,4 (11.3 and 12.3 microns) and 1,2,4,5 (11.3 microns) substitution pattern as would be expected from a polymeric material. The crude material contained 14.79% sulfur which indicated that the average chain length of the polymer was greater than four p-dichlorobenzene units (sulfur analysis 14.1%).

The filtrate from the reaction quench was placed in a separatory funnel and the solvent layer was separated and washed in the usual manner. The solvent was removed by vacuum distillation and a crude fractionation of the residue gave impure p-dichlorobenzene (48 g., 0.328 mole) boiling in the range 60-90°C./2 mm. (internal flask temperature, 290°C.) at which point decomposition set in and it became impossible to maintain a good vacuum. The vacuum line was changed to a water aspirator, heating was continued at the best vacuum obtainable and an orange colored oil was distilled with the decomposition vapors by using a free flame on the column to superheat the liquid. (In a later similar synthesis it was found that the best technique for handling the decomposition was to insert a caustic tower in the vacuum line to absorb the acid fumes in order to maintain a vacuum which prevented excessive heating of the distillation flask.) The distillation flask contained 100 g. of a black carbonaceous tar. The distillate, an orange oil (weight 15 g.), was combined with 13 g. of a similar oil from the initial condensation and the combined material was set aside for two days during which time a crystalline solid precipitated from the oil. This was recovered by filtration and recrystallized from methanol to yield a small amount of a solid material melting at 215.5-216°C.

Anal. Calc'd for $C_{12}H_4Cl_4S_2$: C, 40.70; H, 1.13; Cl, 40.05; S, 18.11

Found: C, 40.68; H, 1.11; Cl, 40.08; S, 18.16

The infra-red spectrum of this material was determined in carbon disulfide (Figure 56) and the strongest peak in the substitution region appeared at 12.25 microns. Weak peaks appeared at 11.15, 11.40 and 13.40 microns. Examination of the spectrum of 1,2,3,4-tetrachlorobenzene (Figure 10) showed peaks at 11.98, 12.35 and 12.96 microns with the strongest peak at 12.35 microns. Such peaks would be expected from the presence of two adjacent hydrogens. Thus the strong peak in the spectrum of the unknown would indicate a 1,2,3,4 type substitution as expected from 1,4,6,9-tetrachlorothianthrene, the anticipated ring closure product.

The methanol mother liquor was evaporated on the steam bath and the residue was added to the oil filtrate initially obtained from the isolation of the solid material. The combined oil was fractionally distilled through a 20 cm. vigreux column separating it into six fractions:

Fraction	Boiling Range
I	93-116°C./6 mm.
II	118-163°C./6 mm.
III	163-183°C./6 mm.
IV	189-205°C./6 mm.
V	208-225°C./6 mm.
IV	254°C./6 mm.

Infra-red examination of the fractions indicated the presence of a thiol (3.92 microns) in the lower boiling fractions and a 1,2,4-substitution product in the various fractions was indicated by absorption peaks at 11.37 and 12.37 microns. Fraction I (weight 5.0 g.) was placed in a 250 ml. round bottom flask equipped with a reflux condenser and 1.8 g. of potassium hydroxide dissolved in 50 ml. of absolute ethanol was added to the oil to obtain the potassium salt of the thiol.[34] The quantity, 5.6 g. (0.028 mole), of 2,4-dinitrochlorobenzene dissolved in 100 ml. of absolute ethanol was added slowly to the reaction flask. A spontaneous exothermic reaction took place with precipitation of an orange solid. After all of the dinitro solution had been added to the reaction mixture it was heated on the steam bath for 30 minutes to insure completion of the reaction. The mixture was cooled and the precipitate was recovered by filtration and recrystallized from a large volume of alcohol to obtain 5.0 g. of a yellow sulfide melting at 167.5-168°C.

Anal. Calc'd for $C_{12}H_6Cl_2N_2O_4S_1$: C, 41.75; H, 1.75; Cl, 20.54; S, 9.29

Found: C, 41.90; H, 1.86; Cl, 20.52; S, 9.15

The 2,5-dichlorophenyl-2,4-dinitrophenyl sulfide (2.0 g.) was oxidized in glacial acetic acid with chromium trioxide by the usual procedure to obtain a 91% yield of the sulfone melting at 177.5-178.5°C.

Anal. Calc'd for $C_{12}H_6Cl_2N_2O_6S_1$: C, 38.21; H, 1.60; Cl, 18.80; S, 8.50

Found: C, 38.29; H, 1.55; Cl, 18.97; S, 8.51

Thus it was definitely shown that the forerun was the decomposition product 2,5-dichlorobenzenethiol. Neither of the two derivatives described above for this aryl mercaptan have been previously described in the literature although the parent thiol (m.p. 27°C.) is known.[167,168]

Fractions III and IV were slurried with absolute alcohol and a yellow solid crystallized from the oily material. The solid was filtered and recrystallized from alcohol to obtain a crystalline solid melting at 114-115°C. Its infra-red spectrum (Figure 37) showed a typical 1,2,4 substitution pattern as would be expected from bis(2,5-dichlorophenyl) sulfide.

Anal. Calc'd for $C_{12}H_6Cl_4S_1$: C, 44.47; H, 1.86; Cl, 43.75; S, 9.89

Found: C, 44.92; H, 2.09; Cl, 43.66; S, 9.87

Oxidation of the sulfide with chromic acid in glacial acetic acid by the usual procedure produced the sulfone (m.p. 178.5-179°C.) in 89% yield. Crowell and Raiford[169] report the melting point to be 179°C. for the bis(2,5-dichlorophenyl) sulfone, as obtained by the sulfonation of p-dichlorobenzene.

Bis(2,4,5-Trichlorophenyl) Sulfide

A 210 g. (1.16 moles) quantity of 1,2,4-trichlorobenzene was placed in a 500 ml. three-neck round-bottom flask equipped for a condensation reaction. The flask was placed in an ice bath, cooled to 10°C., and 40 g. (0.30 mole) of anhydrous aluminum chloride was added. A light orange metal complex slowly formed but quickly changed to a dark red color with the addition of 31 g. (0.30 mole) of sulfur dichloride. The addition required an hour during which hydrogen chloride evolution was spontaneous. The ice bath was removed and the reaction mixture was stirred at room temperature for a period of forty-eight hours (the condenser was protected with a calcium chloride drying tube). At the end of this period the reaction mixture was warmed to 70°C. for one hour and then quenched in cold dilute hydrochloric acid. Quenching caused a solid to crystallize from solution and it was necessary to add additional ethylene dichloride and heat the mixture to 70°C. to effect complete solution. The solvent layer was separated and washed consecutively with dilute hydrochloric acid and water. Solvent removal was accomplished by distillation under vacuum and the residue was fractionated to yield 82 g. (0.45 mole) of 1,2,4-trichlorobenzene (b.p. 86°C./13 mm.) and 78 g. of a higher boiling fraction (b.p. 217°C./2 mm.) which solidified in the receiver. The solid was recrystallized from methyl ethyl ketone to obtain 68 g. (57.5% yield) of white crystalline hexachlorodiphenyl sulfide melting at 149-150°C.

Anal. Calc'd for $C_{12}H_4Cl_6S_1$: C, 36.67; H, 1.02; Cl, 54.13; S, 8.16

Found: C, 36.72; H, 1.16; Cl, 54.32; S, 8.16

The infra-red spectrum of this material in carbon disulfide (Figure 42) was obtained and found to have a single substitution peak with double points at 11.28 and 11.50 microns. The spectrum was compatible with the structure of bis(2,4,5-trichlorophenyl) sulfide which should show a single hydrogen deformation peak in this region (as is illustrated by the spectrum of 1,2,4,5-tetrachlorobenzene, Figure 8). The sulfide was oxidized with chromic acid in glacial acetic acid by the usual procedure to obtain a 91% yield of bis(2,4,5-trichlorophenyl) sulfone melting at 175-175.5°C. after it had been recrystallized twice from absolute ethanol.

Anal. Calc'd for $C_{12}H_4Cl_6O_2S_1$: C, 33.91; H, 0.94; Cl, 50.06; S, 7.78

Found: C, 33.78; H, 1.25; Cl, 50.00; S, 7.52

The spectrum of the sulfone (not listed in the appendix) likewise showed the single hydrogen deformation peak with the major point at 11.35 microns and minor points on the side of the peak at 11.10 and 11.50 microns. The significance of the jagged peak is discussed in the appendix. Neither the sulfide nor the sulfone had been described previously in the literature.

Bis(2,3,4-Trichlorophenyl) Sulfide

This material was prepared, in 250 ml. of ethylene dichloride, by the condensation of 31 g. (0.3 mole) of sulfur dichloride with 150 g. (0.828 mole) of 1,2,3-trichlorobenzene in the presence of 40 g. (0.30 mole) of anhydrous aluminum chloride. The reaction vessel was a 500 ml. flask equipped with a stirrer, thermometer, dropping funnel, and a gas scrubber. All of the charge except the sulfur dichloride was placed in the flask, cooled to 10°C., and the sulfur dichloride was added over a period of three hours. The reaction mixture warmed to room temperature and stirred for an additional forty-eight hours. It was then heated to 70°C. for one hour, poured onto ice, and acidified with hydrochloric acid to decompose the metal complex. Since a small amount of solid precipitated the mixture was warmed to dissolve the solid material and the oil layer was separated and washed with water. The ethylene dichloride was distilled under reduced pressure and the residual material fractionated to obtain hexachlorodiphenyl sulfide (b.p. 215-220°C./4 mm.). The material solidified in the receiver and could be recrystallized from either ethylene dichloride or methyl ethyl ketone to obtain a white crystalline solid melting at 139.5-141°C. The yield of purified product was 61 g. (0.156 mole) which corresponds to a yield of 51.5% based on the sulfur dichloride.

Anal. Calc'd for $C_{12}H_4Cl_6S_1$: C, 36.67; H, 1.02; Cl, 54.13; S, 8.16

Found: C, 36.74; H, 1.23; Cl, 53.85; S, 8.08

The infra-red spectrum of the sulfide (Figure 43) exhibited two major peaks in the substitution region. One of the peaks (12.97 microns) was quite sharp but the other was capped by four individual peals at 12.00, 12.15, 12.30, and 12.45 microns. The infra-red spectrum of 1,2,3,4-tetrachlorobenzene (Figure 10) exhibited peaks at 11.98, 12.35, and 12.96 microns and that of 1,2,3,5-tetrachlorobenzene (Figure 9) exhibited one large peak capped by single peaks at 11.70, 12.00, 12.15, and 12.50 microns. This was confusing since the multiplicity of peaks exhibited did not seem to fit either substitution pattern as was easily done for cases of simpler substitution. Additional evidence was obtained, however, when the spectrum of the sulfone product (Figure 44) was prepared since the spectrum turned out to be surprisingly simple. The two sulfone peaks appeared very strongly at 7.35 and 8.60 microns and strong substitution peaks appeared as a doublet at 11.85 and 12.20 microns with a weaker peak at 13.95 microns. The two spectra could not be interpreted, however, until a sufficient backlog of infra-red spectra had been compiled to allow an interpretation of the influence of the sulfone linkage upon the spectra. The complete explanation of this effect has been placed in the appendix, but the interpretation of this particular case is as follows: If it is considered that the spectrum of bis(2,3,4-trichlorophenyl) sulfide should exhibit the substitution peaks from the out of plane hydrogen deformations of two adjacent hydrogens then a single peak should be observed in the vicinity of 12.25 to 12.75 microns in the spectra of the sulfide and that in the sulfone analog this peak

would be split into two peaks with one peak somewhere near twelve microns and the second near 13 microns. In the case of bis(3,4,5-trichlorophenyl) sulfide the peaks exhibited should arise from the out of plane hydrogen deformations of single hydrogens which normally appear in the region of 11 to 11.5 microns although in this particular case there is more than one single hydrogen on a single benzene ring which tends to shift that peak towards 12 microns and also possibly gives origin to a second peak as is illustrated in the spectra of 1,3,5-trichlorobenzene (Figure 5) as compared to that of meta-dichlorobenzene (Figure 3). In the sulfone analog of that compound the effect of the sulfone linkage would be to damp the amplitude of the peaks in the 11 to 12 micron region and move the peak nearest to 11 microns in that direction. It is rather obvious that the effect noted is that which would be exhibited by bis(2,3,4-trichlorophenyl) sulfide.

The Reaction of Sulfur Dichloride with 1,2,4,5-Tetrachlorobenzene

The quantity, 216 g. (1.0 mole) of 1,2,4,5-tetrachlorobenzene, was placed in a five-liter three-neck round-bottom flask equipped with a stirrer, dropping funnel, thermometer and a reflux condenser. Three liters of ethylene dichloride was added and the mixture was stirred until the majority of the solid had dissolved. Anhydrous aluminum chloride (67 g., 0.5 mole) was then added to the tetrachlorobenzene solution followed by the addition, at room temperature, of 51.5 g. (0.5 mole) of sulfur dichloride during two hours. Hydrogen chloride evolution was slow so that it was difficult to tell if the reaction was proceeding properly. The reaction mixture was stirred for 16 hours, heated to 50°C. for 30 minutes and then quenched in ice water. The oil layer was separated, washed with water, and the solvent removed by distillation under reduced pressure. The residue was transferred to a small distillation flask and the crude product was sublimed, at 30 mm. pressure, into a receiving flask. The internal temperature of the distillation flask reached 300°C. before gaseous decomposition products prevented the maintenance of a vacuum. It was obvious from the nature of the distillation that the majority of the distillate was recovered starting material and that any possible product had co-distilled with the last of the tetrachlorobenzene. Since it had not been possible to fractionate the product it was recrystallized from ethylene dichloride to recover unreacted tetrachlorobenzene. After the first precipitation the mother liquor was reduced in volume and a second precipitation was made to obtain impure tetrachlorobenzene which was recrystallized again to obtain purified tetrachlorobenzene. That mother liquor was added to the previous filtrate and the combined mother liquor was again reduced in volume and a precipitation was made to obtain material melting at 133-135°C. (Note--the melting point of 1,2,4,5-tetrachlorobenzene is 139-140°C.) Infra-red examination of this material revealed that the major substitution peak was at 11.45 microns (which is characteristic of 1,2,4,5 substitution) but that there was a broad peak stump extending from 12.10 to 12.75 microns (which did not appear in the spectrum of pure 1,2,4,5-tetrachlorobenzene) indicating the presence of different substitution product in the impure tetrachlorobenzene. The next precipitation gave material melting at 126-133°C. and the spectrum showed the presence of a new peak at 12.20 microns with a bump appearing on the side of the 1,2,4,5 substitution peak at 11.55 microns. In addition there were new peaks in the spectrum outside of the substitution region (11 to 15 microns) indicating the beginning of a strong concentration of the new compound. A sort of "rare earth type crystallization" was then begun to isolate this material. Several more fractions were isolated from the mother liquor with melting ranges of 10-20°C. and extending below 100°C. in the latter fractions. The high melting fractions were recrystallized from methanol and the mother liquor was added to the solid of next lower melting point range and a recrystallization was made to upgrade the tetrachlorobenzene content of the solid and increase the concentration of the unknown in the mother liquor. This type of procedure was continued until a solid was obtained (from the mother liquor) at the lower end of the melting point ranges which was eventually recrystallized to obtain a solid melting at 72-3°C. The infra-red spectrum of this material (m.p. 72-3°C.) showed peaks in the substitution region (11- to 14.5 microns) with a doublet whose individual peaks were at 11.40 and 11.63 microns and a single peak at 12.18 microns. The melting point of pentachlorobenzene (a possible product of chlorination) was found to be 86°C. and it showed a very similar spectrum (Figure 11) but it was definitely not the same compound since it did not show the doublet peak at 11.40 microns and lacked two strong absorption peaks shown by the unknown material at 8.95 and 9.20 microns. The infra-red spectrum of pentamethyl benzene was obtained and only a single hydrogen peak (which normally would be the only peak exhibited by a 1,2,3,4,5 substituted compound) was found at 11.55 microns indicating that the peak at 12.18 microns (in the unknown spectra and also in the pentachlorobenzene spectrum) was the result of carbon-chlorine vibration rather than ring substitution. The conclusion which must be drawn from this examination is that the compound (m.p. 72-3°C.) exhibits a spectrum which would be compatible with the 1,2,3,4,5 substitution spectrum which would be expected from the desired coupling product, namely, bis(2,3,5,6-tetrachlorophenyl) sulfide. Regretably when the solid (m.p. 72-3°C.) was being recrystallized for analysis the flask was broken and all of the solution was contaminated beyond any hope of recovery so that final conclusive characterization of the material thought to be bis(2,3,5,6-tetrachlorophenyl) sulfide could not be made and there was not sufficient residues left to fractionate additional material.

The Preparation of Bis(4-Chloro-2-Methylphenyl) Sulfide by Condensation

A one-liter three-neck flask was equipped for a condensation reaction and 232 g. (1.83 moles) of meta-chlorotoluene, 500 ml. of ethylene dichloride and 60 g. (0.45 mole) of anhydrous aluminum chloride were added to the reaction flask. The quantity, 51.5 g. (0.5 mole), of sulfur dichloride dissolved in 100 ml. of ethylene dichloride was added to the pre-cooled (10°C.) reaction mixture. The addition of the dichloride solution required one hour; external cooling was removed and the reaction mixture was stirred, at room temperature, for 48 hours. The reaction proceeded vigorously, evolving hydrogen chloride when the reaction mixture was warmed to 60°C. It was kept at this temperature for thirty minutes and then quenched by pouring it into cold water. The oily layer was separated, washed, and vacuum distilled through a 15 cm. vigreux column. The meta-chlorotoluene was recovered in the forerun and the sulfide fraction was collected at b.p. 200-216°C./2 mm. A small highers fraction boiling at 216-250°C./2 mm. was also collected. The final distilling flask temperature was 365°C. and there was only a trace of hydrogen sulfide evolution at the conclusion of the distillation. A black residue of 25 g., which was easily broken up after cooling, remained in the distillation flask. The product fraction was distilled a second time through a 20 cm. vigreux column to obtain 39 g. (27% yield) of a sulfide boiling at 217-219°C./2 mm. (n_D^{25} = 1.6292). Bis(2-methyl-4-chlorophenyl) sulfide as prepared by the sulfoxide reduction had a refractive index, n_D^{25} = 1.6204. The infra-red spectrum of the present material was essentially identical with that prepared by the sulfoxide reduction reaction method (Figure 45). The sulfide obtained by the condensation method was oxidized with potassium permanganate in glacial acetic acid by the method of Bost, Turner and Norton[27] to obtain a 55% yield of the sulfone melting at 139.5-140.5°C. Balasubramanian and Baliah[40] obtained a m.p. 139-140°C. for bis(4-chloro-2-methylphenyl) sulfone so it is reasonable to assume from this data that the material prepared is predominately bis(4-chloro-2-methylphenyl) sulfide. The higher boiling material was redistilled but it gave a very tacky oil and efforts to crystallize it from several solvents were without success. It was discarded since its spectra failed to give any absorption bands which looked like the 1,2,3,5 substitution spectra to be expected from a thianthrene derivative.

Bis(2,4-Dichloro-3-Methylphenyl) Sulfide

The quantity, 193 g. (1.20 moles), of 2,6-dichlorotoluene was placed in a one-liter three-neck round-bottom flask equipped for a condensation reaction. Ethylene dichloride (400 ml.) and 32 g. (0.24 mole) of anhydrous aluminum chloride were added to the reaction flask. The reaction mixture was cooled to 10°C. and 26 g. (0.25 mole) of sulfur dichloride dissolved in 50 ml. of ethylene dichloride was added to it during a one hour period. An initial spontaneous reaction was obtained, as evidenced by hydrogen chloride evolution. When this had subsided external cooling was removed and the reaction mixture was stirred at room temperature for twenty four hours and then quenched by pouring it into cold dilute hydrochloric acid. The solution was warmed to dissolve the solid material which facilitated washing and separating the oily layer in the usual manner. On cooling the oily layer a crystalline solid precipitated from the solvent layer. This was recovered by filtration and recrystallized from acetone to obtain a crystalline material melting at 111-112°C.

Anal. Calc'd for $C_{14}H_{10}Cl_4S_1$: C, 47.75; H, 2.86; Cl, 40.27; S, 9.10

Found: C, 47.66; H, 2.71; Cl, 40.25; S, 9.04

A sample of the sulfide (2.0 g., 0.0057 mole) was oxidized in 200 ml. of glacial acetic acid as a solvent using 2.3 g. (0.014 mole) of

potassium permanganate dissolved in 40 ml. of water following the procedure of Bost, Turner and Norton[34] to obtain a 40% yield, after six recrystallizations from ethanol, of a material melting at 167-8°C. The material was submitted for analysis in the belief that it was the sulfone.

Anal. Calc'd for $C_{14}H_{10}Cl_4O_2S_1$: C, 43.77; H, 2.62; Cl, 36.92; S, 8.35

Found: C, 45.77; H, 2.62; Cl, 38.66; S, 8.68

Obviously the material was not the sulfone so the sulfoxide was then considered as a possibility.

Anal. Calc'd for $C_{14}H_{10}Cl_4O_1S_1$: C, 45.68; H, 2.74; Cl, 38.53; S, 8.71

An infra-red spectrum of the sulfide in carbon disulfide (Figure 49) was determined and absorption peaks were found in the substitution region at 11.3 (weak), 12.2 (strong), 12.5 (strong) and 12.9 (strong) microns. An infra-red examination of the sulfoxide using the potassium bromide pellet technique[169,170,171] showed absorption at 11.32 (weak), 11.63 (medium), 12.02, 12.17, 12.28 (three tips on a strong peak), 12.83 (strong), and 13.84 (medium) microns. In the region from 9-10 microns the sulfide exhibited peaks at 9.25 (strong) and 9.95 (strong) microns whereas the sulfoxide spectrum exhibited absorption peaks in this region at 9.25 (strong), 9.48 (strong) and 9.93 (strong) microns and sulfoxide normally exhibited a peak at approximately 9.5 microns. Analysis of these two spectra establish the structure of the sulfide to be bis(2,4-dichloro-2-methylphenyl) sulfide since there is no strong single hydrogen absorption peak in the 11-12 micron region and since a carbon-chlorine absorption

band (13.84 microns) appears in the spectra of the sulfoxide which is characteristic of a compound containing two adjacent hydrogens as would be found in the assigned structure.

The mother liquor from the initial crystallization solution was placed in a distilling flask and the solvent was removed by vacuum distillation. The residue was distilled to obtain the sulfide (b.p. 225°C./8 mm.) which was again recrystallized from acetone to obtain additional quantities of the bis(2,4-dichloro-3-methylphenyl) sulfide melting at 111-12°C. In all a total of 43.0 g. (0.123 mole, 49% yield) of the sulfide was obtained.

A small higher boiling fraction (b.p. 260°C./8 mm.), after cooling, was recrystallized eight times from acetone to obtain 0.5 g. of a solid melting at 227.5-228°C. The spectrum of this material (using the potassium bromide pellet technique) exhibited absorption at 10.95 (medium), 11.55 (strong), 12.50 (strong), 13.80 (weak) and 14.10 (weak) microns. Pentachlorobenzene (Figure 11) exhibits peaks at 11.6 (medium) and 12.3 (strong) microns indicating the above spectrum to be a typical penta substitution type. If it is assumed that this compound is the ring closure product of a symmetrical sulfide, then the material obtained must be 1,3,7,9-tetrachloro-2,8-dimethyl thianthrene which is the only possible product from the two possible symmetrical sulfides.

Anal. Calc'd for $C_{14}H_8Cl_4S_2$: C, 43.99; H, 2.11; Cl, 37.11; S, 16.78

Found: C, 44.05; H, 2.16; Cl, 37.08; S, 16.72

Bis(2,4-Dichloro-5-Methylphenyl) Sulfide

In a typical condensation reaction, 140 g. (0.87 mole) of 2,4-dichlorotoluene, 32.0 g. (0.25 mole) of anhydrous aluminum chloride and 400 ml. of ethylene dichloride were charged into a reaction flask, equipped as previously described, for such a reaction. A solution of 26 g. (0.25 mole) of sulfur dichloride dissolved in 100 ml. of ethylene dichloride was added, at 20°C., to the stirred mixture during a two hour period. The reaction mixture was stirred an additional forty eight hours and quenched by pouring it into water with vigorous stirring. The oily layer was separated, washed as usual and set aside in a refrigerator overnight. A yellow solid precipitated which was recovered by filtration and dried to obtain 38 g. of a yellowish material which melted at 130-131°C. after recrystllization from acetone.

Anal. Calc'd for $C_{14}H_{10}Cl_4S_1$: C, 47.75; H, 2.86; Cl, 40.27; S, 9.10

Found: C, 47.96; H, 2.81; Cl, 40.27; S, 9.05

An infra-red spectrum of this material (Figure 48) exhibited multiple single hydrogen out of plane absorption peaks at 10.95, 11.25 and 11.45 (all medium) microns with a carbon-chlorine peak at 13.96 (medium) microns. This is compatable with the spectrum to be expected from bis(2,4-dichloro-5-methylphenyl) sulfide which contains four single hydrogen out of the plane absorption peaks.

The sulfoxide was prepared by dissolving 2.0 g. (0.0057 mole) of the sulfide, contained in a one-liter round-bottom flask, in 500 ml. of glacial acetic acid at 60°C. The sulfide was oxidized by adding 2.3 g.

(0.015 mole) of potassium permanganate slurried with 35 ml. of water to the stirred sulfide solution and keeping it at a temperature of 60°C. for thirty minutes. Sodium bisulfite was added to destroy the excess permanganate and the reaction mixture was poured into ice water to isolate the sulfoxide. The solid was filtered, dried and recrystallized from acetone to obtain 1.25 g. (0.0037 mole) (64% yield) of bis(2,4-dichloro-5-methylphenyl) sulfoxide melting at 167-167.5°C.

Anal. Calc'd for $C_{14}H_{10}Cl_4O_1S_1$: C, 45.68; H, 2.74; Cl, 38.53; S, 8.71

Found: C, 45.74; H, 2.66; Cl, 38.58; S, 8.69

Neither of the above compounds has been described previously in the literature.

Bis(2-Methyl-4,5-Dichlorophenyl) Sulfide

The condensation reaction to obtain this sulfide was carried out in the usual fashion. An excess of 3,4-dichlorotoluene (134 g., 0.83 mole) was placed in a one liter flask with 400 ml. of ethylene dichloride as a solvent and 32 g. (0.25 mole) of anhydrous aluminum chloride catalyst was added to the reaction flask. The sulfur dichloride (26 g., 0.25 mole) dissolved in 50 ml. of ethylene dichloride was added, at 15°C., during a one hour period. The reaction mixture was stirred 48 hours following the addition of the sulfur dichloride and then quenched by pouring it into water. The resulting mixture was kept warm and the oily layer was separated and washed in the usual manner. The ethylene dichloride solution was chilled by setting it aside in a refrigerator overnight and the solid which precipitated was recovered by filtration and recrystallized three times from alcohol to obtain a crystalline solid melting at 128.5-129.5°C.

Anal. Calc'd for $C_{14}H_{10}Cl_4S_1$: C, 47.75; H, 2.86; Cl, 40.27; S, 9.10

Found: C, 47.96; H, 2.81; Cl, 40.10; S, 9.05

The infra-red spectrum of the sulfide in carbon disulfide (Figure 47) exhibited multiple single hydrogen out of plane absorption at 11.0 (medium), 11.25 (medium) and 11.5 (medium) microns. This established a 1,2,4,5 type substitution and the structure had to be bis(2-methyl-4,5-dichlorophenyl) sulfide. A total of 32.0 g. (0.091 mole) of purified material was obtained.

The Attempted Condensation of 1-Bromo-2,5-Dichlorobenzene with Sulfur Dichloride

Several attempts had been made to condense the 1,4-dichlorobenzene with sulfur dichloride to form bis(2,5-dichlorophenyl) sulfide before the reaction described here was tried. Failure to produce anything except an amorphous polymer was attributed to a pronounced tendency of the sulfide to condense further in the 4-position (giving 1,2,4,5 substitution in the benzene ring of the sulfide for which there is apparently a strong driving force). Short chain high-molecular weight compounds of indefinite composition were obtained. The following attempt was made to block the reactive position (para to the sulfide linkage) with a bromine atom which could later be removed by zinc reduction to obtain bis(2,5-dichlorophenyl) sulfide.

A 150 ml. volume of ethylene dichloride, 114 g. (0.5 mole) of 1-bromo-2,5-dichlorobenzene, and 33 g. (0.25 mole) of anhydrous aluminum chloride were placed in a 500 ml. round-bottom flask equipped with a stirrer, thermometer, dropping funnel, and a gas escape tube fitted with a calcium chloride tube. Sulfur dichloride, 25 g. (0.25 mole), dissolved in 50 ml. of ethylene dichloride was added to the mixture at room temperature over a half hour period. The reaction temperature rose to 40°C., hydrogen chloride evolution was spontaneous and the metal complex formed was blue-black in color. The reaction mixture was stirred an additional hour and set aside for half a day, during which time it set to a thick slurry. A 50 ml. quantity of solvent was added to the slurry and it was stirred two hours. The mixture was then quenched in 6N hydrochloric acid and a tan solid appeared making hydrolysis of the metal complex quite slow. The solid, removed by filtration, was washed with water and dried in an oven. It weighed 84 g., was insoluble in all of the usual solvents at their boiling points, had an amorphous character and an indefinite melting point. The material was essentially identical with that produced from a similar reaction of 1,4-dichlorobenzene with sulfur dichloride. The oil layer was washed with dilute hydrochloric acid and water, distilled under vacuum to remove the solvent and fractionated to yield 5 g. of 1-bromo-2,5-dichlorobenzene (b.p. 64°C./1.5 mm.) and a solid which sublimed from the residue. The solid was recrystallized from ethanol and gave 6 g. of a material melting at 148-150°C. A mixed melting point of this solid with some of the 1,4-dichloro-2,5-dibromobenzene isolated previously in the bromination of

1,4-dichlorobenzene, showed no depression and the infra-red spectra of the two materials were identical. It was concluded that condensation had occurred with bromine displacement from the ring to give a polymeric material similar to that obtained in the condensation of 1,4-dichlorobenzene with sulfur dichloride. A review of the literature, at this point, readily confirmed the sensitivity of ring bromine to displacement by aluminum chloride and this phenomena was later observed in experiments involving the condensation of bromobenzene.

The Attempted Coupling of Thianthrene with Sulfur Dichloride

The condensation of diphenyl sulfide with sulfur dichloride produced a small amount of a high boiling material melting at 314-315°C. Since the main product of that reaction was thianthrene there seemed a high probability that the unknown material was a condensation product involving two molecules of thianthrene with one of sulfur dichloride. The following experiment was under taken to test this possibility. A 60 g. (0.277 mole) quantity of thianthrene (m.p. 154-5°C.) and 770 ml. of ethylene dichloride were placed in a two-liter three-neck round-bottom flask equipped with a stirrer, thermometer, dropping funnel and a reflux condenser. A beautiful purple metal complex formed, upon the addition of 17.0 g. (0.134 mole) of aluminum chloride to the mixture. The reaction mixture was cooled to 10°C. and 13.7 g. (0.134 mole) of sulfur dichloride dissolved in 100 ml. of ethylene dichloride was added to it during a 45 minute period. The metal complex took on a black coloration during this period. Since the evolution of hydrogen chloride was very moderate, the cooling bath was removed and the reaction mixture was allowed to stir at room temperature for 48 hours after protecting the condenser with a calcium chloride tube to exclude moisture. Acid gas evolution was weak throughout the reaction period at room temperature and the reaction mixture was finally warmed to 45°C. for one and one-half hours and then quenched by pouring it into cold dilute hydrochloric acid. The quenched mixture was filtered to remove a rubbery solid (weight 1.4 g.) which proved to be sulfur. The solvent layer was separated and washed in the customary manner; the solvent was then removed under vacuum distillation and an attempt was made to distill the residue. When the distillation flask temperature reached 170°C. gaseous evolution began and it was impossible to maintain a vacuum. The vacuum pump was disconnected, a caustic trap was placed in the line, the flask was connected to a water aspirator and heating was continued until the decomposition had been completed. The vacuum pump was then replaced and a distillation fraction, weighing 62 g., was collected which boiled in the temperature range of 170-190°C./7 mm. About a 3 g. quantity of a tarry residue remained in the distillation flask. The distillate was recrystallized from glacial acetic acid to obtain an impure thianthrene melting at 140-144°C. The mother liquor was concentrated by heating to obtain a second quantity of a material melting at 112-121°C. The experiment was discontinued at this point since the material being sought had both a higher boiling and a higher melting point than the material isolated. It was concluded from the product isolation

carried out that the reaction which had occurred was not complete since sulfur from the hydrolysis of sulfur dichloride was isolated and that undoubtably chlorination[172,85] had taken place instead of the expected coupling. Evidence for this opinion is that the boiling range of the product isolated was slightly higher than that for thianthrene and the material which contaminated the recovered thianthrene was very probably 2-chlorothianthrene (m.p.[85] 84°C.) since the melting point range was quite low. This experiment was not completely satisfying since the known chemistry of thianthrene[85,173,174,84] indicates that it should have undergone a coupling reaction with sulfur dichloride.

The Condensation of Sulfur Dichloride with Thiophene

A cursory investigation, due to the limitation of time, was made of this reaction in order to try and determine a set of experimental conditions in which the acid sensitivity of the thiophene would not lead solely to tar formation. The "normal" order of addition was that used in analogous condensation reactions with benzene derivatives which consisted of placing the thiophene and the catalyst in the reaction flask and adding sulfur dichloride to the reaction mixture. "Inverse" addition consisted of adding the catalyst last. Data on the experiments with thiophene is summarized in Table VII.

The usual procedure in these experiments was to cool the reaction mixture to 10°C., make the addition of the other reagent and then remove the ice bath from the reaction flask if the reaction seemed to be under control. The reaction mixture was quenched by pouring it into cold water

TABLE VII

THIOPHENE CONDENSATION EXPERIMENTS

Run No.	Moles Thiophene	Moles SCl_2	Catalyst		Type of Addition	Contact Time (Hrs.)	Solvent		Product	
			Type	Moles			Type	Amount (Ml.)	Oil (g.)	Tar (g.)
1	2.55	0.29	$FeCl_3$	0.06	Normal	5	None	-----	10	20
2	5.1	0.31	$SnCl_4$	0.31	Normal	5	None	-----	---	All Polymer
3	2.55	0.34	$AlCl_3$	0.20	Inverse	5	Nitro Ethane	300	Not Isolated	180
4	3.7	0.34	$SnCl_4$	0.13	Inverse	4	Benzene	300	17	Not Weighed
5	3.2	0.34	$SnCl_4$	0.06	Inverse	2.5	Benzene	1000	25	28
6	2.5	0.50	$SnCl_4$	0.06	Inverse	2	CS_2	750	16	8

After several experiments of this type it was found that the best product isolation procedure was to add Filter Cel to the quenched liquor since the tacky nature of the polymer made filtration difficult without its aid.

The oil referred to in the product column is the distillable oil which was obtained on vacuum distillation of the solvent layer after removal of the insoluble polymer and the solvent. These oils were not further purified at once since it was hoped that reaction conditions for a good condensation reaction could be worked out and they would be discarded without further work. However, since this was not realized the distilled oils from experiments 1 and 6 were combined and product isolation was carried out on them. The experiments using benzene as a solvent were not used since there was a possibility that there might be diphenyl sulfide present from side reaction of the solvent although in many cases thiophene condensations with acyl halides have been run in benzene without complication due to side reactions with the solvent.

The oil (from 1 and 6) was distilled under vacuum to obtain three fractions. Fraction I (b.p. 70-80°C./6 mm.) had a strong odor of thiol and was condensed with 2,4-dinitrochlorobenzene as described in another section of the thesis to obtain 2-thienyl-2,4-dinitrophenyl sulfide melting at 119-119.5°C. (Literature value[34] m.p. 119°C.) The sulfide was in turn oxidized (as already described) to the 2-thienyl-2,4-dinitrophenyl sulfone melting at 142-3°C. (Literature value[34] m.p. 143°C.) Thus it was shown that 2-thiophenethiol was a decomposition product in the distillation of the initial condensation product. Fraction II (b.p. 120-130°C./6 mm., weight 9 gm.) was refractionated to obtain a purified product (b.p. 128°C./6 mm.) which analyzed as follows:

Anal. Calc'd for $C_8H_6S_3$: C, 48.44; H, 3.05; S, 48.50

Found: C, 48.37; H, 3.08; S, 48.54

The bis(2-thienyl) sulfide was oxidized to bis(2-thienyl) sulfone (m.p. 130.5-131°C.) using 30% hydrogen peroxide in glacial acetic acid. (Literature value[58] m.p. 130-131°C.) Fraction III (b.p. 140-190°C./5 mm.) was a viscous oil which was discarded since it appeared to be a mixture of compounds since it had a broad boiling point range indicating that it would be very difficult or impossible to separate it into pure components.

The Condensation of Sulfur Dichloride with 2-Chlorothiophene

Two condensation were attempted with 2-chlorothiophene in early experiments under rather poor experimental conditions as later experiments with thiophene demonstrated. The data is summarized in Table VIII. Other experimental reaction conditions were the same as those described in the thiophene condensations. It had been hoped that the blocking of an active ring position in thiophene would prevent polymer formation but the 2-chlorothiophene is also sensitive to polymerization by acid catalysis. Thus, further studies were centered on thiophene to work out better conditions since that molecule was more readily available. Product isolation from the oil isolated in the second experiment was not pursued further as there was too little of it for the necessary isolation procedures to be carried out.

TABLE VIII

2-CHLOROTHIOPHENE CONDENSATION EXPERIMENTS

Run No.	Moles of 2-Chlorothiophene	Moles SCl_2	Catalyst		Type of Addition	Contact Time (Hrs.)	Solvent		Product	
			Type	Moles			Type	Amount	Oil (g.)	Tar (g.)
1	0.85	0.42	$AlCl_3$	0.42	Normal	6	Ethylene Dichloride (500 ml.)		-----	All Tar
2	1.0	0.50	$AlCl_3$	0.52	Inverse	24	CS_2	750	3	99

The Condensation of Sulfur Dichloride with 2,5-Dichlorothiophene

Since Truce and Lotspeich[175] were able to condense 2,5-dichlorothiophene with benzene sulfonyl chloride whereas thiophene gave only tar it was hoped that this molecule would give a good condensation reaction in the thiophene series. The two experiments carried out with this thiophene derivative are summarized in Table IX. The other experimental reaction conditions were the same as those described for the thiophene experiments. Again it was found that the reaction conditions were too vigorous for this material. Product isolation was carried out on the combined oils as had been done for material obtained in the experiments with the parent material, thiophene. An initial fraction was taken which was thought to be the thiol although it did not have a characteristic mercaptan odor. This material was treated with 2,4,-dinitrochlorobenzene and a material melting at 84.5-85°C. was obtained which was believed to be 2,5-dichloro-3-thienyl-2',4'-dinitrophenyl sulfide. Fawcett,[138] however, found this material to melt at 136.5-137°C.

Anal. Calc'd for $C_{10}H_4Cl_2N_2O_4S_2$: C, 34.20; H, 1.15; Cl, 20.19;
S, 18.26

Found: C, 45.21; H, 3.82; Cl, < 0.2; S, < 0.2

An oxidation of this material with potassium permanganate was carried out as described previously for the oxidation of 2-thienyl-2,4-dinitrophenyl sulfide. A material melting at 85-85.5°C. was obtained which was thought to be the sulfone.

Anal. Calc'd for $C_{10}H_4Cl_2N_2O_6S_2$: C, 31.34; H, 1.05; Cl, 18.51;
N, 7.31

Found: C, 45.34; H, 3.87; Cl, 0.2; N, 12.56

TABLE IX

2,5-DICHLOROTHIOPHENE CONDENSATION EXPERIMENTS

Run No.	Moles of 2,5-Dichlorothiophene	Moles SCl_2	Moles $AlCl_3$	Type of Addition	Contact Time (Hrs.)	Solvent		Product	
						Type	Amount	Oil (g.)	Tar (g.)
1	0.65	0.25	0.25	Inverse	24	Pet. Ether (30-60°)	500 ml.	17	Not Weighed
2	1.65	0.19	0.20	Inverse	24	Ethylene Dichloride	500 ml.	9	107

The absence of sulfur and chlorine strongly suggested that 2,4-dinitrophenyl ethyl ether was the only possible product and a check on the melting point (86°C.) and its analysis left no question that the material must have resulted from the reaction of 2,4-dinitrochlorobenzene with the solvent (ethanol).

An oil fraction collected in the boiling point range 190-230°C./15 mm. was believed to be the bis(2,5-dichloro-3-thienyl) sulfide but oxidation of this material with potassium permanganate in acetic acid gave an oil which solidified with difficulty to give a solid melting at 60-90°C. A second crystallization from ethanol raised its melting point to 98-105°C. but it was obvious that the material was very impure and the quantity of material available was insufficient to do any further product isolation with.

Coupling Reactions with Thionyl Chloride

The Preparation of Diphenyl Sulfoxide

To one liter of benzene (879 g., 11.3 moles) contained in a three-liter, three-necked flask and cooled to 10°C. was added 400 g. (3.0 moles) of anhydrous aluminum chloride. To the latter suspension, 357 g. (3.0 moles) of thionyl chloride was added dropwise over a two hour period during which there was a spontaneous evolution of hydrogen chloride gas. The stirred reaction mixture after being allowed to come to room temperature during two hours, was slowly heated on a steam bath to 70°C. in an hour and kept at this temperature for 30 minutes. The reaction mixture was quenched by pouring it into ice water and stirring it vigorously after adding 30 ml. of concentrated hydrochloric acid to break up the complex. The oily layer was separated, washed twice with water, and the excess benzene was removed by distillation under vacuum. The crude product was distilled, b.p. 171°C./5 mm., to give 470 g. (2.32 moles), a 77.4% yield of the pure sulfoxide which solidified in the receiver. It's m.p. was 68-72°C. A single recrystallization from ethanol raised the melting point to 71-2°C. Literature[65] value, m.p. 70.5°C.

Bis(4-Chlorophenyl) Sulfoxide

This material was prepared by the standard Friedel Crafts method using aluminum chloride. One liter of chlorobenzene (9 moles) and 199 g. (1.5 moles) of anhydrous aluminum chloride were placed in a three-liter flask, cooled to 10°C., and 179 g. (1.5 moles) of thionyl chloride was added with vigorous stirring over a two hour period. The condensation proceeded with the spontaneous evolution of hydrogen chloride and the reaction mixture was stirred six hours, without cooling, after all the reactants had been added. The mixture was then warmed to 70°C., held at that temperature for thirty minutes, quenched in ice water, stirred vigorously to hydrolyze the complex, and finally warmed on the steam bath to dissolve the solid which had precipitated. The oil layer was separated, washed with water, and allowed to stand until crystallization had taken place. The solid was removed by filtration, dried, and recrystallized from ethylene dichloride to give 239 g. of the bis(4-chlorophenyl) sulfoxide melting at 141.5-143°C. (Literature value,[85] m.p. 143°C.). The chlorobenzene was removed under vacuum from the original mother liquor, the residue was taken up in the mother liquor from the ethylene dichloride recrystallization, darcoed, and allowed to crystallize. This gave a second quantity of product weighing 61 g. melting at 141-3°C. Reduction of the solvent volume gave still a third quantity of product, 34 g., melting at 139-141°C. The total yield was 334 g. (82%). Although this compound has been prepared by oxidation methods using hydrogen peroxide, nitric acid, and chlorine, no reference to its preparation by the Friedel Crafts method was found in the literature which is rather surprising in view of the yield obtained.

The complete removal of the recrystallization solvent gave 53 g. of an oil which was distilled under reduced pressure (b.p. 193°C./5 mm.). An infra-red spectrum of the oil showed para (12.25 microns) and ortho (13.30 microns) benzene ring substitution. A comparison of this spectra with that of bis(4-chlorophenyl) sulfoxide showed the sulfoxide peak had shifted from 9.50 microns for the symmetrical compound to 9.75 microns for the crude material. An attempt was made to obtain 4-chlorophenyl-2-chlorophenyl sulfone (m.p.[8] 101°C.) from this material by oxidizing it with 30% hydrogen peroxide in acetic acid but the product obtained on isolation was a viscous oil and efforts to crystallize it were unsuccessful.

The Reaction of Thionyl Chloride with o-Dichlorobenzene

The quantities, 882 g. (6.0 moles) of o-dichlorobenzene (99+% purity) and 67 g. (0.5 mole) of anhydrous aluminum chloride, were placed in a two liter three neck round bottom flask equipped for a condensation reaction. Thionyl chloride (59.5 g., 0.5 mole) dissolved in 100 ml. of ethylene dichloride was added to the aluminum chloride dichlorobenzene suspension during a six hour period without external cooling of the reaction mixture. There was no metal complex color formation until about a half hour after the addition of the thionyl chloride solution had commenced and then only a light transparent blue appeared which gradually deepened to a dark sky blue as the reaction proceeded. Hydrogen chloride evolution, which was slow until the appearance of the light blue complex coloration, increased measureably as the reaction mixture took on a deeper blue coloration. The reaction mixture was allowed to stir for four days following the addition of the thionyl chloride and then it was poured onto crushed ice. The metal complex hydrolyzed readily leaving a light yellow colored oily layer. A sample of the oil was set aside in the refrigerator overnight during which no precipitation or crystallization occurred. The oily layer was then washed consecutively with 6N hydrochloric acid and water and the excess o-dichlorobenzene was removed by vacuum distillation (b.p. 70°C./17 mm.). Distillation was continued until the internal temperature of the distillation flask reached 140°C. The residue was cooled and an infra-red spectrum was determined on the crude material. Absorption peaks in the substitution region (11-15 microns) appeared at 11.5 (strong), 12.4 (strong), 13.0 (weak), 13.40 (weak) and 14.3 (weak) microns. There was also a peak at 9.45 microns that was taken to be sulfoxide (see Figure 33). Thus the spectrum showed the 1,2,4 substitution pattern (11.4 and 12.4 microns) and sulfoxide as would be expected from the desired bis(3,4-dichlorophenyl) sulfoxide. A sample of the distillation residue was slurried in acetone and a solid precipitated which on recrystallization from ethanol gave a solid melting at 244-6°C. The infra-red spectrum of this material showed a strong single hydrogen out of plane absorption peak at 11.4 microns. The material was later identified as impure 2,3,7,8-tetrachloro thianthrene (m.p. 272-3°C.). The residue was then distilled under vacuum to obtain six fractions. Solid precipitating, as a mush, in the forecut was later identified as 1,2,4,5-tetrachlorobenzene (from chlorination). One of the middle fractions also precipitated a mush of crystals and the solid was filtered and recrystallized from acetone to obtain a material melting at 147-8°C. As this material exhibited absorption peaks at 11.26 and 11.50 microns (see Figure 42) it appeared to have 1,2,4,5 substitution and was assumed to be the oxide of 2,3,7,8-tetrachlorothianthrene. The analysis (C, 36.81; H, 1.02; Cl, 54.13; S, 8.16), however, did not agree with this possibility. Further purification showed the material to be slightly impure bis(2,4,5-trichlorophenyl) sulfide (m.p. 149-150°C.)

Anal. Calc'd for $C_{12}H_4Cl_6S_1$: C, 36.81; H, 1.14; Cl, 53.93; S, 8.15
Attempts to isolate the bis(3,4-dichlorophenyl) sulfoxide from the other oily fractions failed and further work with the initial experiment was abandoned in favor of making a second experiment under more optimum experimental conditions.

In the second experiment 1000 g. (7.0 moles) of o-dichlorobenzene, 133 g. (1.0 mole) of anhydrous aluminum chloride and 119 g. (1.0 mole) of thionyl chloride were used. The reaction flask was cooled to 10°C. before the addition of the thionyl chloride had commenced and then 15 ml. of the thionyl chloride was added. Coloration due to complex formation was very slow at this point and it was an hour before any hydrogen chloride evolution could be detected. The cooling media was removed from the reaction flask and the remainder of the chloride was added during a three hour period after which the reaction mixture was stirred for five hours, warmed to 50°C. for thirty minutes and quenched by pouring it into ice water. An orange yellow oily layer formed which was separated and washed as before. The excess solvent was removed by vacuum distillation, 513 g. being recovered. Final internal temperature of the distillation flask was 160°C./10 mm. A spectra determined on the crude residue again showed the correct elements for the spectra of the desired sulfoxide. The crude material was warmed on the steam bath and poured into acetone with vigorous stirring to precipitate the higher melting material. A 30 g. quantity of crude product precipitated which was filtered and recrystallized from ethylene dichloride to obtain partially purified 2,3,7,8-tetrachlorothianthrene melting at 255-9°C. Several additional crystallizations of this material resulted in a fractionation into thianthrene (m.p. 272-3°C.) and some higher melting material that was undoubtably a mixture of thianthrene oxide. This was not purified further since the relative insolubility of these materials made separations extremely difficult.

Attention was then turned to the acetone filtrate from the original solid isolation. The solvent from this mother liquor was removed and the residue was distilled under vacuum to obtain eight fractions. Infra-red spectra were taken of these fractions to locate the heaviest concentrations of the sulfoxide and hexachlorodiphenyl sulfide. It was found that the two could be separated fairly readily since the sulfoxide was quite a bit more soluble in acetone than the hexachlorodiphenyl sulfide. It was also found that the sulfide distilled at a slightly higher boiling point (223°C./2 mm.) than the sulfoxide (b.p. 210°C.) and that it was possible to separate the two materials on this basis. A total of 31 g. (0.08 mole) of the bis(2,4,5-trichlorophenyl) sulfide was purified. Crystallization of the bis(3,4-dichloro phenyl) sulfoxide fractions from ethanol resulted in obtaining 42 g. (0.12 mole) of a purified material which melted at 102.5-103.5°C.

Anal. Calc'd for $C_{12}H_6Cl_4O_1S_1$: C, 42.38; H, 1.77; Cl, 41.70; S, 9.42

Found: C, 42.07; H, 1.89; Cl, 41.51; S, 9.91

No attempt was made to isolate any of the pentachlorodiphenyl sulfide (m.p. 84.5-85.5°C.) nor any of the mixed sulfoxide whose presence in small amounts was indicated by the infra-red spectrum of the crude oils.

The Reaction of Thionyl Chloride with p-Dichlorobenzene

As the reaction of sulfur dichloride with p-dichlorobenzene produced primarily polymeric material there was a possibility that thionyl chloride would function better as a coupling reagent since it had been found in other such coupling reactions to stop at the sulfoxide stage with little or no multiple substitution. Para-dichlorobenzene (294 g., 2.0 moles), 850 ml. of ethylene dichloride and 67 g. (0.5 mole) of anhydrous aluminum chloride were placed in a two-liter three-neck flask properly equipped to carry out the condensation reaction. Thionyl chloride (60 g., 0.50 mole) dissolved in 100 ml. of ethylene dichloride was then added, at room temperature, to the contents of the reaction flask. The reaction proceeded very slowly and when half of the thionyl chloride had been added the temperature of the reaction mixture was raised to 40°C. but the addition of the balance of the chloride solution resulted in only a weak evolution of hydrogen chloride. The reaction mixture was stirred for an additional two hours during which no increase in rate of hydrogen chloride evolution occurred. An additional 15 g. of aluminum chloride was then added without any apparent effect. However, five minutes following this addition, hydrogen chloride began to evolve briskly from the reaction mixture. Stirring was continued for an additional hour and the reaction mixture was quenched by pouring it into cold dilute hydrochloric acid. A brown solid precipitated from the quenched liquor which was recovered by filtration and dried. On heating, the crude solid fused into a dark gummy resin at 305-315°C. The material was insoluble in both boiling ethylene dichloride and chlorobenzene indicating it had a polymeric nature. The oily layer was separated from the filtrate, washed in the usual manner and the solvent was removed by vacuum distillation. The residue was distilled under vacuum to obtain a crude fraction of p-dichlorobenzene (weight 171 g., b.p. 70°C./25 mm.). A short column was then placed on the flask and the balance of the distillable material was distilled at a distillation head temperature of 110-225°C./10 mm. Copious quantities of hydrogen chloride were given off during this stage of the product isolation procedure and a caustic tower had to be inserted into the vacuum line to maintain a low distillation pressure. A residue of 77 g. of a non-distillable tar remained in the distillation flask. The crude high boiling material was refractionated through a 10 cm. vigreux column to obtain a second small fraction of p-dichlorobenzene (weight 19 g.), a mixed intermediate fraction, a solid material distilling at 205-10°C./10 mm. and a trace of very high boiling material which sublimed into the vacuum fraction cutter. The sublimate was washed out of the fraction cutter with acetone and the solid material was filtered and dried. The crude material melted at 203-210°C. but it was not characterized further as it was set aside for further purification by recrystallization and was lost in a minor laboratory accident. The solid fraction (b.p. 205-10°C./9 mm.) was recrystallized from acetone three times to yield a crystalline solid melting 136.5-137°C.

Anal. Calc'd for $C_{12}H_6Cl_4O_1S_1$: C, 42.38; H, 1.77; Cl, 41.70; S, 9.42

Found: C, 42.27; H, 1.79; Cl, 41.75; S, 9.45

The bis(2,5-dichlorophenyl) sulfide, previously prepared by the condensation of p-dichlorobenzene with sulfur dichloride, was oxidized using hydrogen peroxide in acetic acid at room temperature to obtain a sulfoxide identical to the material obtained in the above synthesis showing that it was bis(2,5-dichlorophenyl) sulfoxide. Two grams of the purified material was obtained although there was considerable material remaining in the solvent and in the mixed fraction which could have been purified further if needed.

The Preparation of Bis(4-Chloro-2-Methylphenyl) Sulfoxide

This preparation was a repetition of a synthesis used by Balasubramanian and Baliah.[40] The structure of the product was established by them using an independent synthesis.

Ethylene dichloride (400 ml.), 383 g. (3.02 moles) of meta-chlorotoluene, and 100 g. (0.75 mole) of anhydrous aluminum chloride were placed in a two-liter three-neck round-bottom flask properly equipped for the condensation. The reaction flask was cooled to 5°C. and 89 g. (0.75 mole) of thionyl chloride dissolved in 100 ml. of ethylene dichloride was added over a period of an hour and a half. The reaction had a short induction period during which a purple metal complex formed and then the reaction proceeded readily, as evidenced by hydrogen chloride evolution. After the thionyl chloride had been added the reaction mixture was allowed to stir at room temperature for two hours and then at 50°C. for fifteen minutes before it was quenched by pouring it into water. The oil layer was separated, washed consecutively with 6N hydrochloric acid and water and the solvent was removed by distillation under vacuum. The oil residue was fractionated to obtain 150 g. (1.18 moles) of meta-chlorotoluene (b.p. 47°C./7 mm. or 161°C. at atmospheric pressure) and 210 g. of the sulfoxide condensation product (b.p. 238°C./ 7 mm.). Only traces of hydrogen sulfide were given off at the end of the distillation and there was no difficulty in maintaining the vacuum at an internal temperature of 300°C. There was only 5 g. of carbonaceous residue left in the flask after the distillation indicating a low percentage of side reaction.

The crude sulfoxide (m.p. 101-4°C.) was recrystallized twice from acetone to obtain a crystalline solid melting at 104.5-105.5°C. (Literature[40] m.p. 102-3°C.) The material was slow in crystallizing and was allowed to stand at room temperature for several hours before filtration in order to get good precipitation. The first purified material obtained weighed 118 g. and additional material was obtained from the mother liquor, but each successive quantity required an additional crystallization to get the same purity. It became apparent there was an impurity in the crude material which was being concentrated in the mother liquor with each crystallization. No investigation was made to determine whether this impurity was another sulfoxide isomer, a chlorination product, or the sulfide which might be produced by the reduction of the predominate sulfoxide product. A total of 180 g. (0.60 mole, 80% yield) of highly purified bis(4-chloro-2-methylphenyl) sulfoxide (m.p. 104.5-105.5°C.) was obtained. Particular care was taken to upgrade all of the material isolated since the structure of the sulfoxide had been proven previously[40] and it was desired to convert this material to the sulfide (which would therefore have a known structure) for attempted ring closures.

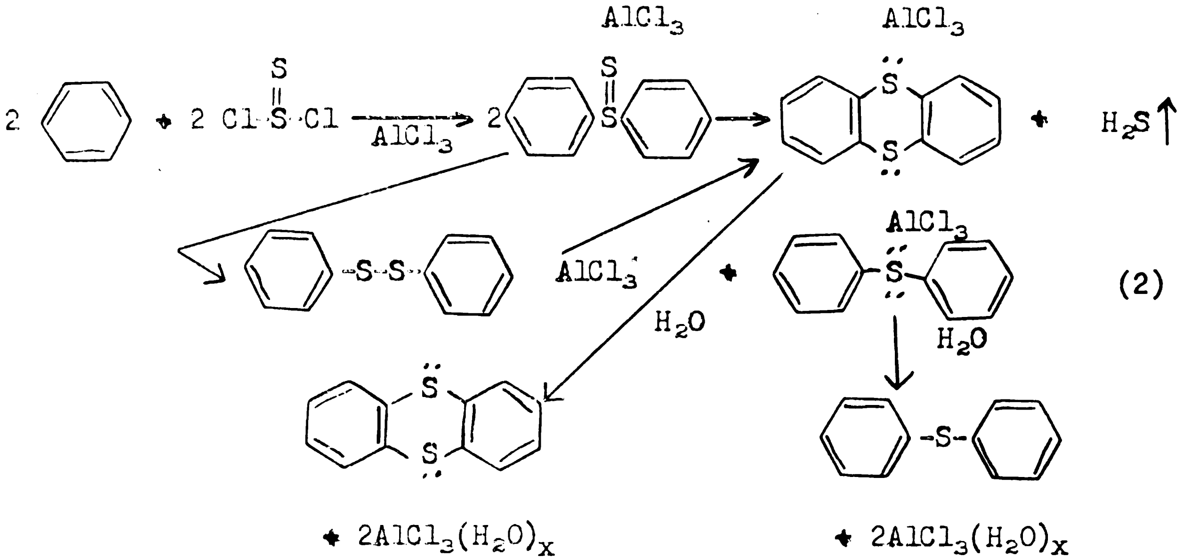
Ring Closure Reaction with Sulfur Chloride and Oxychloride

The Reaction of Sulfur Monochloride with Benzene to Obtain Diphenyl Sulfide and Thianthrene

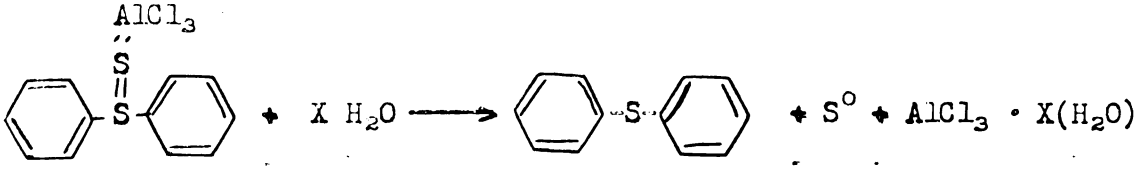
The preparation of diphenyl sulfide using sulfur monochloride has been described extensively in the literature. When the method was used the product was accompanied by a small amount of thianthrene and the odor of hydrogen sulfide was noted in the gas effluent. Varying amounts of thianthrene had also been found by other investigators[142] in using this reaction. The position of the second sulfur atom, during this reaction, is open to question although Ray[5] and others claim to have isolated water-sensitive intermediates that contain di- and tetravalent sulfur as indicated in the equations below. If this type of intermediate is present it should be relatively easy to cause ring closure to thianthrene. Gilman and Swayampati[119] who added sulfur monochloride to refluxing benzene to prepare thianthrene said, "the yields are best expressed on the basis of the reaction (1):

$$2\ C_6H_6 + 2\ S_2Cl_2 \xrightarrow{AlCl_3} C_{12}H_8S_2 + 4\ HCl + 2\ S^o \quad (1)$$

However, they operated under conditions such that the sulfur would be used for ring closure purposes.[117] It is believed the reaction is better expressed by the following series of reactions (2)


(2)

Whenever this reaction was carried out at low temperature[176,142] and low contact time, the product has been diphenyl sulfide and free sulfur. This is apparently formed by the following reaction (3):


(3)

If the above equations are correct, then when the reaction has proceeded far enough it requires that approximately equal molar quantities of diphenyl sulfide and thianthrene be produced. This was shown to be the case by the following experiment.

The quantity, 1.5 liters (16.9 moles, thiopene-free) of benzene and 333 g. (2.5 moles) of anhydrous aluminum chloride were placed in a three-liter three-necked round-bottom flask equipped with a stirrer, thermometer, dropping funnel, and a gas escape tube leading to a reflux condenser. The sulfur monochloride (337 g., 2.5 moles) was added at room temperature without cooling over a period of six hours. The maximum reaction temperature reached during this period was 40°C. The complex coloration began as a reddish color and progressed through a purple-black to a deep black. The first hydrogen sulfide noticed was toward the end of the sulfur monochloride addition. It was present continuously in the hydrogen chloride evolution after its initial appearance as evidenced by odor and lead acetate test paper until the end of the reaction period. Following the addition of the chloride the reaction mixture was allowed to stir at room temperature for forty-eight hours, at the end of which time gas evolution had ceased. The reaction mixture was warmed to 85°C. in a hot water bath, held there for one hour, and then quenched in ice water and stirred thoroughly to hydrolyze the metal complex. The benzene layer rose to the top and a red viscous oil settled to the bottom of the flask below the acid layer. The benzene and acid layers were removed by decantation and the benzene layer was separated and washed with 6N hydrochloric acid to remove the last trace of aluminum and then with water. The red oil was extracted into chloroform and washed similarly to the benzene layer. The benzene layer and the chloroform extract were combined and the solvents removed under vacuum. The oily residue was distilled using a 15 cm. vigreux column, collecting the material boiling over the range 145-200°C.<7 mm. When the distillation flask temperature reached 263°C. decomposition started and gaseous products prevented the maintenance of a sufficient vacuum for further distillation. A black carbonaceous residue weighing fifty grams was found in the distillation flask. The distillate was then refractionated through a 45 cm. vigreux column to obtain 175 g. (0.94 mole) of diphenyl sulfide (b.p. 137°C./6 mm.), an intermediate fraction, and a thianthrene fraction (b.p. 180°C./7 mm.). The thianthrene fraction was recrystallized from ethylene dichloride to give 190 g. (0.870 mole) of thianthrene melting at 154-155.5°C. The ethylene dichloride was removed from the mother liquor under vacuum and the oily residue was combined with the intermediate fraction and they were refractionated into five fractions. Inspection of the infra-red spectrum of these fractions indicated the presence of 4-chlorophenyl phenyl sulfide, thianthrene, and 1,4-bis(phenyl mercapto) benzene. The crystals from fractions 2,3, and 4 were filtered from the oily material on a Buchner suction funnel and recrystallized from glacial acetic acid to give 20 g. (0.092 mole) of thianthrene melting at 154-5°C. Fraction 5 was recrystallized from methanol to give 1.0 g. (0.0034 mole) of 1,4-bis(phenyl mercapto) benzene melting at 80-81°C. (Literature value,[47] m.p. 81.5°C.) This sulfide (0.5 g., 0.0017 mole) was oxidized with 1 g. (0.01 mole) of chromium trioxide in boiling acetic acid to yield the 1,4-bis(benzenesulfonyl) benzene which was recrystallized from acetone and melted at 230-231°C. (Literature value,[177] m.p. 229°C.) The oil from the thianthrene filtration and the mother liquor from the thianthrene recrystallization were combined with fraction 1 and refractionated to give 5 g. (0.023 mole) of 4-chlorophenyl phenyl sulfide, b.p. 167°C./9 mm. A sample (1 g., 0.0045 mole) of the sulfide was oxidized with 1.4 g.

(0.0135 moles) of chromium trioxide to obtain 4-chlorophenyl phenyl sulfone melting at 92-3°C. (Literature value,[178] m.p. 91°C.) Examination of the infra-red spectrum of the original diphenyl sulfide fraction in a concentrated solution indicated that it was slightly contaminated with the 4-chlorophenyl phenyl sulfide as shown by the para substitution band at 12.25 microns. There was no evidence to show whether the 4-chloro material arose from the chlorination of diphenyl sulfide or from chlorination of benzene with subsequent condensation, although the former case was more probable. The total yield figures were as follows:

	Weight	Moles
diphenyl sulfide	175 g.	0.94
thianthrene	210 g.	0.97
4-chlorophenyl phenyl sulfide	5 g.	0.0225
1,4-bis(phenyl mercapto) benzene	1 g.	0.0034
tar	50 g.	?
	Total moles	1.936

The theoretical yield, based on S_2Cl_2, of diphenyl sulfide and thianthrene according to the equations proposed would be 1.25 moles of each product.

The Preparation of Diphenyl Sulfide and Thianthrene

The necessity of obtaining additional diphenyl sulfide for condensation reactions prompted the following experiment.

Two liters of thiopene-free benzene (22.0 moles) and 464 g. (3.25 moles) of anhydrous aluminum chloride were placed in a five-liter three-neck round-bottom flask equipped with a stirrer, dropping funnel, and a gas scrubber. The stirred mixture was cooled to 10°C. in an ice bath and 520 g. (5.04 moles) of sulfur dichloride was added over a period of seven hours. The reaction mixture was then allowed to stir at room temperature for an additional 48 hours. Hydrogen sulfide was first noticed in the hydrogen chloride effluent 14 hours after the addition of sulfur dichloride and it was present in noticeable amounts until the end of the reaction. Since the sulfur dichloride used in this experiment was the last quantity of an originally large amount it probably contained a fair amount (about 5%) of sulfur monochloride formed by the loss of chlorine in repeated openings of the bottle which shifts the mobile equilibrium between sulfur dichloride and sulfur monochloride. Ring closure involving the sulfur monochloride would release hydrogen sulfide as a by-product. As the last of the sample of sulfur dichloride was used up in this experiment it was not possible to check its specific gravity to determine to what extent the conversion to monochloride had taken place due to loss of chlorine. At the end of the reaction period the mixture was quenched in cold 6N hydrochloric acid and stirred vigorously to hydrolyze the complex. A viscous benzene insoluble oil made the hydrolysis difficult, but it was eventually successful, and when stirring was stopped, three separate layers formed. On being set aside overnight crystalline thianthrene formed at the lower interface of the benzene layer. The latter was decanted, washed separately and the thianthrene collected on a Buchner funnel with the viscous oil. On attempting to filter this material the oil partially solidified indicating the viscous material was crude thianthrene which is benzene insoluble. The oily material and crystals were taken up separately in chloroform and each solution was washed successively with 6N hydrochloric acid and water before removing the solvent under vacuum. The oily residue obtained was distilled under vacuum using a 2.5 cm. by 40 cm. asbestos wrapped vigreux column to separate the diphenyl sulfide, thianthrene, 1,4-bis(phenylmercapto) benzene, and tars. The fractionation was made taking frequent intermediate cuts so that it was easy to distinguish fractions containing thianthrene due to its easy crystallization on cooling. The distillation residue, insoluble in boiling ethanol, weighed 31 g. In the lower thianthrene fractions where it occurred as a mush of cyrstals the thianthrene was recovered by filtration. The combined crude thianthrene was recrystallized from glacial acetic acid to obtain a product in the form of shining white needles. These were washed with alcohol to remove most of the acetic acid and then oven-dried to obtain 174 g. (0.805 mole) of thianthrene melting at 154-5°C. The main fraction (288 g., 1.54 moles) of diphenyl sulfide (b.p. 143°C./5 mm.) was examined by infra-red and found free of 4-chlorophenyl phenyl sulfide. All other fractions were combined with the residue obtained by evaporating the acetic acid mother liquor from the thianthrene recrystallizations and refractionated. A tarry residue of 15 g. was obtained from this distillation. Diphenyl sulfide (30 g., 0.16 mole) and thianthrene (30 g., 0.139 mole) were obtained in the same manner as described previously and a higher boiling fraction (b.p. 250°C./4 mm.) was recrystallized from methanol to yield 23 g. (0.078 mole) of 1,4-bis(phenylmercapto) benzene melting at 81-2°C. The residues and impure fractions were again collected, as in the second distillation, and after solvent removal were subjected to careful fractionation to obtain 28 g. (0.15 mole) of diphenyl sulfide, 20 g. (0.091 mole) of 4-chlorophenyl phenyl sulfide, and 12 g. (0.056 mole) of thianthrene. The combined intermediate fractions weighed 25 g. and the over-all results were:

	B.p. and M.p.	Total Weight (gms.)	Moles	Moles SCl_2 Used
diphenyl sulfide	143°C./5 mm.	346	1.85	1.85
4-chlorophenyl phenyl sulfide	165°C./6 mm.	20	0.091	0.091
thianthrene	191°C./6 mm. 154-5°C.	216	1.00	2.00
1,4-bis(phenylmercapto)benzene	250°C./4 mm. 81-2°C.	23	0.078	0.156
total intermediate fractions	-----	25	---	---
non-distillable residues	-----	46	---	---
	Total moles SCl_2 used =			4.097

The total moles of sulfur dichloride accounted for in purified products was 4.097 compared with 5.04 moles of sulfur dichloride used as a starting material. The 4-chlorophenyl phenyl sulfide arises from the free chlorine which is always present in sulfur dichloride due to the equilibrium between sulfur dichloride and sulfur monochloride. The high yield of thianthrene may be accounted for partially by the probable presence of sulfur monochloride in the starting material but the large amount is undoubtedly attributable to the fact that the ratio of aluminum chloride to sulfur dichloride was low, (i.e., 3.25/5.04). This is consistent with the findings of Dougherty and Hammond[117] who found that when condensing benzene and sulfur in the presence of aluminum chloride the formation of thianthrene over diphenyl sulfide was favored by a low catalyst to sulfur ratio other things being equal. The formation of 1,4-bis(phenylmercapto) benzene occurs by the condensation of a diphenyl sulfide molecule with a benzene molecule and the non-distillable materials arise from similar reactions to yield longer chain materials. Evidence from other experiments also indicates that these materials may be formed by dismutation reactions.

The Reaction of Sulfur Monochloride with Chlorobenzene

Equipment for a condensation reaction was assembled and 1930 g. (17.2 moles) of chlorobenzene and 333 g. (2.5 moles) of anhydrous aluminum chloride were placed in the flask. The mixture was cooled to 10°C. and 337 g. (2.5 moles) of sulfur monochloride (S_2Cl_2) was added to the reaction mixture during a period of six hours. The ice bath was removed from the reaction flask and the reaction mixture was stirred an additional forty-eight hours at room temperature. The reaction was vigorous from the beginning of the addition of the sulfur monochloride as evidenced by the copious evolution of hydrogen chloride. Hydrogen sulfide was first detected in the gaseous effluent, using lead acetate test paper, near the end of the addition of the dichloride and it was evolved continuously in small quantities all during the reaction period. At the end of that period the reaction mixture was heated on the steam bath until its temperature reached 70°C. and it was held there until hydrogen sulfide evolution had nearly ceased. Heating caused an abundant evolution of hydrogen sulfide which decreased to a very slow rate after approximately three hours. The reaction mixture was then quenched by pouring it into ice water and the resulting solution was stirred vigorously to hydrolyze the metal complex. A yellow oily layer formed after the hydrolysis was complete but there was also a small amount of a third phase, a red oil, present which was not soluble in the water nor chlorobenzene layer. The chlorobenzene layer was decanted from the other two layers and washed in the usual manner. The unreacted chlorobenzene was removed by vacuum distillation and the residue was transferred to a smaller flask for distillation. The product was distilled using a short path column to obtain 505 g. of a crude product boiling in the range 158-220°C./2 mm. A small amount of decomposition occurred near the end of the distillation, evolving both hydrogen chloride and hydrogen sulfide, and leaving 71 g. of carbonaceous tar in the distillation flask. The crude product was then fractionated into two primary fraction containing respectively dichlorodiphenyl sulfide (b.p. 169-179°C./2 mm.) and dichlorothianthrene (b.p. 193-210°C./2 mm.). The sulfide fraction (weight 273 g.) did not solidify until twenty-four hours after it had been set aside at room temperature. No further work was done with this material since it was adjudged from other work to be primarily bis(4-chlorophenyl) sulfide contaminated with 4-chlorophenyl-2'-chlorophenyl sulfide and bis(4-chlorophenyl) disulfide.

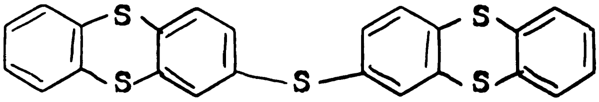
The thianthrene fraction (weight 170 g.) solidified immediately on cooling. An infra-red determination was made on the crude material and absorption was found in the substitution region (11-15 microns) at 10.63 (weak), 11.53 (medium), 12.35 (strong), 12.95 (weak), 13.38 (medium), 14.15 (weak) and 14.40 (weak) microns. The crude material melted at 125-8°C. Approximately 20 g. of this material was recrystallized from methyl ethyl ketone to obtain a solid melting at 136-141°C. This solid was again recrystallized to obtain material melting at 145-8°C. It appeared at this junction that the material might be the unidentified dichlorothianthrene isomer reported by Ray[5] which melted at 147°C. The infra-red absorption spectrum of this material (m.p. 145-8°C.) no longer exhibited the absorption at 12.95 and 13.38 microns indicating the elimination of one or more substitution types. However, when this material was again recrystallized from acetone and was allowed to crystallized slowly at room temperature the solid isolated melted at 163-6°C. and its spectrum no longer exhibited the peak at 14.40 microns. A further recrystallization raised its melting point to 170-171.5°C. and it appeared the solid might be the 2,8-dichlorothianthrene but an additional recrystallization raised the melting point to 174-5°C. and it was then certain that the material was actually 2,7-dichlorothianthrene (m.p. 180-180.5°C.) since the infra-red spectrum of this material was now identical with that of the pure isomer. It was obvious at this point that the reaction of chlorobenzene with sulfur monochloride apparently gave fairly large amounts of more than one dichlorothianthrene isomer. As this experiment was initiated late in the present investigation and it was then apparent that identification of the isomers formed by fractional crystallization would be a tedious process, no further investigation of this reaction was done. It was apparent that fractional crystallization had succeeded in isolating only the highest melting isomer and that reaction of a chlorobenzene with sulfur monochloride was quite complex. A summary of what may have occurred appears in the discussion section of the thesis.

The Reaction of Sulfur Dichloride with Diphenyl Sulfide

When this experiment was performed there had been no data available to indicate the correct amount of aluminum chloride to use in thianthrene ring closure reactions. It was anticipated that if such information could be determined with diphenyl sulfide that it would eliminate the loss of starting materials which were difficult to obtain.

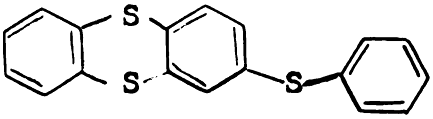
The quantities, 186 g. (1.0 mole) of diphenyl sulfide, 33 g. (0.25 mole) of anhydrous aluminum chloride and 300 ml. of ethylene dichloride were placed in a one-liter three-neck round-bottom flask and cooled, in an ice water bath, to 10°C. Sulfur dichloride (51.5 g., 0.5 mole) dissolved in 80 ml. of ethylene dichloride was added to the contents of the reaction flask during a two hour period. This resulted in the formation of a deep-brown metal complex. The ice bath was removed from the reaction flask and the reaction mixture was allowed to stir, at room temperature, for 36 hours. Hydrogen chloride continued to be evolved during the entire period and very slight traces of hydrogen sulfide were detected with lead sulfide paper. The reaction mixture was warmed to 50°C. for thirty minutes, quenched by pouring it into ice water followed by acidification with hydrochloric acid. No brown colored insoluble material was isolated in this condensation reaction. The oily layer was separated and washed as usual with subsequent solvent removal under vacuum. The residue was vacuum distilled to obtain eight fractions and a residue of only 5 g. of a non-distillable tar. Fraction I (39 g., b.p. 113-120°C./2 mm.) was identified as diphenyl sulfide by its infra-red spectrum. Fraction II (20 g., b.p. 120-130°C./2 mm.) was found to be diphenyl sulfide contaminated with a trace of 4-chlorophenyl phenyl sulfide as evidenced by the appearance of the para absorption peak at 12.3 microns. Fraction III (b.p. 140-156°C./2 mm.) partially solidified on being set aside and the solid was recovered by filtration and washed with alcohol to remove the oil. The solid was identified as thianthrene as were fractions IV, V, VI and VII. The solid material was all collected and recrystallized from glacial acetic acid to obtain 65 g. (0.30 mole) of thianthrene melting at 154-5°C. It gave an infra-red absorption curve typical of 4 adjacent hydrogens at 13.3 microns (see Figure 50). Fraction VIII partially solidified in the receiver and it was diluted with acetone to assist the solidification of the mushy oil. A crude solid was obtained by filtration and found to melt at 290-305°C. Recrystallization of this material from ethylene dichloride gave 0.2 g.

of a crystalline solid melting at 314-315°C. In the absence of analytical data it was assumed that the material was the thianthrene coupling product (I)



(I)

since thianthrene had been the major product isolated and since a compound with a structure like (I) would be likely to exhibit a high melting point. An attempt to condense thianthrene with sulfur dichloride failed to give any coupling product. Analysis of the unknown material gave: C, 60.97; H, 2.86; S, 36.35. Calculations for structures I-VI which could conceivably be present failed to give any suggestion



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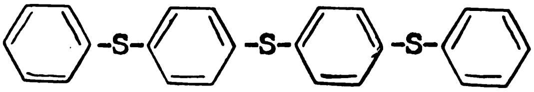

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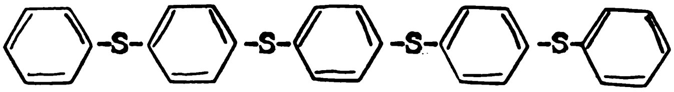

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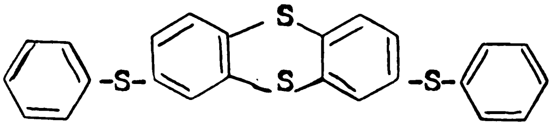

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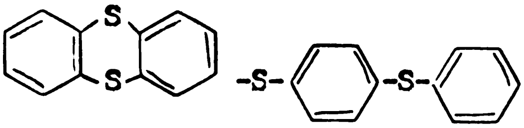
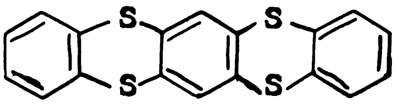


(VI)

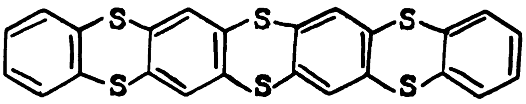
as to the correct structure of the solid.

Structure No.	%C	%H	%S
I	62.30	3.05	34.65
II	66.5	3.7	29.6
III	71.59	4.50	23.89
IV	70.54	4.34	25.11
V	66.62	3.73	29.65
VI	66.62	3.73	29.65

An infra-red spectrum of this material was determined using the potassium bromide pellet technique (0.35% solid) and absorption in the substitution region (11-15 microns) was found at 11.45 and 13.25 microns. This data would also eliminate structures I-VI since they would exhibit different absorption peaks due to the presence of five adjacent hydrogens and two adjacent hydrogens in such structures. It was concluded from the spectrum that the compound would have single hydrogens (11.45 micron absorption) and four adjacent hydrogens (or the substitution at 13.25 microns). The only structures which might be present which would exhibit such a spectra were structures VII and VIII.



(VII)



(VIII)

Calculations were made for these structures and it was found that

Structure No.	%C	%H	%S
VII	61.19	2.83	35.98
VIII	58.50	2.44	35.98

the results for structure VII agreed with the experimental data. As all of the material had been used for an analytical sample it was not possible to pursue this structure determination further. It is presumed that the material was derived from 1,4-bis(phenylmercapto) benzene which would be present due to migration of a phenylmercapto group from 4,4'-bis(phenylmercapto) diphenyl sulfide which was shown later to actually be present. It should be possible to prepare this same material from 1,4-bis(phenylmercapto) benzene which had already been prepared previously as a by-product in the synthesis of 4-chlorophenyl phenyl sulfide. The condensation of 4-chlorophenyl phenyl sulfide with alkali thiophenate should easily give this material. It is significant that this structure has not previously been recorded in the literature and appears to be a new ring structure. This problem was not further investigated since it arose too late in the present investigation, but should be an interesting problem for future study.

The investigation then returned to the residues obtained from the original distillation. The mother liquor from the recrystallization of thianthrene, the acetone wash from fraction VIII and the oil from fraction III were all combined and the solvents were removed leaving an oily residue which was again distilled to obtain nine separate fractions. Fraction IA and IIA solidified and upon crystallization from methanol gave a material melting at 54-9°C. A second recrystallization of this material raised its melting point to 59-64°C. The material had infrared absorption peaks at 13.65 and 14.6 microns. This is usually typical of either mono substitution or a mixture of mono and ortho substitution. Inasmuch as there was not enough of this material to make an extensive fractionation no further work could be done with it. Impure thianthrene was isolated from fraction IIIA and para substitution at 12.40 microns began to appear in this fraction. The amount of a para substitution product increased in the succeeding fractions as did the absorption peak at 9.75 microns. The latter absorption was shown to be characteristic of 1,4-bis(phenylmercapto) benzene (Figure 61) and 4,4'-(phenylmercapto) diphenyl sulfide (Figure 64). Fraction IXA, the best appearing solid material, was recrystallized from ethanol to obtain a somewhat waxy solid melting at 110.5-111°C. which analyzed correctly for 4,4'-bis(phenyl mercapto) diphenyl sulfide (Structure III).

Anal. Calc'd for $C_{24}H_{18}S_3$: C, 71.59; H, 4.50; S, 23.89

Found: C, 71.56; H, 4.54; S, 23.80

The 4,4'-bis(phenylmercapto) diphenyl sulfide (III) was oxidized using chromic acid in glacial acetic acid to obtain the 4,4'-bis(benzenesulfonyl) diphenyl sulfone melting at 303.5-304°C. after recrystallization from ethylene dichloride which had previously been prepared as a derivative in the condensation of diphenyl sulfide with thionyl chloride. No further attempt was made to isolate pure materials from the other oils.

The Preparation of 2-Methyl-8-Chlorothianthrene

The quantities, 13 g. (0.055 mole) of 4-chlorophenyl-4'-tolyl sulfide, 8.0 g. (0.06 mole) of anhydrous aluminum chloride and 200 ml. of ethylene dichloride were placed in a 500 ml. round-bottom flask equipped with a stirrer, thermometer, dropping funnel and a condenser fitted with a calcium chloride tube. A gray metal complex formed in a few minutes. The reaction mixture was cooled to 10°C. and 6.0 g. (0.058 mole) of sulfur dichloride dissolved in 30 ml. of ethylene dichloride was added to the reaction mixture during a one hour period. The reaction solution took on a bluish-black coloration during the addition of the dichloride. The reaction mixture was allowed to stir for an additional 27 hours at room temperature following the addition of the dichloride solution and was then quenched by pouring it into cold dilute hydrochloric acid. A light brown oily layer was separated, washed in the usual manner and subjected to solvent removal under vacuum. The residue was distilled under vacuum to obtain two fractions (b.p. 155-178°C./10 mm. and 178-200°C./ 10 mm.) and 6.5 g. of a tarry residue. The lower boiling fraction (weight 3.0 g.) solidified on cooling to room temperature and was recrystallized from methanol to obtain a material melting at 71-3°C. which was identified by its infra-red spectrum to be unreacted starting material (m.p. 73-4°C.). The second fraction was then subjected to infrared examination and was found to have substitution peaks at 11.50 and 12.35 microns which indicated the 1,2,4 substitution pattern expected from the anticipated ring closure product. The material was taken up in boiling methanol and chilled in the refrigerator to obtain a small quantity of solid material which melted at 128-9°C. following three recrystallizations from methanol.

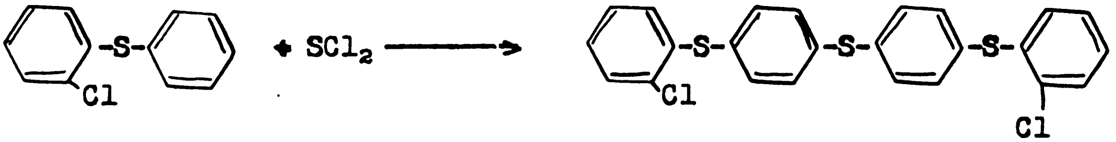
Anal. Calc'd for $C_{13}H_9Cl_1S_2$: C, 58.96; H, 3.42; Cl, 13.29; S, 24.21

Found: C, 58.94; H, 3.40; Cl, 13.28; S, 24.26

No previous record of the 2-methyl-8-chlorothianthrene was found in the literature. The tetroxide of this material was not prepared due to the small amount of material isolated and the experiment was not repeated to obtain additional material since a procedure for preparing the tetroxide of a thianthrene molecule containing a methyl group on the ring had not been worked out.

The Reaction of Sulfur Dichloride with 2-Chlorophenyl Phenyl Sulfide

A 500 ml. three-neck round-bottom flask was equipped in the usual manner for a condensation reaction. The quantity, 23.0 g. (0.104 mole), of 2-chlorophenyl phenyl sulfide was placed in the flask with 100 ml. of ethylene dichloride and 14.0 g. (0.11 mole) of anhydrous aluminum chloride. The reaction mixture was cooled to 10°C. and 10.7 g. (0.104 mole) of sulfur dichloride dissolved in 100 ml. of ethylene dichloride was added during a period of three hours. The ice bath was then removed from the flask and the reaction mixture was stirred for twenty-four hours before warming it to 70°C. for thirty minutes and then quenching it by pouring the mixture into dilute hydrochloric acid. The oily layer was separated and washed in the usual manner and the solvent was removed by vacuum distillation. An attempt to distill the residue under high vacuum led to extensive decomposition with the evolution of copious quantities of gaseous products resulting in the loss of the vacuum in the distillation system. Insertion of a caustic tower in the vacuum line permitted the distillation of 9 gms. of an oil (b.p. 70-230°C./5 mm.) using a short path fractionating column. A residue of 14 g. of a brittle carbonaceous tar remained in the flask after the distillation (final temperature of the distillation flask was 350°C.). The oil was refractionated through a 10 cm. vigreux column into eight fractions. Infra-red spectra were determined of each fraction and absorption peaks were found at 12.40, 13.00, 13.50 and 14.5 microns. The peak at 12.40 was interpreted as due to para substitution which could arise from chlorination or condensation of the monosubstituted benzene ring as indicated in reaction (4).



(4)

The band at 13.45 was attributed to ortho substitution in the absence of any absorption band at 14.5 microns while the combination of those two bands indicated monosubstitution with the possibility that there was ortho substitution as well. (Note--a study of infra-red absorption curve, Figure 19, will help to make this point clear.) Fraction V (b.p. 190-200°C./3 mm.) which showed a longer absorption peak at 13.00 microns was diluted with ethanol and allowed to set aside in the refrigerator. After two weeks a few crystals precipitated and were recovered by filtration. These were recrystallized from methanol to obtain approximately 0.2 g. of a solid melting at 84-5°C. The infra-red spectrum showed substitution peaks at 13.00 and 13.41 microns. The material was oxidized with chromic acid in glacial acetic acid to obtain the tetraxide which melted at 240.5-242°C. Gilman and Swayampati[97] prepared 1-chlorothianthrene from the corresponding 1-amino derivative and found it to melt at 85-85.5°C. and to have an infra-red absorption curve showing 1,2,3-substitution absorption at 13.0 microns and 1,2-substitution absorption at 13.4 microns. Their tetroxide melted at 242°C. The other oil fractions were not investigated further.

The Condensation of Sulfur Dichloride with 3,4-Dichlorophenyl Phenyl Sulfide

Since 3,4-dichlorophenyl phenyl sulfide would give 3,4-dichloro thianthrene, a 1,2,4,5 substitution product upon ring closure with sulfur dichloride it was decided to test the theory that the formation of a 1,2,4,5 substitution product in such condensation reactions is a strong driving force. Ethylene dichloride (250 ml.), 40 g. (0.155 mole) of 3,4-dichlorophenyl phenyl sulfide and 12.5 g. (0.095 mole) of anhydrous aluminum chloride were placed in a 500 ml. round-bottom three-neck flask. The addition of 16 g. (0.155 mole) of sulfur dichloride dissolved in 50 ml. of ethylene dichloride to the cooled reaction mixture during a period of an hour produced a green coloration due to metal complex formation. The suspension of metal complex reaction mixture was stirred for twenty-four hours and quenched by pouring it into dilute hydrochloric acid. The oily layer was separated and washed as usual. After solvent removal the residue was vacuum distilled with attendant heavy decomposition through a short path column leaving a tarry residue of 15 g. in the distillation flask. The oily distillate (20 g., b.p. 150-220°C./5 mm.) was refractionated through a 10 cm. vigreux column into five fractions which were examined by infra-red. Absorption peaks in the substitution region (11-15 microns) were found at 11.50, 12.35, 13.4 and 14.5 microns. The absorption peak amplitude varied as the boiling point of the fraction increased indicating the disappearance of monosubstitution product (14.5 microns), with an increase in ortho (13.4 microns) and para substitution products (12.35 microns). An attempt at the isolation of any solid material from the fractions by chilling in solvent failed to effect a separation of any pure material. Compounds containing two adjacent hydrogens (chlorination products, 1,2-dichlorothianthrene or higher condensation products were so extensively contaminated with the other material (as evidenced by the para substitution absorption at 12.35 microns) that it was not possible to purify such a small amount of material. As 2,3-dichlorothianthrene would undoubtably be very low melting (less than 60°C.) further work with these materials was abandoned in lieu of repeating the experiment on a larger scale using an excess of starting material to reduce the side reactions. However, time used on other phases of this research did not permit the experiment ever being carried out.

The Preparation of 2,8-Dichlorothianthrene

The quantity, 70 g. (0.27 mole), of bis(4-chlorophenyl) sulfide (m.p. 95-6°C., prepared via the sulfoxide) was placed in a one-liter flask with 200 ml. of ethylene dichloride. Anhydrous aluminum chloride (37 g., 0.028 mole) was added to the reaction flask and it was then cooled to 15°C. Sulfur dichloride (28 g., 0.027 mole) was added to the chilled reaction mixture during a period of one hour and was accompanied by spontaneous hydrogen chloride evolution. The reaction mixture was stirred at room temperature for 24 hours and then at 50°C. for fifteen minutes and quenched by pouring it into ice water. A small amount of solid precipitated upon hydrolysis of the metal complex which redissolved on warming the hydrolyzed mixture. The solvent layer was separated, washed consecutively with dilute hydrochloric acid and water, and the solvent was removed by vacuum distillation. The residue was fractionated under vacuum to obtain a product fraction (b.p. 193-200°C./10 mm.) which was recrystallized from acetone three times to obtain 39 g. (0.124 mole, 49% yield) of 2,8-dichlorothianthrene melting at 172-172.5°C.

Anal. Calc'd for $C_{12}H_6Cl_2S_2$: C, 50.53; H, 2.12; Cl, 24.86; S, 22.48

Found: C, 50.53; H, 2.28; Cl, 24.72; S, 22.44

The infra-red spectrum of this material was found to be essentially identical with that of the 2,7-dichlorothianthrene (Figure 52) which was not unexpected since both compounds would exhibit a 1,2,4-type of substitution pattern.

Oxidation of the material with chromic acid in glacial acetic acid by the usual procedure produced an 88% yield of 2,8-dichlorothianthrene-5,5,10,10-tetroxide melting at 288-9°C.

Anal. Calc'd for $C_{12}H_6Cl_2O_4S_2$: C, 41.26; H, 1.73; Cl, 20.30; S, 18.36

Found: C, 41.26; H, 2.01; Cl, 20.25; S, 18.18

An infra-red spectrum of the tetroxide was made and peaks in the substitution region (11-15 microns) were found at 10.90, 11.30, 11.75, 11.90, 12.41 and 14.00 microns. The first two were weak bands from the single hydrogen out of plane vibrations while the next three arise from the adjacent hydrogen out of plane vibrations. The peaks at 11.75 and 11.90 were twin peaks of a doublet. The strongest peak at 14.00 arises from the carbon-chlorine vibrations. A detailed discussion of this spectra will be found in the appendix of this thesis.

The Reaction of Sulfur Dichloride with Phenyl Ether

Some preliminary studies with diphenyl methane indicated that it was very probably necessary to have an electronegative element such as sulfur, nitrogen, or oxygen between the two phenyl rings in order to obtain a satisfactory ring closure with the sulfur halides. As a result of these preliminary observations, ring closure of phenyl ether as an oxygen type compound was attempted.

A 510 g. (3.0 moles) quantity of phenyl ether was placed in a two-liter three-neck round-bottom flask equipped with a stirrer, thermometer, dropping funnel and a gas scrubber. The flask and its contents were cooled to 10°C. in an ice bath, and 15 g. (0.12 mole) of anhydrous aluminum chloride was added to the aryl ether followed by the addition of 216 g. (2.0 moles) of sulfur dichloride dissolved in 500 ml. of ethylene dichloride during a two hour period. Hydrogen chloride evolution was vigorous during the addition of the thiohalide and continued at a diminished rate following the addition of the sulfur halide. When the halide had been added the ice bath was removed and the reaction mixture was stirred for an additional five hours at room temperature then warmed to 50°C. for 20 minutes and finally quenched by pouring it into cold dilute hydrochloric acid. After hydrolysis of the metal complex the oily layer was separated and washed initially with acid and then with water. The ethylene dichloride was removed by vacuum distillation and the residue was distilled through a 15 cm. vigreux column. A fraction boiling in the range 60-150°C./3 mm. was collected before hydrogen chloride evolution increased to the point which prevented maintenance of a vacuum. The insertion of a tower filled with potassium hydroxide and anhydrous calcium chloride into the vacuum line combined with a change to water aspiration for pumping also failed to secure a sufficient vacuum to continue the distillation. Allowing the distillation apparatus to cool caused the residue to solidify to a black glassy resin and it was necessary to discard the distillation flask. By comparison with an empty flask of the same size it was estimated that 260 g. of the tarry material was discarded. A careful refractionation of the initial 260 g. of distillate through a 50 cm. vigreux column produced

150 g. (0.88 mole) of unreacted phenyl ether (b.p. 88°C./3 mm.), 61 g. (0.296 mole) of 4-chlorophenyl phenyl ether (b.p. 107°C./3 mm., n_D^{25} = 1.5863) and 29 g. (0.145 mole) of phenoxathiin (b.p. 120°C./3 mm.). The chlorinated product was identified from its infra-red spectrum which had substitution peaks at 12.3 and 13.6 microns as would be expected from a compound containing mono and para substitution. Suter and Green[44] report n_D^{25} = 1.5865 for the refractive index of 4-chlorophenyl phenyl ether. The phenoxathiin was recrystallized from methanol to obtain a white crystalline solid melting at 56-7°C. Literature value[33] m.p. 56-7°C. Oxidation of the sulfide link with chromic acid in glacial acetic acid by the usual procedure gave an 85% yield of the phenoxathiin-10,10-dioxide melting at 147-8°C. after a single recrystallization from ethanol. Literature value[179] m.p. 147-8°C.

A second condensation of phenyl ether was made using the same quantities of reactants with the exception of the catalyst, aluminum chloride, which was increased to 266 g. (2.0 moles). This change produced considerable improvement in the reaction although it was still not satisfactory. The initial distillation again had to be stopped due to decomposition, leaving a brittle glassy residue of 106 g. in the distillation flask. The initial distillate was again refractionated to obtain 158 g. (0.93 mole) of unreacted phenyl ether, 140 g. (0.68 mole) of 4-chlorophenyl phenyl ether and 90 g. (0.45 mole) of phenoxathiin. In this experiment there was also formed about 10 g. of a higher boiling distillate which was undoubtably the product resulting from the coupling of two moles of phenyl ether in the para position. No further work was done on this material since the amount was too small to work with effectively. There was undoubtably some monochlorophenoxathiin in the residues but no attempt was made at this time to isolate the material.

Although this work proved to be quite promising at the time it was not pursued further since it was felt that due to the tedious distillation of products it would be better to study the ring closure of diphenyl sulfide to thianthrene since the latter material had a much higher melting point (154-5°C.) which made the isolation of the product much less difficult. A number of conclusions regarding future work on this ring closure appear in the discussion part of the present thesis.

The Preparation of 2,8-Dichlorophenoxathiin

The ether, bis(4-chlorophenyl) ether, was prepared in an effort to extend the phenoxathiin ring closure procedure beyond the use of diphenyl ether. A 25 g. (0.104 mole) quantity of bis(4-chlorophenyl) ether was placed in a 500 ml. three-neck round-bottom flask suitably equipped for the condensation reaction. A 200 ml. volume of ethylene dichloride and 6.9 g. (0.052 mole) of anhydrous aluminum chloride were added to the reaction flask and the mixture was cooled to 10°C. The quantity, 10.7 g. (0.104 mole) of sulfur dichloride dissolved in 50 ml. of ethylene dichloride was added to the reaction flask during a one hour period. External cooling of the reaction mixture was removed and it was stirred for 48 hours, then warmed to 50°C. for fifteen minutes and finally quenched by pouring it into cold dilute hydrochloric acid. A small amount

of material precipitated which redissolved on warming the mixture and then the oily layer was separated and washed. The solvent was removed by vacuum distillation and the product (b.p. 201°C./11 mm.) was distilled in a short path column. The solid was recrystallized from ethanol to obtain a white solid melting at 135-135.5°C. Smiles and Hilditch[103] prepared 2,8-dichlorophenoxathiin by the sulfuric acid ring closure of bis(2-hydroxy-5-chlorophenyl)sulfoxide with subsequent zinc reduction of the 2,8-dichlorophenoxathiin-10-oxide to obtain 2,8-dichlorophenoxathiin melting at 135°C. Suter, McKenzie, and Maxwell[33] chlorosulfonated phenoxathiin with chlorosulfonic acid and then heated the phenoxathiin-2,8-disulfonyl chloride with phosphorous trichloride to obtain 2,8-dichlorophenoxathiin melting at 134-5°C.

Oxidation of the 2,8-dichlorophenoxathiin, obtained by the procedure described in the present work, with chromic acid in glacial acetic acid by the usual oxidation procedure produced an 84% yield of 2,8-dichlorophenoxathiin-10,10-dioxide melting at 196-196.5°C. after a single recrystallizatinn from ethanol. Literature value[103] m.p. 196°C.

The Reaction of Sulfur Dichloride with Diphenyl Methane

This reaction was the initial experiment in the present investigation. A two-liter three-neck round-bottom flask was equipped with a stirrer, thermometer, dropping funnel and hydrogen chloride scrubber. A 168 g. (1.0 mole) quantity of diphenyl methane, 600 ml. of ethylene dichloride and 133 g. (1.0 mole) of anhydrous aluminum chloride were placed in the reaction flask. The flask was cooled to 10°C. and 103 g.

(1.0 mole) of sulfur dichloride dissolved in 100 ml. of ethylene dichloride was added during a three hour period. Hydrogen chloride evolution was spontaneous and heat of reaction was evident upon rapid addition of the sulfur dichloride. Following the addition of the dichloride the reaction mixture was warmed on the steam bath to 60°C. for thirty minutes and then quenched by pouring it into ice water. The metal complex hydrolyzed readily and the oily layer was separated and washed consecutively with dilute hydrochloric acid and water. The solvent was removed by vacuum distillation and an attempt was made to distill the residue in vacuo. Approximately 10 g. of an orange oil distilled in the temperature range 88-160°C./2 mm. by heating the flask contents to 250°C. Some solidification took place in the oil and an attempt was made to find a recrystallization solvent for the material. The rest of the material was non-distillable and on cooling it solidified to a hard brittle tar. A second reaction of diphenyl methane with sulfur dichloride was carried out employing the same quantities of reactants and experimental conditions with the exception that heating the reaction mixture at the end of the experiment was eliminated and the reaction mixture was stirred at room temperature for 30 minutes. The solvent layer isolated from the quenched reaction mixture was considerably lighter in color than the previous case but the same net result was obtained.

The work was discontinued at this point since it was apparent that the desired ring closure reaction of diphenyl methane to thiaxanthene was not occurring due either to polymerization or attack on the methylene

bridge and that an electronegative atom such as O, S or N might be necessary for coordination of the catalyst near the ortho position in order to obtain a ring closure. Studies with diphenyl sulfides and diphenyl ethers subsequently proved fruitful and after it had been shown that an excess of the reactant was necessary to avoid polymerization tendencies two more reactions of diphenyl methane with sulfur dichloride were made with better end results.

In the third experiment 282 g. (1.68 moles) of diphenyl methane, 350 ml. of ethylene dichloride, and 13.3 g. (0.10 mole) of anhydrous aluminum chloride were placed in the reaction vessel. The mixture was cooled to 10°C. but the diphenyl methane (m.p. 26-7°C.) crystallized from the solution and it was necessary to add 250 ml. of additional ethylene dichloride and warm the reaction mixture to 20°C. to effect solution. The addition of 41.0 g. (0.40 mole) of sulfur dichloride dissolved in 100 ml. of ethylene dichloride required two hours and then the reaction mixture was stirred at room temperature for twenty-four hours. A dark-brown metal complex formed during the reaction but hydrogen chloride evolution was slow due to the low catalyst ratio to reactants. The reaction mixture was quenched, without heating, by pouring it into cold dilute hydrochloric acid. This resulted in the formation of a red-colored oil layer which was separated and washed as in previous experiments. Distillation of the solvent followed by fractionation of the residue produced eleven fractions as follows:

Fraction Number	Boiling Point	Comments
I	37-120°C./3 mm.	
II	120-142°C./3 mm.	
III	142-145°C./3 mm.	Faint green fluorescence in distillate
IV	145-151°C./3 mm.	Green fluorescence
V	151-154°C./3 mm.	Green fluorescence with trace of H_2S from pump
VI	154-160°C./3 mm.	Green fluorescence with trace HCl
VII	160-162°C./3 mm.	Green fluorescence
VIII	162°C./5 mm.	H_2S and HCl from pump
IX	160°C./23 mm.	Lost vacuum and had to install KOH trap
X	210°C./4 mm.	Crystals in distillate
XI	210-260°C./5 mm.	Crystals in distillate

A non-distillable tar residue weighing 63 g. remained in the distillation flask. The green fluorescence in the distillation fractions faded on standing exposed to the atmosphere indicating that it was probably due to some sort of a complex resulting from traces of hydrogen sulfide or hydrogen chloride both of which were present in the distillation vapors. Fraction I through VII were combined and refractionated to recover 173 g. (1.03 moles) of diphenyl methane. A small amount of benzophenone (about 1 g.) was isolated at the very tail end of this distillation. It solidified in the receiver and was recrystallized from alcohol to obtain a white crystalline solid melting at 47-8°C. The infra-red spectrum of this material showed a carbonyl peak at 6.0 microns and it was identical to the spectrum of a known sample of benzophenone. Fraction X precipitated solid on standing which was filtered and recrystallized from ethanol to obtain a yellow solid melting at 118-120°C. It was found to be elemental sulfur since it produced a characteristic blue flame and smelled strongly of sulfur dioxide when burned. The handbook lists a melting point of 120°C. for amorphous and 119°C. for monoclinic sulfur. Fraction XI also precipitated a crystalline solid which was filtered and recrystallized from acetone to obtain a yellow colored solid melting at 213-215°C. The material showed a strong ortho peak at 13.60 microns and a carbonyl peak at 6.10 microns and was eventually identified as thiaxanthenone. (Literature value[74] m.p. 212-214°C.) This material was oxidized with chromic acid in glacial acetic acid in the usual manner to obtain 10-thiananthenone-5,5-dioxide in an 87% yield melting at 184.5-185.5°C. (Literature value[74,180] m.p. 184°C.) The filtrates from fractions X and XI were combined and refractionated. Five fractions were taken from this redistillation. The first three fractions boiling in the range 190-215°C./5 mm. precipitated additional quantities of thiaxanthenone on standing. This was filtered off and recrystallized as before. However, efforts to obtain further information from the filtrates from these first three fractions and the two higher fractions boiling in the range of 215-260°C./5 mm. and 260-280°C./5 mm. proved fruitless.

The fourth reaction of diphenyl methane and sulfur dichloride was made with the largest excess of diphenyl methane (6 to 1) and with more catalyst than the third experiment.

The quantities, 513 g. (3.06 moles) of diphenyl methane, 250 ml. of ethylene dichloride and 45 g. (0.34 mole) of anhydrous aluminum chloride were placed in a three-liter three-neck round-bottom flask equipped as before. The reaction mixture was cooled to 20°C. and 51.5 g. (0.5 mole) of sulfur dichloride dissolved in 100 ml. of ethylene dichloride was added during a one hour period. Hydrogen chloride evolution was vigorous as long as the addition of sulfur dichloride was continued. The metal complex coloration was blood red. The cold water bath was removed at the end of the addition of the dichloride and the reaction mixture was stirred for four hours before quenching it by pouring it into dilute hydrochloric acid. The product isolation was carried out in the same manner as the previous experiment. The initial distillation was made with a short path column and the presence of a potassium hydroxide tower in the vacuum system was necessary to maintain a good vacuum. The residue (weight 128 g.) solidified to a hard glassy material on cooling. It was dissolved in boiling chlorobenzene and given three successive treatments with Norite and allowed to cool slowly. Since no precipitation of any kind occurred on standing for a week this material was discarded with the conclusion that the material was probably a low molecular weight polymer. The crude distillate was fractionated through a 20 cm. vigreux column and separated into low, medium and high boiling fractions. The low boiling range fraction was refractionated to recover 106 g. (0.63 mole, b.p. 101°C./5 mm.) of unreacted diphenyl methane. Examination, by the infra-red technique, of the terminal portions of the distillation from this fractionation showed only traces of para- substitution which would have been present if chlorination had taken place. The terminal portions of the low boiling fraction were added to the intermediate fraction from the initial distillation and this material was fractionated into four fractions as follows:

Fraction	Boiling Range	Comment
I	107-155°C./6 mm.	
II	164-190°C./6 mm.	Partially solidified
III	190-200°C./6 mm.	Greenish fluorescence
IV	176-187°C./2 mm.	Greenish fluorescence

Fraction II was filtered and the solid was washed with alcohol and dried to obtain a crude product with a melting point of 121-125°C. The material on recrystallization from ethanol gave a colorless crystalline solid melting at 128.5-129.5°C. Its infra-red spectrum showed an ortho peak at 13.5 microns and a methylene peak at 3.35 microns and was identified as thiaxanthene. (Literature value[108,46] m.p. 128°C.) The thiaxanthene was oxidized with chromic acid by the usual procedure (described elsewhere in this thesis) to obtain an 81% yield of 10-thiaxanthenone-5,5-dioxide which melted at 184.5-185.5°C. (Literature value[74,180] m.p. 184°C.)

Fraction I and the filtrate from fraction II were combined and redistilled to obtain additional thiaxanthene (b.p. 155-160°C./2 mm.). This was recrystallized to obtain a total of 12.5 g. (0.063 mole) purified thiaxanthene. It should be noted at this point that no previous record of direct ring closure to thiaxanthene has appeared in the literature except the hot tube oxidation of 2(phenylmercapto) toluene.[46] Its usual preparation is the reduction[108,46] of thiaxanthenone which can be readily obtained by the sulfuric acid condensation of thiosalicylic acid with benzene.[32,110,107]

The residue from the isolation of thiaxanthene and fraction III were combined and refractionated as follows:

Fraction No.	Boiling Point	Comment
IA	170-176°C./2 mm.	Solid plus oil
IIA	178-185°C./2 mm.	Yellow crystals on cooling
IIIA	185-205°C./2 mm.	Oil

The solid obtained from fraction IA turned out to be thiaxanthene and the solid from fraction IIA turned out to be thiaxanthenone. The filtrate from fraction IIA was transferred, with the aid of methylene chloride, to a distillation flask for refractionation. However, on vacuum distillation of the solvent at room temperature the contents of the flask solidified. This solid was separated, washed with methanol, and was found to melt at 71-86°C. Recrystallization of the material from absolute alcohol gave a colorless crystalline product melting at 86-7°C. The infared spectrum of the material showed essentially monosubstitution with absorption peaks at 14.0 and 14.5 microns with a low intensity peak at 13.0 microns and in a very concentrated solution it showed a low intensity peak at 12.00 microns. A sodium fusion indicated the absence of chlorine and sulfur and an elemental analysis showed it to be 1,4-(dibenzyl) benzene. (Literature value[181] m.p. 87-87.5°C.)

Anal. Calc'd for $C_{20}H_{18}$: C, 92.97; H, 7.02

Found: C, 92.96; H, 7.01

This material was oxidized to the 1,4-(dibenzoyl) benzene using chromic acid in glacial acetic acid by the usual procedure.[77] The oxidized material melted at 160-161°C. (Literature value[77] m.p. 160-161°C.) and analyzed correctly for 1,4-(dibenzoyl) benzene.

Anal. Calc'd for $C_{20}H_{14}O_2$: C, 83.89; H, 4.92

Found: C, 83.91; H, 4.86

A total of 23.0 g. (0.089 mole) of this material was purified in all.

The higher boiling range fractions were also refractionated and after long standing some of them precipitated solid which was filtered and an unsuccessful attempt was made to recrystallize the solid but the materials failed to crystallize from solution. These fractions were eventually discarded since it was believed that they were a mixture of several compounds and that more would be gained by working in other areas since it was now apparent that it would be quite difficult to evolve a satisfactory procedure for this ring closure reaction.

The Attempted Ring Closure of 1,1-bis(4-Chlorophenyl) Ethane

The quantity, 50 g. (0.22 mole) of 1,1-bis(4-chlorophenyl) ethane was placed in a one-liter flask containing 250 ml. of ethylene dichloride and 20 g. (0.15 mole) of anhydrous aluminum chloride. The mixture was stirred and cooled to 10°C. prior to adding 23 g. (0.22 mole) of sulfur dichloride. Chemical reaction was spontaneous and following the addition of the dichloride the reaction mixture was stirred for 6 hours at room temperature, warmed to 50°C. for 30 minutes and then quenched by pouring it into dilute hydrochloric acid. The solvent layer was separated and washed in the usual manner after which the excess solvent was removed by distillation at atmospheric pressure. The residue was found to be insoluble in boiling acetone, benzene, methanol, ethanol and acetic acid. An attempt was made to distill the residue under vacuum but extensive decomposition occurred and only a carbonaceous residue was obtained.

The Attempted Preparation of Thianthrene-5-Oxide

This experiment was the first of a series of reactions carried out to prepare thianthrene-5-oxide using diphenyl sulfide. Diphenyl sulfide (200 g., 1.07 moles), ethylene dichloride (300 ml.) and 67 g. (0.5 mole) of aluminum chloride were placed in a one-liter three-neck round-bottom flask and cooled to 10°C. Thionyl chloride (59.5 g., 0.5 mole) dissolved in 100 ml. of ethylene dichloride was then added dropwise to the above mixture over a three hour period. Hydrogen chloride evolution was spontaneous. When the addition of thionyl chloride had been completed the ice bath was removed and the reaction mixture was stirred at room temperature for 18 hours, after which it was warmed to 70°C., allowed to stir for an additional thirty minutes and then quenched in ice water with vigorous stirring to hydrolyze the metal complex. Insoluble material appeared almost immediately and the mixture was warmed with additional solvent in a futile attempt to dissolve the material. An emulsion formed on further stirring and ice had to be added to solidify the gummy material and the solid was removed by filtration. The oil layer was separated from the filtrate and washed successively with 6N hydrochloric acid and water. The solvent was removed by distillation under reduced pressure and the oil residue was fractionally distilled under vacuum. The initial fraction contained 51 g. of diphenyl sulfide contaminated badly with 4-chlorophenyl phenyl sulfide (as evidenced by the para absorption peak at 12.25 microns). The intermediate fraction solidified on cooling and after three recrystallizations from methanol yielded 2.0 g. of thianthrene melting at 154.5-155.5°C. The final fraction also solidified and was recrystallized three times from methanol to give 21 g. of a material melting at 81.0-81.5°C. In order to decide whether this material contained a sulfoxide group, a zinc reduction in acetic acid was carried out. The material was recovered unchanged showing that sulfoxide was absent. The material was then oxidized with chromic acid in boiling acetic acid to obtain a polysulfone melting at 230.5-231°C. after recrystallization from acetone. Before analysis of these materials were completed it was realized that the melting points of these two materials agreed with the constants for 1,4-bis(phenyl mercapto) benzene[47] and its sulfone,[177] and their analysis verified this conclusion.

Anal. Calc'd for $C_{18}H_{14}S_2$: C, 73.42; H, 4.79; S, 21.78

Found: C, 73.37; H, 4.92; S, 21.94

Anal. Calc'd for $C_{18}H_{14}O_4S_2$: C, 60.31; H, 3.93; S, 17.89

Found: C, 60.53; H, 3.80; S, 17.75

The isolation of 1,4-bis(phenyl mercapto) benzene from this reaction leads to the inescapable conclusion that migration of a phenyl mercapto group must have occurred during the reaction. Tarbell and Wilson[150] in their studies of the cleavage of phenyl benzyl sulfide state that electron attracting groups speed up sulfide cleavage. Since phenyl mercapto groups activate halogen displacement on the benzene ring it can be assumed that they are electron withdrawing and that in a phenylene sulfide chain the end group is relatively easily displaced and then it adds onto the end of a second phenylene sulfide chain to increase its length, eventually producing large amounts of polymer in a reaction where there is a sufficient amount of Friedel Crafts catalyst present. It was found that the insoluble material isolated during this reaction was partially soluble in hot chloroform while the majority of it was not indicating its polymeric nature.

The absence of any oxygenated compounds in the isolated materials emphasizes the lability of the oxygen in sulfoxide groups when subjected to an environment of aluminum chloride and hydrogen chloride as will be emphasized in other experimental sections of this thesis.

The Second Attempt to Ring Close Diphenyl Sulfide with Thionyl Chloride

Since the first attempt to prepare thianthrene-5-oxide by a ring closure reaction showed there was too much catalyst present (as evidenced by phenyl mercapto migration and deoxygenation) the ratio of catalyst to reactant in this experiment was decreased and the solvent volume was increased for higher dilution.

Diphenyl sulfide (200 g., 1.07 moles), 33 g. (0.25 mole) of anhydrous aluminum chloride and 900 ml. of ethylene dichloride were placed in a two-liter three-neck round-bottom flask, suitably equipped to conduct a ring closure reaction, and the mixture was cooled to 10°C. The addition of 59.5 g. (0.5 mole) of thionyl chloride dissolved in 100 ml. of ethylene dichloride was made during a three hour period. It was necessary to remove the ice bath to maintain a suitable reaction rate during the initial addition of the thionyl chloride. The mixture after the chloride had been added was stirred at room temperature for twenty-six hours, heated to 60°C. for forty-five minutes on the steam bath and quenched by pouring it into ice water. The sky-blue metal complex broke up readily leaving a rust-brown organic layer from which insoluble material precipitated on setting the mixture aside for a period of time. The insolubles were removed by filtration and the organic layer was separated and washed consecutively with 6N hydrochloric acid and water, the solvent was removed by vacuum distillation and the oily residue was fractionated. The initial fraction (b.p. 152-8°C./6 mm.) was shown by infra-red analysis to be diphenyl sulfide (41 g., 0.22 mole) and the next four successive fractions (28, 13, 10 and 5.5. g. respectively) were shown to be progressively contaminated with 4-chlorophenyl phenyl sulfide. The last two higher boiling fractions (IV and V) were practically pure chlorinated material as shown by the infra-red spectrum and a sample of fraction V was oxidized with chromic acid in glacial acetic acid to obtain 4-chlorophenyl phenyl sulfone melting after three recrystallizations from methanol, at 90-91°C. (Literature value[150] m.p. 91.2° C.) The infra-red spectrum of the sulfone was identical with that obtained from the same sulfone prepared in other experiments.

Fraction VI (b.p. 190° C./6 mm. partially solidified on being set aside at room temperature. The solid was recovered by filtration and recrystallized from ethanol to obtain crystalline thianthrene (weight 1.0 g.) melting at 154-5°C. In order to distill the higher boiling material the 10 cm. vigreux column was removed from the apparatus and only the still head was used directly in the distillation since the boiling ranges were so high. Fractions VII and VIII (b.p. 213-230 and 230-300°C./3 mm. respectively) were distilled using a direct flame to heat the column and assist the distillate through the head. Fraction VII was found to contain thianthrene (m.p. 154-5°C.) which was identified by oxidizing it to its tetroxide (m.p. 320-322°C.) with chromic acid in glacial acetic acid. (Literature value[182] m.p. 321°C.) Fraction VIII was recrystallized from petroleum ether to obtain a somewhat waxy solid melting at 90-94°C. Further crystallization separated the material into several fractions melting in both higher and lower melting ranges.

All of the fractions gave infra-red spectra showing substitution bands at 12.30, 13.45 and 14.5 microns as would be shown by five adjacent hydrogens (mono substitution) and two adjacent hydrogens (para substitution). Such substitution would be found in molecules formed by the condensation of two diphenyl sulfide molecules coupling in the para position. The absorption peaks at 9.75 and 9.90 microns shown by these fractions are characteristic of 1,4-bis(phenylmercapto) benzene (m.p. 81-85.5°C., Figure 61 in the appendix). The lowest melting range for material obtained was 87-90°C. and the highest was 94-7°C. Further attempts to separate pure isomers were abandoned since the fractions could not be induced to crystallize. The highest melting fraction (m.p. 94-7°C.) was oxidized with chromic acid in glacial acetic acid to obtain a crystalline solid melting, after recrystallization from ethylene dichloride, at 303-304°C.

Anal. Calc'd for $C_{24}H_{18}O_6S_3$: C, 57.81; H, 3.63; S, 19.29

Found: C, 57.08; H, 3.63; S, 19.35

Thus, it would appear that the crude material contained four phenyl rings connected by three sulfur atoms and this suggests that very probably the crude fraction was a mixture of 1,4-bis(phenylmercapto) diphenyl sulfide and sulfoxide. Unfortunately a zinc reduction which undoubtably would have eliminated the sulfoxide leaving only the sulfide was not carried out. The spectral evidence (absorption at 9.75 and 9.90 microns) also indicates that the lower melting fractions contained material [1,4-bis(phenyl mercapto) benzene] resulting from phenylmercapto migration as was found in the first attempt at this ring closure reaction.

2,8-Dichlorothianthrene-10-Oxide

The quantity, 60 g. (0.24 mole), of bis(4-chlorophenyl) sulfide (m.p. 95-6°C.) obtained by the reduction of the sulfoxide was placed in a 500 ml. round-bottom flask suitably equipped for a condensation reaction. Ethylene dichloride (150 ml.) and 35 g. (0.26 mole) of anhydrous aluminum chloride were added to the reaction flask and the mixture was cooled to 10°C. A solution of 32 g. (0.27 mole) thionyl chloride dissolved in 75 ml. of ethylene dichloride was added to the reaction mixture during a two hour period. The evolution of hydrogen chloride was rapid during the addition of the chloride solution. The ice bath was removed from the reaction flask and the reaction mixture was stirred for 10 hours, warmed to 50°C. for 15 minutes and then quenched by pouring it into ice water. A crystalline solid precipitated from the quenched reaction mixture on setting it aside. This was recovered by filtration and dried. The solid (weight 11 g.) was recrystallized from acetone to obtain a material melting at 166-7°C.

Anal. Calc'd for $C_{12}H_6Cl_2O_1S_2$: C, 47.84; H, 2.00; Cl, 23.54; S, 21.29

Found: C, 47.90; H, 2.03; Cl, 23.50; S, 21.24

No further product isolation work was carried on the quenched liquor filtrate.

The Attempted Preparation of 2,3,7,8-Tetrachlorothianthrene-5,5-Dioxide

This was the first endeavor to use sulfuryl chloride in the presence of a Friedel Crafts catalyst for producing a sulfone linkage. An attempt was made to ring close a diphenyl sulfide, blocked in the para position, to develop a method of preparing thianthrenes with two oxygens on the same sulfur which are not readily obtainable by other methods.[14,16,20]

Bis(3,4-dichlorophenyl) sulfide (30 g., 0.0925 mole), 12.3 g. (0.0925 mole) of anhydrous aluminum chloride, and 500 ml. of ethylene dichloride were placed in a one-liter three-neck round-bottom flask properly equipped and 12.5 g. (0.0925 mole) of sulfuryl chloride was added at 25°C. over a two hour period. The mixture was stirred two hours at room temperature and it was heated at reflux temperature for one hour. It was then quenched in water and the oil layer was separated and washed in the usual manner. The solvent was removed by distillation under vacuum and an attempt was made to recrystallize the residue from eleven different solvents without success. An infra-red spectrum of the crude showed peaks at 7.6 and 8.5 microns which were indicative of sulfone formation although the benzene ring substitution still appeared to be 1,2,4 since peaks appeared at 11.5 and 12.35 microns. However, the spectrum was markedly different from that of the starting material. The residue was then distilled and five fractions were taken over the range 190-225°C./5 mm. Infra-red spectra of the five fractions showed no detectable differences in them. Partial crystallization occurred in the fifth fraction upon standing, the solid was filtered and after being recrystallized four times from acetone melted at 149-150°C. An infra-red spectrum of this material showed a typical 1,2,4,5 substitution pattern, exhibited by a doublet with peaks at 11.25 and 11.50 microns (see Figure 42).

Since the spectrum also had peaks in the typical sulfone positions it appeared that this was the desired ring closure product. However, due to their similar melting points, the infra-red spectrum of bis(2,4,5-trichlorophenyl) sulfide was compared with that of the material which had just been prepared. The curves proved to be identical and oxidation of the material with chromic acid to the sulfone confirmed the fact that the material which had been isolated was bis(2,4,5-trichlorophenyl) sulfide which had apparently been formed by chlorination of the original sulfide. This suggested that the major product of the reaction was pentachlorodiphenyl sulfide which would exhibit an infra-red spectrum whose substitution pattern would seem to be unsymmetrical trisubstituted (1,2,4). An examination of the spectra obtained from bis(3,4-dichlorophenyl) sulfide (see Figure 32) and bis(2,4,5-trichlorophenyl) sulfide (see Figure 42) showed that the spectrum exhibited from 7-14.5 microns by the major portion of the product was a composite of the peaks shown by those two sulfides. This indicated the material was 2,4,5,3',4'-pentachlorodiphenyl sulfide. The third fraction was then recrystallized twice from acetone and twice from methanol to obtain 2,4,5,3',4'-pentachlorodiphenyl sulfide melting at 85-85.5°C.

Anal. Calc'd for $C_{12}H_5Cl_5S_1$: C, 40.19; H, 1.40; Cl, 49.45; S, 8.94

Found: C, 39.53; H, 1.47; Cl, 50.09; S, 9.04

The sulfide was oxidized to the sulfone with chromic acid by the usual procedure. This was recrystallized from methanol to obtain 2,4,5,3',4'-pentachlorodiphenyl sulfone melting at 142-142.5°C.

Anal. Calc'd for $C_{12}H_5Cl_5O_2S_1$: C, 36.90; H, 1.29; Cl, 45.29; S, 8.21

Found: C, 36.67; H, 1.50; Cl, 44.89; S, 8.04

The sulfone was also prepared by the reaction of 3,4-dichlorobenzenesulfonyl chloride and excess 1,2,4-trichlorobenzene in the presence of aluminum chloride to obtain identical material. The other fractions proved to be fairly impure and were discarded. This original experiment was reported in detail since it was one of the first experiences in which the use of the infra-red technique proved to be of inestimable value in working up the reaction mixture and identifying the products.

The Reaction of bis(4-Chlorophenyl) Sulfide with Sulfuryl Chloride

The quantity, 30 g. (0.12 mole) of bis(4-chlorophenyl) sulfide, 16 g. (0.12 mole) of anhydrous aluminum chloride and 500 ml. of ethylene dichloride were placed in a one liter flask and cooled to 5°C. Sulfuryl chloride (16 g., 0.12 mole) was added slowly to the reaction mixture over a 45 minute period. It was necessary to allow the temperature of the mixture to rise to 20°C. to get steady evolution of hydrogen chloride. The mixture was allowed to stir at room temperature for 18 hours and then it was refluxed for one hour. The material was quenched in cold dilute hydrochloric acid and the oil layer was separated and washed further with acid and water. The solvent was then removed by vacuum distillation and recrystallization attempts on the residual material were made in a large number of solvents. The material was soluble at room temperature in methanol and ethanol. It was insoluble hot in acetone, ethyl acetate, water, and carbon disulfide. It was sparingly soluble in carbon tetrachloride and ethylene dichloride, benzene, petroleum ether (80-100°C.) and chloroform but did not precipitate on cooling. After standing for some time crystals were found in the chloroform sample and further investigation revealed that it could be crystallized from a minimum amount of chloroform to obtain 20 g. of solid melting at 188.5-189°C.

Anal. Calc'd for $C_{12}H_6Cl_2O_2S_2$: C, 45.43; H, 1.91; Cl, 22.36; S, 20.22

Found: C, 50.72; H, 2.74; Cl, 34.67; S, 10.37

The total for the elements analyzed was 98.44% and a survey of possible products failed to find any structure which would fit this data. The material was again recrystallized without any change in its melting point and it was reanalyzed as follows:

Found: C, 49.47; H, 2.40; Cl, 38.08; S, 10.37 giving a total of 100.37

Again no structure could be found which would fit the data. Time did not permit further checking of this analysis of this material. An infra-red spectrum of the material using the potassium bromide pellet method showed absorption at 11.60 (a medium shoulder on the broad peak) a very broad strong peak from 12.0 to 12.40 and a sharp peak at 13.45 microns such as might be expected from 2,8-dichlorothianthrene-10,10-dioxide although there were no usual sulfone peaks in the 7-8 micron region. An attempted oxidation of this material to obtain 2,8-dichlorothianthrene-5,5,10,10-tetroxide using chromic acid in glacial acetic acid yielded a non-crystallizable tar. Termination of the current investigation did not allow further study of this material.

Ring Closure Reactions in Sulfuric Acid

2,7-Dichlorothianthrene and 2,7-Dichlorothianthrene-5-Oxide

This material was desired for comparison with the product obtained from the interaction of sulfur dichloride and bis(4-chlorophenyl) sulfide since Baw, Bennet, and Dearns[4] report that the product which they obtained from this sulfuric acid condensation of 4-chlorobenzenethiol was identical with that which they obtained from the interaction of sulfur monochloride and chlorobenzene. Fifty-four grams (0.374 mole) of 4-chlorobenzenethiol was added a few grams at a time over a one-hour period to a mixture of 370 ml. of concentrated sulfuric acid and 200 ml. of 60% oleum in a one-liter round-bottom flask. The mixture was swirled with each addition (fumes were given off) and its final temperature was 60°C. The mixture stood, except for an occasional shaking, for forty-eight hours at room temperature and then it was poured onto ice with vigorous stirring. The precipitated solid was filtered off and recrystallized from a large volume of acetone. The material did not precipitate well on cooling and three successive concentrations of the mother liquor were required to obtain a total of 18 g. of solid in four fractions which progressively covered the melting point range of 183-195°C. (with 2-3 degree melting points). These were combined and recrystallized from boiling acetic acid to obtain solid sintering at 195 and melting at 204°C. This material was recrystallized again from acetic acid to obtain 13 g. of solid sintering at 193 with actual melting at 199-203°C. Baw, Bennett, and Dearns[4] give the melting point of 2,7-dichlorothianthrene as 181.5°C. (186°C. corr.). Fries and Volk[16] suggested that the thianthrene oxides were intermediates in this reaction so the assumption was made that the product obtained was contaminated by oxide and its reduction was attempted using a procedure previously employed by Gilman and Swayampati.[84]

Ten grams of the crude product (m.p. 199-203°C.), 500 ml. of glacial acetic acid and 10 ml. of water were placed in a one-liter flask and brought to reflux. A 10 g. quantity of zinc dust was added through the reflux condenser in small portions and the reaction mixture was refluxed for five hours. The liquid was decanted from the zinc residues onto crushed ice with vigorous stirring and the precipitated solid was filtered off and dried. It was recrystallized from acetic acid twice and once from absolute alcohol to obtain 7.0 g. of white crystals melting at 180-180.5°C. (Literature[4] m.p. for 2,7-dichlorothianthrene was 181.5°C.).

Anal. Calc'd for $C_{12}H_6Cl_2S_2$: C, 50.53; H, 2.12; Cl, 24.86; S, 22.48

Found: C, 50.54; H, 2.14; Cl, 24.82; S, 22.49

The other three grams of impure product (m.p. 199-203°C.) was fractionally crystallized from absolute ethanol to obtain a solid which after final purification melted at 228-228.5°C. (uncorr.).

Anal. Calc'd for $C_{12}H_6Cl_2O_1S_2$: C, 47.84; H, 2.00; Cl, 23.54; S, 21.29

Found: C, 48.09; H, 2.17; Cl, 23.58; S, 21.24

Baw, Bennett, and Dearns[4] gave the melting point of 2,7-dichlorothianthrene-5-oxide as 235-7°C. (decomp.). If one assumes that this melting point has been corrected (as they indicated for several other compounds in their article) then the uncorrected melting point would undoubtably agree with that which was obtained. However, there were definitely no signs of decomposition upon melting and none has been experienced with other compounds of this type. Oxidation of the 2,7-dichlorothianthrene (m.p. 180-180.5°C.) with nitric acid in glacial acetic acid (a known procedure for preparing monoxides) gave identical material melting at 228-228.5°C. The infra-red spectrum of 2,7-dichlorothianthrene-5-oxide (Figure 53) was compatible with the structure of this material and provides a very interesting example of the effect of sulfoxide interaction with adjacent ring hydrogen (see appendix discussion of this effect).

Since the 2,7-dichlorothianthrene had not been obtained directly it was desirable to repeat the ring closure reaction to gain additional information about reaction conditions since further use of this reaction was contemplated. A 500 ml. flask was equipped with a stirrer, thermometer, and a dropping funnel and 185 ml. of concentrated sulfuric acid was placed in it and cooled to 5°C. A 27 g. (0.182 mole) quantity of 4-chlorophenyl) disulfide intermediate quickly appeared (as indicated by the precipitation of a yellow solid) and then 95 ml. of 65% fuming sulfuric acid was dripped into the flask over a one-half hour period at 10°C. The ice bath was removed and the mixture was allowed to stir for 14 hours before pouring it onto ice. The quenched mixture was set aside overnight and the precipitated solid was filtered off, washed thoroughly with water and dried. The solid was recrystallized from acetic acid and alcohol successively to obtain 8.0 g. (0.028 mole) of 2,7-dichlorothianthrene melting at 180-180.5°C.

Study of the two ring closure reactions leads to the conclusion that it is highly probable that the thianthrene oxide is not an intermediate but is formed by oxidation after ring closure had taken place. This is consistent with some work by Gillespie and Passerini[183] who found that sulfides were oxidized to sulfoxides in sulfuric acid and who postulated some mechanisms for oxidations of this type.

The Preparation of 2,3,7,8-Tetrachlorothianthrene

Since bis(3,4-dichlorophenyl) disulfide had been prepared, accidentally, by the incomplete reduction of 3,4-dichlorobenzenesulfonyl chloride using lithium aluminum hydride it was decided to use this material in an attempted ring closure reaction using sulfuric acid as the cyclizing agent. Disulfides have previously been mentioned in condensations of thiophenols with benzene derivatives,[32] in condensations of disulfides with benzene derivatives,[110] and as intermediates in the ring closures of thiophenols to thianthrenes[16] in the presence of sulfuric acid.

Concentrated sulfuric acid (200 ml.) and 10.0 g. (0.028 mole) of bis(3,4-dichlorophenyl) disulfide were placed in a 500 ml. round-bottom three-neck flask equipped with a stirrer, thermometer, dropping funnel and a gas exit tube connected to a collecting apparatus. Since a slightly pinkish coloration developed in the reaction mixture at this point it was stirred, at 20°C., for four hours. When no further change occurred, 50 ml. of 65% fuming sulfuric acid was slowly added while the reaction flask was chilled in an ice bath. The color of the reaction solution changed from pink to a transparent blue but the disulfide did not immediately dissolve, so the reaction mixture was stirred an additional two hours during which no further change was observed. An additional 40 ml. of 65% fuming sulfuric was then added to the reaction mixture resulting in a very marked change in coloration with the formation of a very deep greenish blue color. The remaining solid dissolved immediately and apparently a threshold level of acid concentration had been passed since the color change was so marked. Three hours after the last addition of sulfuric acid there was another change in coloration of the reaction mixture to a pale blue and precipitation of a mushy complex. The formation of an insoluble material of this nature had not previously been observed in reactions of this type. The reaction mixture was stirred an additional five hours without any further observable change after which it was poured onto ice. Considerable washing of the precipitate was necessary to dissipate its blue coloration which suggested that some sort of complex hydrolysis was occurring. During this cyclization reaction there was no detectable evolution or absorption of gas as had been observed in previous sulfuric acid condensations using thiols.

The hydrolyzed mixture was set aside overnight in order to allow coagulation of the finely divided precipitate after which it was recovered by filtration and washed thoroughly with water. Following air drying the solid was recrystallized from ethylene dichloride to obtain 3.0 g. of a solid melting at 272-3°C. This solid was found to be identical with the 2,3,7,8-tetrachlorothianthrene which had been prepared earlier from the reaction of sulfur dichloride with o-dichlorobenzene. Their melting points were identical; their mixed melting points showed no depression and their infra-red spectra (see Figure 57) were identical. The cyclization product obtained from bis(3,4-dichlorophenyl) disulfide was oxidized with chromic acid in glacial acetic acid by the usual procedure to give a colorless solid melting at 314-314.5°C. which was identical with the 2,3,7,8-tetrachlorothianthrene-5,5,10,10-tetroxide previously obtained by another synthetic route.

The sulfuric acid filtrate from the tetrachlorothianthrene filtration had a very strong odor of sulfur dioxide and on being set aside for a week deposited a colorless precipitate. This material was recovered by filtration, dried (weight 4.2 g.) and found to have a melting point of 63-6°C. Three recrystallizations of this material from water raised the melting point to 78-9°C., which agreed with that reported by Vickery[184] for 3,4-dichlorobenzenesulfonic acid which he had prepared by the sulfonation of o-dichlorobenzene. A sample of the o-toluidine salt, prepared by the method of Dermer and Dermer,[185] melted at 170.5-172°C. Dermer and Dermer report 170-172°C. for the melting point of the o-toluidine salt of 3,4-dichlorobenzenesulfonic acid.

The Attempted Preparation of 1,6-Dichlorothianthrene

This compound had been prepared previously as a by-product by Dalgliesh and Mann[99] in their preparation of 7-chlorothioindoxyl from 5-chloro-3-keto-3,4-dihydro-1,4-benzothiazine. They opened the ring of the lactam with caustic and then diazotized the sodium salt. The diazotization product lost nitrogen and ring closed to 4-chlorothioindoxyl. A side reaction also occurred in which two of the diazotized molecules eliminated acetic acid and formed 1,6-dichlorothianthrene. Based on this information and the availability of 2-chlorothiophenol it was decided to take advantage of the opportunity to attempt to extend the sulfuric acid condensations of thiols to thianthrenes. Sulfuric acid, 200 ml., (30% fuming) was placed in a 500 ml. round-bottom flask and 29 g. (0.20 mole) of 2-chlorothiophenol was added during a two hour period in portions of one gram. The evolution of heat and fumes accompanied each addition and the reaction flask temperature rose to 55°C. When the addition of 2-chlorothiophenol had been finished the flask was set aside for eighteen hours with occasional swirling of the contents to insure good mixing. Half of the reaction mixture was poured onto ice giving a reddish black solution with a strong odor of sulfur dioxide, but 1,6-dichlorothianthrene did not precipitate. It was assumed that the material had not had sufficient contact time and the other half of the reaction mixture was allowed to stand an additional ten hours before being poured into a separate beaker of ice with the same result. Neither quench contained even a trace of insoluble material that might be the desired thianthrene or phenylene sulfide polymer. This material was discarded and another attempt was made using the technique of adding the thiol to the concentrated sulfuric acid and allowing disulfide formation to take place before the fuming sulfuric acid was added. The quantity, 25 g. (0.17 mole) of 2-chlorothiophenol was added to 185 ml. of concentrated sulfuric acid in a 500 ml. round-bottom flask at 5°C. with stirring. The yellow disulfide precipitated almost immediately and the addition of the 90 ml. of 65% fuming sulfuric (the same acid concentration used in the preparation of 2,7-dichlorothianthrene) was begun shortly afterward. There was essentially no change in the solution except that where the fuming sulfuric acid hit the solution it became deep blue-green but the color dissipated as soon as mixing occurred. When three-quarters of the acid had been added a dark brown coloration suddenly appeared where there had been essentially a clear solution. The rest of the fuming acid was then added and the reaction mixture was stirred for an additional two hours before the removal of the ice bath, and then for twelve hours at room temperature before quenching on ice. A red-wine colored solution was obtained and again no solid precipitate was found. The material was again discarded with the conclusion that either sulfonation or oxidation had taken place to give a sulfonic acid which was water soluble and that the ortho isomer is apparently much more sensitive to acid concentration than the para isomer.

Bis(4-Chlorophenyl) Disulfide

In the attempted ring closure of 2-chlorobenzenethiol to 1,6-dichlorothianthrene with 30% fuming sulfuric acid, no product was obtained. As no detailed description of the experimental reaction conditions for this ring closure appears in the literature no definite conclusions could be drawn concerning the strength of the acid to be used. Thus, it was decided to investigate the reaction more closely using the most readily available material (4-chlorobenzenethiol) since the latter avoided polymer formation.

The quantity, 26 g. (0.18 mole) of 4-chlorobenzenethiol was placed in a 500 ml. round-bottom flask equipped with a stirrer, thermometer, dropping funnel, and a gas outlet tube leading to an inverted gas measuring bottle filled with water. The acid (200 ml. of concentrated sulfuric, d=1.843) was run into the flask and the original displacement of water was measured. The reaction mixture was stirred for forty-eight hours during which time measurements of the gas volume were determined and color changes in the mixture were noted. A total of 290 ml. of SO_2 was collected and the color of the reaction mixture changed from an initial white through yellow into a very dark-purple containing yellow specks of material floating in the acid. At the completion of the reaction period the contents of the flask were poured onto ice and stirred. A yellowish-white solid crystallized from solution and was recovered by filtration, dried, and recrystallized from methanol to give 17.5 g. (0.0805 mole, 44.5% yield) of a shiny yellow solid melting at 71-2°C. The material was identified as bis(4-chlorophenyl) disulfide (Literature value[186] m.p. 70-1°C.) which agrees with the finding of Stenhouse[165] who observed a similar oxidation of benzenethiol with sulfuric acid. According to Fries and Volk[16] the disulfide is the first intermediate in the oxidation, using sulfuric acid, of thiols to thianthrenes.

2,7-Dichlorothianthrene was not isolated in this case and since it has a high melting point (180°C.) it should have been readily detectable. Apparently it is necessary to have SO_3 present to obtain ring closure of the disulfide, although Hilditch[17] claimed that he obtained thianthrene from benzenethiol using cold concentrated sulfuric acid to accomplish ring closure.

The Reaction of Thiophenol and Benzene in the Presence of Concentrated Sulphuric Acid

In reviewing the literature on the ring closure of benzenethiols to thianthrenes using concentrated or fuming sulphuric acid, the articles of Davis and Smiles,[112] and Archer and Suter[32] on the condensation of thiosalicylic acid with benzene derivatives (to obtain thiaxanthones) suggested the possibility of using the condensation of chlorinated thiophenols with chlorinated benzenes in the presence of sulphuric acid as a method to prepare substituted diphenyl sulfides. Apparently, thiosalicylic was the only thiol which previous investigators had been able to condense with benzene derivatives.

Concentrated sulphuric acid (300 ml., d = 1.8437) was placed in a one-liter three-neck round-bottom flask equipped with a stirrer, thermometer, dropping funnel and a gas outlet tube leading to a gas measuring bottle inverted over water. The reaction flask was cooled to 10°C. and a mixture of thiophenol (55 g., 0.50 moles) and 300 ml. (3.4 moles) of benzene (thiopene free) was added over a period of an hour and a half after which the mixture was stirred for eight additional hours. The volume of SO_2 evolved was 225 ml. and it was very noticeable that during the addition period a definite decrease in gas volume occurred, as indicated by water being drawn back into the trap, which was possibly due to the uptake of oxygen by the reaction solution. This same phenomena had been noted in other runs in a similar phase of the reaction. The color changes passed through the sequence cream, orange-yellow, deep red, purple, and finally a purple-black. The reaction mixture was quenched on ice at the end of the reaction period and a yellowish semi-solid formed beneath the benzene layer. The oil and water layers were separated by decantation and the semi-solid was washed as thoroughly as possible with benzene, then with acetone which helped to solidify it, after which it was air-dried and found to weigh 95 grams. The combined benzene wash and oil layer were separated from the acid layer, washed and dried. The solvent was removed under vacuum and thirty grams of residual oil was obtained. This was fractionated into four fractions from which it was determined that the material consisted of diphenyl sulfide (by infra-red spectra comparison), thianthrene (by isolation of a small amount of the solid, m.p. 154-5°C.), and 1,4 bis(phenyl mercapto) benzene (by isolation of the solid, m.p. 81-2°C.) A nujol mull taken on the dried solid showed a typical mono (13.25 microns) and para (12.24 microns) substitution pattern as would be expected from a phenylene sulfide polymer. It appeared from this experiment that there is a pronounced tendency for the thiophenol to attack the product of the reaction in preference to the benzene (which was present in excess) and that better results would be obtained by using substituted compounds which would prohibit polymer formation.

Diphenyl Sulfides by Diazo Condensation

The Preparation of 2-Chlorophenyl Phenyl Sulfide

Caution: Anyone performing this experiment or any variation of it should study this experiment and the discussion related to it in detail. It should not be performed on the scale which is described here due to the inherent danger of diazonium compound decomposition.

The procedure of Rolla, Sanesi and Leandri[10] as described in the abstract was used for this synthesis. A solution of sodium thiophenate was prepared in a three-liter three-neck flask using 140 g. (1.18 moles) of thiophenol, 500 ml. of water and 160 g. (3.88 moles), 97% of sodium hydroxide pellets. The diazonium chloride was formed in a two-liter three-neck round-bottom flask equipped with a stirrer and thermometer. The reaction flask was placed in an ice bath and 500 ml. of water and 300 ml. of concentrated hydrochloric acid were added. The 2-chloroaniline (127 g., 1.0 mole) was added slowly to the acid solution to form the white aniline hydrochloride. The salt solution was stirred until its temperature was lowered to 10°C. and then a solution containing 80 g. (1.15 moles) of sodium nitrite dissolved in 200 ml. of water (previously chilled to 0°C. in an ice-calcium chloride bath) was added slowly to the aryl amine salt solution. The white aniline hydrochloride slowly dissolved to give a clear solution of the diazonium chloride except for a few brown insoluble particles. The temperature of the sodium thiophenate solution was adjusted to 40°C. and the cold diazonium chloride solution was added to it with good stirring (behind a shield) during a six hour period. A red oil formed during the addition of the diazonium chloride and there seemed to be nitrogen evolution as evidenced by a foaming of the reaction solution. The temperature of the reaction mixture was kept in the range 40-50°C. during the addition of the diazonium chloride and then it was allowed to stir, at room temperature, overnight The following morning the red oil was extracted with ether and the ether extract was washed consecutively with dilute sodium hydroxide, dilute hydrochloric acid and water. Most of the ether was removed by warming the ether solution on a steam bath and the residual oil was transferred to a distilling flask using a little ether to rinse the evaporation flask. A thermometer was placed in the distilling flask to determine when the majority of the ether had been removed as would be indicated by a temperature rise above the boiling point of the ether. The temperature of the residual oil reached slightly over 70°C. when the oil began to foam a little. The foaming increased to the point that it started to overflow the flask so that the flask was picked up by the neck and allowed to froth over into a beaker to save the contents. Suddenly the evolution of liquid became extremely violent and as the flask was dropped the force of the evolution violently propelled the flask three feet across the hood and against the hood wall demolishing the flask. If the contents of the flask had been contained in a semi-closed system there would no doubt have been an explosion.

It was known previously from the preparation of thiophenols[128] by an analogous reaction that these decompositions can become violent. However, since there was no caution expressed in the abstract of Rolla, Sanesi and Leandri's work[10] it was mistakenly believed that the decomposition took place at lower temperatures as was experienced in the previous thiophenol preparation. A literature survey was made and it was found that this type of diazonium compound was more stable although not many examples[52,53,10,54,55] were to be found. Armed with this information an attempt was made to salvage the material (about 50 ml.) which had been poured into the beaker at the beginning of the decomposition. A solvent (n-butyl ether) was selected with a sufficiently high boiling point (142°C.) to insure decomposition of any diazo compound. The ether was first washed with sulfite to decompose any peroxides and then 100 ml. of it were placed in a 500 ml. round-bottom flask under a reflux condenser and the residue oil dissolved in 300 ml. of n-butyl ether was added slowly to the refluxing material to decompose any remaining diazo compound. The mixture was heated at its reflux temperature for an hour after the addition of the o-chloro phenyl diazonium thiophenolate and then the ether was removed by distillation under vacuum (b.p. 33°C./9 mm.) and the residue was fractionated to obtain 23 g. (0.104 mole) of 2-chlorophenyl phenyl sulfide (n_D^{25} = 1.6381) which was identical to the product obtained by the interaction of 1-bromo-2-chlorobenzene and potassium thiophenolate, as indicated by its infra-red spectrum and oxidation to the 2-chlorophenyl phenyl sulfone (m.p. 105-6°C.) using hydrogen peroxide in acetic acid. (Literature value[8] m.p. 105°C.)

(See the discussion section of this thesis for a more detailed treatment of this reaction.)

Diphenyl Sulfides by Sulfoxides Reduction

Bis(4-Chlorophenyl) Sulfide by Sulfoxide Reduction

The following method was found to be the best for preparing the pure isomer which was used later in a ring closure reaction. A one-liter three-neck flask was equipped with a stirrer and a straight tube condenser and 60.0 g. (0.22 mole) of bis(4-chlorophenyl) sulfoxide (m.p. 142-3°C.) and 300 ml. of glacial acetic acid were placed in it. The reaction mixture was brought to its reflux temperature and 45 g. of zinc dust was added through the condenser during a two hour period after which the mixture was kept at its reflux temperature for an additional two hours. The reaction mixture was filtered hot to remove the unreacted zinc and the filtrate was poured into vigorously stirred ice water. A white solid precipitated which was filtered, dried and recrystallized twice from ethanol to obtain 47.0 g. (0.18 mole, 84% yield) of bis(4-chlorophenyl) sulfide melting at 95-6°C. The literature [12,85,187,143] lists melting points ranging from 88-98°C. for this sulfide which appears to be due to the presence of isomers or impurities rather than thermometer stem corrections since the material prepared by direct condensation of chlorobenzene with sulfur dichloride was found to be highly contaminated and did not purify easily.

Bis(4-Chloro-2-Methylphenyl) Sulfide

This material was prepared from the sulfoxide which had been specially purified for this purpose in order to obtain a known structure for a ring closure reaction. The quantity, 91 g. (0.304 mole), of bis(4-chloro-2-methylphenyl) sulfoxide was placed in a two-liter three-neck round-bottom flask equipped with a stirrer and a straight-tube reflux condenser. One liter of glacial acetic acid and 100 ml. of water were added, the mixture was brought to reflux, 60 g. of zinc dust was added in small portions over a period of two hours, and the mixture was allowed to reflux for an additional hour. A white precipitate formed in the reaction mixture on standing overnight. Some of the white solid was removed, pressed on a filter paper and found to melt at 232-37°C. It was assumed to be zinc acetate (m.p. 240°C.) and was filtered off. Since a large amount of unused zinc remained in the reaction flask a good reduction had not been obtained and the acetic acid solution was transferred to a clean flask, 10 ml. of acetic anhydride was added and the reduction repeated using 30 g. of zinc dust. The reaction mixture was cooled to precipitate as much zinc acetate as possible and filtered. The acetic acid was removed at 20 mm. pressure until the internal flask temperature reached 140°C. The concentrated mixture was cooled below 100°C., water was added to dissolve the remaining zinc acetate, and the organic material was extracted with ethylene dichloride. The solvent layer was washed with water to remove the last of the inorganic material and the ethylene dichloride was removed by distillation under vacuum. The product was fractionated to obtain 53.5 g. (0.184 moles, 62.5% yield) of bis(4-chloro-2-methylphenyl) sulfide, (b.p. 178°C./2 mm., n_D^{25} = 1.6304 and n_D^{29} = 1.6289). This material solidified on standing in a cold room for several days. The solid was pressed on a filter paper to remove traces of oil and was found to melt at 29-30°C. Recrystallization of this material from methanol gave white solid melting at 30.5-31°C. Balasubramanian and Baliah[40] had previously prepared this compound by the condensation of the appropriate sodium thiophenate and the analogous iodo compound and found n_D^{29} = 1.6295. Bis(4-chloro-2-methylphenyl) sulfoxide (b.p. 220°C./2 mm.) was recovered in the amount of 23 g. (0.076 mole) from incomplete reduction. In referring back to the work of Gilman and Swayampati[84] it was found that the proportion of water used in the reaction had been too high and in checking other similar procedures[136,183] there would appear to be no need for the dilution. It was noted that the sulfide obtained from this reduction was water white as compared to the yellow oil obtained later by direct condensation of meta-chlorotoluene using sulfur dichloride.

Fusion Condensations

2-Chlorophenyl Phenyl Sulfide

The quantities, 110 g. (1.0 mole) of thiophenol, 338 g. (1.76 moles) of 1-bromo-2-chloro benzene, 5 g. of precipitated copper powder, and 500 ml. of absolute ethanol were placed in a one-liter three-neck flask equipped with a stirrer, thermometer, and distilling head. The mixture was warmed to 50°C. and 65 g. (1.0 mole, 86%) of potassium hydroxide pellets were added cautiously in two equal portions. The alcohol was then removed by distillation and heating was continued until the temperature of the reaction mixture reached 170°C. where it was held for five hours. The phase changes were similar to those previously described for other condensations of this type. At the end of the reaction period the mixture was poured onto ice; 300 ml. of ethylene dichloride was added to dissolve the oil layer and the mixture was acidified with concentrated hydrochloric acid. The insolubles were coagulated with Celite (filter cell) and removed by filtration. The oil layer was separated from the filtrate, washed successively with 6N hydrochloric acid, 10% aqueous sodium hydroxide, and water. The solvent was removed by distillation at atmospheric pressure and the oily residue was fractionally distilled under vacuum. The quantities, 208 g. (1.09 moles) of 1-bromo-2-chloro benzene (b.p. 85°C./9 mm.), 51 g. (0.231 mole, 23.1% yield based on the thiophenol) of 2-chlorophenyl phenyl sulfide (b.p. 149°C./5 mm., 159°C./10 mm., $n_D^{25} = 1.6383$), and 2.0 g. (0.0067 mole) of 1,2-bis(phenylmercapto) benzene (b.p. 226-230°C./4 mm.) were isolated. The 2-chlorophenyl phenyl sulfide has been prepared previously by the diazonium coupling process[10,51] and its boiling point reported as 186°C./40 mm. and 163-4°C./11 mm. but no other physical constants were given. The sulfide was oxidized to the 2-chlorophenyl phenyl sulfone using 30% hydrogen peroxide in a acetic acid-acetic anhydride mixture to obtain a white solid which melted at 105-106.5°C. after recrystallization from methanol. Literature,[8] m.p. 105°C.

The 1,2-bis(phenylmercapto) benzene has not been described in the literature and it was not further characterized due to accidental loss of the material. An infra-red spectrum of this material was, however, taken before the loss and it had a spectrum almost identical to the 2-chlorophenyl phenyl sulfide except in the region between 5 and 6 microns which showed four absorption peaks instead of the three exhibited by the chloro compound indicating the greater percentage of mono-substitution which is present in the molecule. The low yield of the 2-chlorophenyl phenyl sulfide indicates the reaction temperature was either too low or the heating period was not sufficiently long. This conclusion is verified by the small amount of 1,2-bis(phenylmercapto) benzene formed.

Synthesis of 4-Chlorophenyl Phenyl Sulfide

This preparation was the initial attempt to prepare chlorinated diphenyl sulfides using alkali salts of thiophenols and pseudoactivated halobenzenes. The attempt was made without a catalyst and failed to produce a sulfide. The quantity, 53 g. (0.48 moles) of thiophenol, 191.5 g. (1.0 mole) of 1-bromo-4-chloro benzene, and 300 ml. of absolute ethanol were placed in a 500 ml. round-bottom flask and warmed to 60°C. To this mixture, 31 g. (0.48 mole, 86%) of potassium hydroxide pellets and 3.0 g. of precipitated copper powder were added; the alcohol and water, liberated in salt formation were removed by distillation. The potassium thiophenate precipitated as the last of the alcohol was removed but the mixture remained fluid due to the excess halobenzene employed as a diluent. The reaction temperature was raised to just a few degrees below the boiling point of the halobenzene (200°C.) and held there for four hours. The solid (potassium phenate), which initially precipitated, slowly disappeared as reaction took place and reformed as the potassium bromide began to precipitate. The reaction mixture was poured onto ice and acidified with concentrated hydrochloric acid to dissolve the copper salts. Ethylene dichloride (400 ml.) was added to take up the oil layer and the mixture was filtered to remove a small amount of insoluble material. The filtrate was washed first with dilute caustic to remove any unreacted thiophenol, and then with water. The solvent was removed by vacuum distillation and the residue fractionated to give 78 g. (0.35 mole, 73% yield) of 4-chlorophenyl phenyl sulfide boiling at 167-8°C./ 9 mm., n_D^{25} = 1.6354.

Anal. Calc'd for $C_{12}H_9Cl_1S_1$: C, 65.29; H, 4.11; Cl, 16.06; S, 14.52

Found: C, 65.27; H, 4.11; Cl, 15.85; S, 14.31

This material had been prepared previously by other methods[162,78,150] and was found to have a boiling point of 167-8°C./10 mm. The distillation residue was recrystallized from ethanol to give 1 g. (0.034 mole) of 1,4-bis(phenylmercapto) benzene melting at 81-2°C. Its reported[47] melting point is 81.5°C.

The quantity, 25 g. (0.113 mole), of the 4-chlorophenyl phenyl sulfide was placed in a 500 ml. round-bottom flask with 200 ml. of glacial acetic acid and 30 ml. of acetic anhydride and the well-stirred mixture was heated on the steam bath, while a 26 g. (0.226 mole) quantity of 30% hydrogen peroxide was added over a one hour period. The reaction was heated an additional six hours, then poured onto ice, and stirred until it solidified. The solid was removed by filtration and recrystallized from 95% ethanol to yield 25.5 g. (0.102 mole, 90% of theory) of 4-chlorophenyl phenyl sulfone (white needles) melting at 92.5-93.5°C. Literature value[150] m.p. 91-2°C.

3,4-Dichlorophenyl Phenyl Sulfide

The sulfide was prepared by the interaction of 110 g. (1.0 mole) thiophenol, 500 g. (2.2 moles) 1,2-dichloro-4-bromobenzene, and 65 g. (1.0 mole) of 85% potassium hydroxide pellets in the presence of 4.0 g. of precipitated copper powder. All of the reactants except the caustic were placed in a two-liter round-bottom flask with 800 ml. of absolute alcohol and warmed to 50°C. with good agitation. The caustic was then added slowly to form the potassium thiophenate after which the alcohol was removed by distillation carrying with it the water liberated by salt formation. The potassium thiophenate precipitated as the last of the alcohol was removed and a thick slurry formed. Heating was continued until the temperature of the slurry reached 200°C. at which point the slurry slowly began to break up and became more fluid again in about thirty minutes of additional heating. The reaction mixture was held at that temperature for six hours, transferred into ice water, and acidified with concentrated hydrochloric acid to dissolve the copper salts. Ethylene dichloride was added to take up the oil layer and the insoluble material was removed by filtration. The oil layer was separated, washed with water, and distilled under reduced pressure to give 140 g. (0.55 mole, 55% based on the thiophenol) of 3,4-dichlorophenyl phenyl sulfide, b.p. 152°C./5 mm., n_D^{25} = 1.6460.

Anal. Calc'd for $C_{12}H_8Cl_2S$: C, 56.48; H, 3.16; Cl, 27.80; S, 12.56

Found: C, 56.24; H, 3.13; Cl, 27.70; S, 12.44

The amount of the higher condensation product from the above reaction was too small to characterize in this case.

Since this sulfide had not been previously described in the literature it was oxidized to the sulfone. Thirty grams (0.118 mole) of the 3,4-dichlorophenyl phenyl sulfide, and a mixture prepared from 100 ml. of glacial acetic acid and 80 ml. of acetic anhydride, were heated to the reflux temperature of the solvent mixture and 80 g. (0.704 mole) of 30% hydrogen peroxide were added, dropwise, through the condenser over a four hour period. The reaction mixture was kept at its reflux temperature for an hour after the addition of the peroxide and then poured onto crushed ice and stirred vigorously. The solid was recovered by filtration after crystallization, dried in an oven at 50°C., and recrystallized from absolute ethanol to give 27.5 g. (0.096 mole, 81%) of a white crystalline sulfone melting at 123.5-125°C. Huismann[8] had previously prepared the material from o-dichlorobenzene and benzene sulfonyl chloride and records the melting point of 3,4-dichlorophenyl phenyl sulfone as 125°C.

The Preparation of 2,4,5-Trichlorophenyl Phenyl Sulfide

A 110 g. quantity of thiophenol (1.0 mole), 400 g. (1.85 moles) of 1,2,4,5-tetrachlorobenzene, 3.0 g. of precipitated copper powder and 1200 ml. of absolute ethanol were placed in a two-liter three-neck round-bottom flask equipped with a distilling column, thermometer, and stirrer. The mixture was warmed to 60°C. and potassium hydroxide pellets (65 g., 1.0 mole) were added in two portions to avoid excessive heat evolution resulting from the formation of the potassium thiophenoxide. The alcohol was distilled from the reaction mixture at atmospheric pressure after which heating was continued until the temperature of the residue reached 240°C. A fair amount of the tetrachlorobenzene sublimed into the distilling column as the last of the alcohol was removed and care had to be taken to prevent plugging of the column with solid until the reaction temperature had been reached at which point the melt again became fluid. The reaction mixture was stirred for eight hours at 240°C. and then it was poured into cold 6N hydrochloric acid. A liter and a half of ethylene dichloride was added and the mixture was warmed to 70°C. on the steam bath to dissolve the organic material. About 25 g. of Celite (filter aid) was added to the mixture and the copper insolubles were removed by filtration. The oil layer was separated and washed consecutively with dilute hydrochloric acid and water after which the solvent was removed by vacuum distillation. The oil residue was fractionated roughly into three fractions which were primarily 1,2,4,5-tetrachlorobenzene (b.p. 160°C./20 mm.), 2,4,5-trichlorophenyl phenyl sulfide (b.p. 200°C./3 mm.), and the first higher condensation product of the sulfide with potassium thiophenoxide (b.p. 220°C./3 mm.). The tetrachlorobenzene was recrystallized from ethylene dichloride to recover 199 g. (0.92 mole) of this material melting at 138-140°C. The solvent was removed from the mother liquor and the residue was added to the trichlorophenyl phenyl sulfide fraction for redistillation. The product distilled at 200°C./3 mm. and the semi-pure 2,4,5-trichlorophenyl phenyl sulfide solidified in the receiver and was found to have a melting point of 82-3°C. Recrystallization of it from absolute ethanol gave 86 g. (0.297 mole, 29.7% yield based on the thiophenol) of pure product in the form of white needles melting at 84.5-85°C. Huismann, Uhlenbroek, and Meltzer,[9] who prepared this material by the condensation of 2,4,5-trichlorothiophenol and para-nitro chlorobenzene with subsequent removal of the nitro group by reduction and diazotization, record its melting point as 82°C. The sulfide was oxidized with chromic acid in boiling acetic acid by the usual procedure to obtain 2,4,5-trichlorophenyl phenyl sulfone melting at 127-8°C. after two recrystallizations from methanol.

Anal. Calc'd for $C_{12}H_7Cl_3O_2S_1$: C, 44.81; H, 2.19; Cl, 33.07; S, 9.97

Found: C, 44.92; H, 2.10; Cl, 32.90; S, 9.90

When this material was analyzed it was believed that it had not been previously described in the literature but a thorough examination of the tables given by Huismann, Uhlenbroek, and Meltzer[9] revealed that they had prepared the compound (m.p. 127-8°C.) by interaction of 2,4,5-trichlorobenzenesulfonyl chloride and benzene.

The third cut from the original fractionation was recrystallized from ethylene dichloride three times to obtain 21 g. of a white solid melting at 185-6°C. The infra-red spectrum of this material in carbon disulfide was taken and mono- and 1,2,4,5 type benzene ring substitution peaks were found (Figure 63). The two mono- substitution peaks appeared at 13.35 and 14.5 microns while the 1,2,4,5 peak appeared as a doublet with points at 11.15 and 11.40 microns. The relative heights of the two types of substitution peaks indicated that the percentage of mono-substitution in the compound was greater than that of the 1,2,4,5 type substitution as would be expected from the condensation of two thiophenol groups with a single 1,2,4,5-tetrachlorobenzene. Analysis of the material confirmed that this was the case.

Anal. Calc'd for $C_{18}H_{12}Cl_2S_2$: C, 59.50; H, 3.33; Cl, 19.52; S, 17.65

Found: C, 59.58; H, 3.24; Cl, 19.37; S, 17.37

This material was oxidized with chromic acid in boiling glacial acetic acid by the usual procedure to obtain the disulfone melting at 236-7°C. after two recrystallizations from methanol.

Anal. Calc'd for $C_{18}H_{12}Cl_2O_4S_2$: C, 50.59; H, 2.83; Cl, 16.59; S, 15.01

Found: C, 50.67; H, 2.86; Cl, 16.41; S, 14.82

The sulfone was not very soluble in carbon disulfide and only a weak infra-red spectrum could be obtained. The peak from the 1,2,4,5-type substitution did not appear at this concentration as would be predicted since it is recessive in sulfone compounds due to the interaction of the ring hydrogen and the sulfone oxygen. The mono-substitution peak which the sulfide exhibited at 13.35 microns was split in the sulfone spectrum exhibiting peaks at 13.25 and 13.75 microns which is normal for unsubstituted benzenesulfonyl groups. The peak which the sulfide showed at 14.5 microns is shifted to higher wavelengths, beyond the range of the sodium chloride prism, in the sulfone spectrum.

There are theoretically three possible structures which would give the above spectra since the substitution of a phenylmercapto group into the 2,4,5-trichlorophenyl phenyl sulfide could replace any of the three chlorines and give the same substitution pattern. The 1,2-di(phenylmercapto)-4,5-dichlorobenzene can be ruled out since the probability of such a large group attacking the chlorine atom ortho to an equally large group is sterically unfavorable when other more accessible reaction sites are available. There is no readily available method to prepare the other two isomers and determine the structure so that the best that may be said in the absence of further data is that the material is probably 1,4-di(phenylmercapto)-2,5-dichlorobenzene. It would seem that having the phenylmercapto group para to the chlorine in the 4 position of 2,4,5-trichlorophenyl phenyl sulfide would activate it enough to allow a preferential substitution which apparently is the case as only one isomer was formed. The relatively high melting point (185-6°C.) of the disulfide would also seem to confirm this structure since it would be the most symmetrical isomer, a fact which is normally compatible with a high melting point.

An attempt was made to recrystallize the 21 g. of black tarry residue from the original distillation to obtain a sample of the trisubstitution product, 1,2,4-tri(phenylmercapto)-5-chlorobenzene. The material was dissolved in boiling ethylene dichloride and treated twice with Norite (activated charcoal) but the solution did not decolorize well and no solid formed on being set aside so that the material was discarded.

The low yield (29.7%) of the 2,4,5-trichlorophenyl phenyl sulfide must be attributed to a slow reaction rate due to the fact that the chlorines in such a highly substituted benzene are sterically hindered to the attack of such a large group.

4-Chlorophenyl-4'-Tolyl Sulfide

This reaction was the second condensation of a bromobenzene with a potassium salt of a thiophenol to obtain a substituted aryl sulfide. The product has been made previously[11] by the coupling of the diazonium salt of p-chloroaniline with the sodium salt of p-thiocresol.

The quantity, 124 g. (1.0 mole) of p-toluenethiol, 400 ml. of absolute alcohol, 3 g. of precipitated copper powder, and 450 g. (2.32 moles) of 1-bromo-2-chloro benzene were placed in a one liter three-necked round-bottom flask and warmed to 60°C. Potassium hydroxide pellets (65 g., 1.0 mole, 85%) were then added cautiously with stirring to the above mixture. The ethanol was slowly removed by distillation taking with it the water of salt formation, and the reaction temperature was allowed to rise to 200°C. where it was held for 8.5 hours. The reaction mixture was poured onto ice, acidified with concentrated hydrochloric acid and 750 ml. of ethylene dichloride was added to dissolve the oily material. A voluminous brown precipitate (probably hydrated copper oxides) was removed by filtration and the oil layer was separated and washed successively with water, aqueous sodium hydroxide, and water. p-Toluenethiol, 13 g. (0.104 mole), was recovered from the caustic wash by the usual procedure. The oil layer was distilled to give 220 g. (1.15 moles) of 1-bromo-4-chlorobenzene (b.p. 88-90°C./15 mm.), 4-chlorophenyl-4'-tolyl sulfide (b.p. 195-200°C./5 mm.), and 1,4-bis(4-tolyl mercapto) benzene (b.p. 240-250°C./5 mm.). The 4-chlorophenyl-4'-tolyl sulfide was recrystallized from methanol to give 135 g. (0.575 mole, 57.5% yield) of white plates melting at 73-4°C. (Literature value,[11] m.p. 72-3°C.) The 1,4-bis(4-tolyl mercapto) benzene was recrystallized from methanol to give 8 g. (0.025 moles) of white plates melting at 98.5-99.5°C. The latter compound had been previously prepared[48] by the condensation of the lead salt of p-toluenethiol and p-dibromobenzene (m.p. 99°C.).

Bis(4-Chlorophenyl) Ether

This compound was prepared following the method of Suter and Green[44] to obtain an intermediate needed for later ring closure to 2,8-dichlorophenoxathiin by means of sulfur dichloride.

A two-liter three-neck round-bottom flask equipped with a stirrer, immersion thermometer and distilling head for the condensation reaction. The quantity, 128.5 g. (1.0 mole), of p-chlorophenol was placed in the reaction flask with one liter of absolute ethanol, 300 g. (1.56 moles) of 1-bromo-4-chlorobenzene, and 2.0 g. of precipitated copper powder. The reaction mixture was warmed to 40°C. and 66.0 g. (1.0 mole, 85%) of potassium hydroxide pellets were cautiously added to the reaction mixture. The alcohol was slowly distilled, at atmospheric pressure, and the reaction mixture was heated until the temperature of the melt reached 195°C. where it was held for five hours. The reaction mixture was then poured into ice water and acidified with hydrochloric acid. Ethylene dichloride (one liter) was added to dissolve the oily material. Filter cel was next added to the solution and it was filtered to remove the copper insolubles. The organic layer was separated from the filtrate and washed consecutively with dilute hydrochloric acid and water. The solvent was removed by vacuum distillation and the residue was fractionated through a 20 cm. vigreux column. A forecut containing p-chlorophenol and 1-bromo-4-chlorobenzene was collected as the lower boiling fraction and a crude product fraction boiling in the range of 140-158°C./5 mm. was next collected. The higher boiling fraction containing the condensation products of p-chlorophenol with itself was not further purified as they were of no interest to the problem at hand. The crude bis(4-chlorophenyl) ether was refractionated to obtain an oil (b.p. 147°C./5 mm.) which solidified on chilling. It was recrystallized from ethanol to obtain

131 g. (0.55 mole, 55% yield) of bis(4-chlorophenyl) ether melting at 30-31°C. Brewster and Stevenson[188] prepared this aryl ether by the chlorination of phenyl ether to obtain a solid melting at 30°C. (b.p. 168-172°C./7 mm.).

It should be noted that this preparation represents an extension of the method used by Suter and Green[44] and others in that the phenol contained a labile chlorine whereas previous investigators had used only phenol and alkylated phenols. In this present instance the dimer of the phenol is separable since it is slightly higher boiling than the desired product.

Benzene Sulfonyl Chloride Condensations

Diphenyl Sulfone

This reaction was carried out to become acquainted with the general method of condensing benzene derivatives with benzene sulfonyl chlorides which was used to obtain sulfones of known substitution and to prepare intermediates required for synthesis involving ring closures. One and one-half liters (1320 g., 16.9 moles) of benzene (thiopene free) and 400 g. (3.0 moles) of anhydrous aluminum chloride were placed in a three-liter three-necked flask and 528 g. (3.0 moles) of benzenesulfonyl chloride were added to the reaction mixture over a three hour period at room temperature. Since the reaction appeared sluggish (as evidenced by slow evolution of hydrogen chloride) the reaction mixture was gradually warmed to 80°C. and held at that temperature for an hour before quenching it in cold dilute hydrochloric acid. The oil layer was separated, washed thoroughly with water, and cooled to induce crystallization. The solid was filtered, air dried, and recrystallized from a large volume of absolute ethanol to give 502 g. (2.30 moles, 76.7% yield) of diphenyl sulfone (white platelets) melting at 121-2°C. Beilstein reports several melting points for this compound in the range 122.5-129°C. The same material, diphenyl sulfone, was also prepared in 94% yield by the chromic acid oxidation of diphenyl sulfide to give a material melting at 122-122.5°C. after two recrystallizations from absolute ethanol.

The Preparation of 4-Chlorophenyl Phenyl Sulfone

The quantities, 221 g. (2.0 moles) of chlorobenzene and 66 g. (0.5 mole) of anhydrous aluminum chloride were placed in a 500 ml. three-neck round-bottom flask equipped for a condensation reaction. The reaction flask and its contents were placed in a hot water bath, heated to 50°C. and 88 g. (0.5 mole) of benzene sulfonyl chloride was added during a 45 minute period. The mixture was stirred for an hour before the reaction temperature was raised to 80°C. where it was held for an additional hour and then the reaction mixture was poured into ice water. Some crystalline material precipitated from solution and so the quenched reaction mixture was warmed to dissolve the solid and to complete hydrolysis of the metal complex. The chlorobenzene layer was separated and washed consecutively with dilute hydrochloric acid and water. The chlorobenzene was removed under reduced pressure. The residue was distilled through a 20 cm. vigreux column (b.p. 195°C./3 mm.) to obtain 113 g. of crude product which solidified in the receiver. The solid was recrystallized from 95% ethanol to obtain 100 g. (0.41 mole, 82% yield) of 4-chlorophenyl phenyl sulfone melting at 92.5-93.5°C. (Literature value[150] m.p. 91-2°C.).

The Preparation of 3,4-Dichlorophenyl Phenyl Sulfone

A three-neck round-bottom flask (500 ml.) was equipped with a stirrer, thermometer, dropping funnel and hydrogen chloride scrubber. The quantities, 261 g. (1.78 moles) of o-dichlorobenzene and 66 g. (0.5 mole) of anhydrous aluminum chloride, were placed in the flask and the addition of 88 g. (0.5 mole) of benzene sulfonyl chloride was started. It was found that the reaction was slow (as evidenced by hydrogen chloride evolution) until the temperature of the reaction mixture was raised to 85°C. The addition of the aryl sulfonyl chloride required 45 minutes. Following the addition of the aryl sulfonyl chloride the reaction mixture was stirred for two hours and then poured into ice water. The product isolation procedure used was identical to that described for the synthesis of 4-chlorophenyl phenyl sulfone. The product, 3,4-dichlorophenyl phenyl sulfone, distilled at 183°C./1 mm. The solid was recrystallized from 95% ethanol to obtain 61 g. (0.21 mole, 43% yield) of 3,4-dichlorophenyl phenyl sulfone melting at 124.5-126°C. (Literature value[8] m.p. 125°C.).

The Preparation of 2,4,5-Trichlorophenyl Phenyl Sulfone

The initial attempt to prepare this sulfone was made since a similar attempt to obtain 2,4,5-trichlorophenyl-3',4'-dichlorophenyl sulfone using 3,4-dichlorobenzene sulfonyl chloride with 1,2,4-trichlorobenzene and aluminum chloride failed to produce satisfactory results. The starting materials, 1,2,4-trichlorobenzene and benzenesulfonyl chloride, for this reaction were both readily available whereas the 3,4-dichlorobenzenesulfonyl chloride had to be prepared. The 2,4,5-trichlorophenyl phenyl sulfone was needed to check the sulfone previously prepared by the oxidation of 2,4,5-trichlorophenyl phenyl sulfide and more importantly it was desired to check the experimental method for synthesizing 2,4,5-trichlorophenyl phenyl sulfone since it was planned to use this experimental procedure extensively for preparing derivatives of known structure.

The quantity, 75 g. (0.41 mole), of 1,2,4-trichlorobenzene was placed in a 300 ml. round bottom flask equipped with a stirrer, reflux condenser, thermometer, and dropping funnel. Aluminum chloride catalyst (27 g., 0.205 mole) was added to this and then 25 g. (0.205 mole) of benzenesulfonyl chloride was dripped into the stirred trichlorobenzene aluminum chloride mixture over a 45 minute period. The reaction temperature rose slightly to 32°C. but without any evolution of hydrogen chloride. The reaction mixture was then heated and the first slow evolution of hydrogen chloride started at 55°C. with strong evolution of hydrogen chloride occurring at 90°C. When the reaction temperature reached 110°C. it was held there for a period of an hour and then it was increased to 140°C. for ten minutes just prior to pouring the reaction mixture onto ice. The quenched mixture was acidified with hydrochloric acid, extracted with ethylene dichloride and the oily layer was separated and washed with water. The solvent was removed by vacuum distillation and the residue was fractionated through a 25 cm. vigreux column to obtain 21 g. (0.11 mole) of unreacted 1,2,4-trichlorobenzene (b.p. 112°C./35 mm.) and 19 g. of a solid fraction (b.p. 145°C./35 mm.). A 29 g. quantity of a non-distillable tar remained in the distillation flask. The solid fraction was recrystallized from ethanol to obtain a white crystalline solid melting at 139-140°C. An infra-red spectrum of this material identified it as 1,2,4,5-tetrachlorobenzene (m.p. 139-140°C.). The above synthesis, however, failed to yield any of the desired sulfone.

The above results suggested that the conditions which had been satisfactory for producing simple chlorinated diphenyl sulfone derivatives from the sulfonyl chloride were not applicable for obtaining the highly chlorinated members. Further investigation of this synthetic route to obtain highly substituted sulfones was dropped at this point and it was not until much later in this investigation that the article of Huismann, Uhlenbroek and Meltzer[9] was found describing a modification of the above procedure which they had used with fair success to obtain the desired sulfone. Their experimental method was then tried using the same quantities of reactants as given in the first attempt. The 1,2,4-trichlorobenzene and the benzenesulfonyl chloride were placed in the reaction flask and warmed to 100°C.; the aluminum chloride catalyst was added a few grains at a time over a period of one hour after which the reaction mixture was heated to 130°C. for fifteen minutes. The reaction mixture was quenched and the crude product was isolated as described previously. It was vacuum distilled to obtain a solid boiling at 225°C./3 mm. which on recrystallization from ethanol gave 29 g. (0.09 mole, 45% yield) of the 2,4,5-trichlorophenyl phenyl sulfone melting at 127-8°C. Huismann, Uhlenbroek and Meltzer[9] obtained the same sulfone from the condensation of 2,4,5-trichlorobenzenesulfonyl chloride and benzene as well as from the 2,4,5-trichlorophenyl-4-nitrophenyl sulfide by synthesis involving several steps. Their sulfone had the same melting point as the sulfone obtained in this work and it was also identical with the sulfone obtained by the oxidation, with chromium trioxide in glacial acetic acid, of 2,4,5-trichlorophenyl phenyl sulfide.

The Preparation of 2,4,5,3',4'-Pentachlorodiphenyl Sulfone

When the initial sample of 2,4,5,3',4'-pentachlorodiphenyl sulfide was obtained by the chlorination of bis(3,4-dichlorophenyl) sulfide with sulfuryl chloride it was oxidized to the sulfone. Since the sulfone had not been previously reported its preparation was attempted using the benzene sulfonyl chloride condensation method.

A 108 g. (0.595 mole) quantity (75 ml.) of 1,2,4-trichlorobenzene and 4.0 g. (0.03 mole) of anhydrous aluminum chloride were placed in a 500 ml. three-neck round-bottom flask equipped with a stirrer, dropping funnel and a reflux condenser. The mixture was warmed to 35°C. and 5.0 g. (0.02 mole) of 3,4-dichlorobenzene sulfonyl chloride was slowly added to it. Hydrogen chloride evolution was very slow and the reaction temperature was slowly raised after half of the chloride had been added. Acid evolution became significant at about 95°C. and the remainder of the sulfonyl chloride was added. The total time required to add the sulfonyl chloride was an hour after which the reaction temperature was raised to 120°C. for two hours and the reaction was then quenched by pouring it into cold dilute hydrochloric acid. A small amount of an insoluble material separated at once. This was removed by filtration and an attempt was made to recrystallize it from ethanol. Since the material was quite insoluble a hot saturated solution of it was prepared, filtered and allowed to cool. A fine light precipitate was obtained which was filtered, dried and found to melt at 270-3°C. An attempt was made to obtain an infra-red spectrum of the material in carbon disulfide but the material was so insoluble that only a low peak amplitude could be obtained with a saturated solution of it. A short broad peak with a flat top appeared at 11.40-11.80 microns. Since the material did not appear to be the compound sought it was set aside since there was such a small amount of it. The solvent layer was separated from the quenched reaction mixture and washed in the usual manner using ethylene dichloride to extract the oily material in the final wash. The solvent was removed by vacuum distillation and the excess 1,2,4-trichlorobenzene (b.p. 112°C./ 35 mm.) was recovered. The residue was recrystallized from ethanol to obtain a white solid melting at 139-140°C. This was identified as 1,2,4,5-tetrachlorobenzene by means of its infra-red spectrum which exhibited an out of the plane hydrogen deformation peak at 11.50 microns. An additional quantity of solid material was isolated from the mother liquor and found to show a new infra-red peak at 12.30 microns as would be expected from the desired 2,4,5,3',4'-pentachlorodiphenyl sulfone (see Figure 41). However, it was apparent that it was present in such a small amount that its isolation would not be profitable. The experiment was discontinued at this point and an attempt was made to perfect the condensation method using the more readily available material, benzene sulfonyl chloride. This condensation also failed and further attempts to carry it out were discontinued until the article of Huismann, Uhlenbroek and Meltzer[9] appeared giving a modified procedure for this condensation reaction. The condensation reaction was again tried employing benzenesulfonyl chloride and found to be successful whereupon a second experiment using 3,4-dichlorobenzenesulfonyl chloride was attempted. Using twice the quantities of reactants as in the original experiment, 1,2,4-trichlorobenzene and 3,4-dichlorobenzenesulfonyl chloride were placed in the reaction flask, heated to 130°C. and the aluminum chloride was added in small amounts during a two hour period. Heating of the reaction mixture was continued for an hour after the addition of the catalyst and then a product isolation was made in the manner described earlier. A small amount of tetrachlorobenzene was sublimed from the distilling flask before the residue was recrystallized from ethanol to obtain 7.1 g. (0.18 mole, 45% yield) of 2,4,5,3',4'-pentachlorodiphenyl sulfone melting at 142-142.5°C. This material was shown to be identical to that previously prepared by the oxidation of 2,4,5,3',4'-pentachlorodiphenyl sulfide by its infra-red spectrum (see Figure 41) and mixed melting points. Huismann, Uhlenbroek and Meltzer[9] gave 144-145°C. as the melting point of this sulfone as prepared from o-dichlorobenzene and 2,4,5-trichlorobenzene sulfonyl chloride. It would appear that the difference reported in the melting points is due to a stem correction for the thermometers.

Oxidation Procedures

Bis(2,5-Dichlorophenyl) Sulfoxide

The quantity, 2.0 g. (0.0062 mole), of bis(2,5-dichlorophenyl) sulfide was dissolved in 350 ml. of glacial acetic acid at room temperature and one equivalent (0.71 g., 0.0062 mole) of 30% hydrogen peroxide was added to the sulfide solution. The oxidation mixture was set aside for 5 days at room temperature and then poured into ice water. A white solid precipitated which was filtered, dried and recrystallized three times from ethanol to obtain 1.1 g. (0.0032 mole, 52% yield) of bis(2,5-dichlorophenyl) sulfoxide melting at 136.5-137°C. The material was identical in all respects with that obtained from the condensation of thionyl chloride with 1,4-dichlorobenzene.

Bis(2,4,5-Trichlorophenyl) Sulfoxide

In the initial attempt to prepare this compound 3.0 g. (0.0076 mole) of bis(2,4,5-trichlorophenyl) sulfide (m.p. 149-150°C.) was partially dissolved in 300 ml. of acetone and 1.0 g. (0.0088 mole) of 30% hydrogen peroxide was added to the sulfide suspension. It was set aside, with occasional shaking, for six days. The solid never completely dissolved in the oxidation media. On the sixth day the acetone was removed under vacuum and the residue was recrystallized from ethylene dichloride to obtain 2.1 g. of a solid melting at 149-150°C. This was obviously recovered starting material and the mother liquor was not investigated further.

A second experiment was made using 2.0 g. (0.0051 mole) of bis(2,4,5-trichlorophenyl) sulfide dissolved in 200 ml. of glacial acetic acid. Since the material appeared to be resistant to oxidation the conditions were made more vigorous. The quantity, 1.5 g. (0.013 mole) of 30% hydrogen peroxide was added to the reaction mixture and its temperature was raised slowly to 90°C. where it was held for three hours. The reaction mixture, after cooling to room temperature, was set aside until the next day (18 hours later) during which time crystals precipitated. The solid was filtered and recrystallized from acetone to obtain a white solid melting at 144-5°C. An infra-red spectrum of this material was made using the potassium bromide pellet technique.[169,170,171,189] Absorption peaks were found at 9.0 (strong), 9.05 (weak), 9.34 (medium), 9.50 (strong), 11.05 (weak), 11.25 (strong), 11.45 (strong), and 11.65 (medium) microns. The starting material, bis(2,4,5-trichlorophenyl) sulfide (Figure 42), exhibited peaks at 9.0 (strong), 9.5 (strong), 11.25 (strong) and 11.50 (strong) microns. The peak at 9.45 microns was interpreted as confirmation of the sulfoxide group in bis(2,4,5-trichlorophenyl) sulfoxide.

Anal. Calc'd for $C_{12}H_4Cl_6O_1S_1$: C, 35.24; H, 0.99; Cl, 52.02; S, 7.84

Found: C, 35.20; H, 0.93; Cl, 52.10; S, 7.85

The mother liquors were partially evaporated on a steam bath and allowed to cool. The solid which precipitated was filtered and dried. The material commenced to melt at 142°C. but residual solid remained in the capillary until a temperature of 174°C. was reached. An additional recrystallization of this material from acetone raised the melting point to 171-174°C. The residues were obviously contaminated by the sulfone which melts at 175-175.5°C.

Bis(2,3,4-Trichlorophenyl) Sulfone

A 3.0 g. (0.0075 mole) quantity of bis(2,3,4-trichlorophenyl) sulfide and 30 ml. of glacial acetic acid were placed in a 250 ml. round-bottom flask equipped with a straight tube condenser and heated to its reflux temperature. Solid chromium trioxide (2.5 g., 0.025 mole) was added to the acid solution of the sulfide through the condenser during an hour period using 75 ml. of glacial acetic acid to wash the oxide down the condenser when necessary. The reaction was exothermic and the heating mantle was turned down low during the addition of the oxide to prevent eruption of the material through the condenser. This procedure[65] is preferable to attempting to dissolve the chromium trioxide in the glacial acetic as others[75,76,172] have reported since the oxide is only sparingly soluble in the acid and it requires too large a volume of acetic acid to handle conveniently by that technique. Following the addition of the oxidizing agent the reaction mixture was refluxed an additional fifteen minutes and then it was poured onto ice with vigorous stirring. The white precipitate was removed by filtration, washed thoroughly with water to remove a green coloration, dried and recrystallized from acetone to obtain 3.0 g. (0.007 mole, 93% yield) of bis(2,3,4-trichlorophenyl) sulfone melting at 205.5-206°C.

Anal. Calc'd for $C_{12}H_4Cl_6O_2S_1$: C, 33.91; H, 0.94; Cl, 50.06; S, 7.78

Found: C, 34.13; H, 1.12; Cl, 49.82; S, 7.54

The spectrum of this material (Figure 44) was determined and has been cited as structure proof [see the preparation of bis(2,3,4-trichlorophenyl) sulfide and the infra-red discussion in the appendix] for the condensation product of 1,2,3-trichlorobenzene and sulfur dichloride as well as the bis(2,3,4-trichlorophenyl) sulfone prepared by this oxidation. The latter sulfone has not been previously described in the literature.

The Preparation of Thianthrene-5-Oxide

The ring closure of diphenyl sulfide with thionyl chloride gave a material which melted at 154-5°C. Beilstein lists two melting points for thianthrene-5-oxide, 148° and 143°C. Since the melting point of thianthrene is 154-5°C. it was desired to prepare the oxide by a known procedure[66] to check the melting point with a pure sample and to determine its infra-red spectrum to ascertain the presence and location of the sulfoxide band, since the ring closure product of bis(4-chlorophenyl) sulfide with thionyl chloride shows no such band.

The oxidation was carried out by adding dropwise 20 ml. of concentrated nitric acid (d = 1.416) diluted with 55 ml. of water to a refluxing solution, containing 43 g. of thianthrene dissolved in 700 ml. of glacial acetic acid, over a period of an hour and a half. The reaction mixture was kept at its reflux temperature for an additional 15 minutes after the addition of acid was complete and then it was poured into two and one-half liters of vigorously stirred ice water. The solid was recovered by filtration, washed with water, and then dried in an oven at 60°C. for twenty four hours. The crude dry product weighed 43 g. (92.5% of theory) and melted at 141-2°C. A sample recrystallized from methanol melted at 142-3°C. corresponding with that prepared by Gilman and Swayampati,[66] m.p. 143-143.5°C. A comparison of the infra-red spectrum of this material with that of thianthrene showed a band at 9.30 microns believed to be due to sulfoxide.

2,3,7,8-Tetrachlorothianthrene-5-Oxide

The quantity, 10.0 g. (0.028 mole) of 2,3,7,8-tetrachlorothianthrene was placed in a one-liter three-neck round-bottom flask equipped with a stirrer, dropping funnel, and reflux condenser. Glacial acetic acid was added until the material dissolved at the reflux temperature of the mixture (this required 750 ml.) and then 3 ml. of concentrated nitric acid (d = 1.416) in 10 ml. of water was added over a period of one hour. The reaction mixture was refluxed for five hours during which time precipitation of a white solid occurred. The mixture was poured into three liters of ice water, the solid was filtered and washed thoroughly with water. The solid was dried and recrystallized from ethylene dichloride to obtain a white crystalline material melting at 275-6°C. Since samples of purified 2,3,7,8-tetrachlorothianthrene had melted very close to 275-6°C. it was mistakenly assumed that the solid isolated was starting material and a search of the mother liquor was made for the expected oxidation product. Six separate precipitations were made from the mother liquor with the last fraction melting at 185-195°C. Infra-red spectra were taken on all six fractions and an examination of the spectra was made for the sulfoxide peak and the single hydrogen out of plane deformation peak. Since the materials were not very soluble in carbon disulfide it was hard to obtain good spectra and interpretation was difficult. Two humps were found at 11.25 and 11.75 microns and a possible sulfoxide peak appeared at 9.45 microns (see Figure 58). An interpretation of the spectra was found when it was noted that the spectrum of the solid melting at 275-6°C. did not coincide with that of a known sample of 2,3,7,8-tetrachlorothianthrene (see Figure 57). It was recognized that the original material must be the oxidation product and that the normal 1,2,4,5 substitution pattern which this type of compound usually exhibits had been modified due to the interaction of the oxygen of the sulfoxide group with the adjacent hydrogens on the thianthrene skeleton. A discussion of the effect of this interaction on the spectrum of this compound will be found in the appendix. The material melting at 275-6°C. was then recrystallized further to obtain material melting at 278.5-279°C. and analysis of this material confirmed that it was the monoxide.

Anal. Calc'd for $C_{12}H_4Cl_4O_1S_2$: C, 38.93; H, 1.08; Cl, 38.32;
S, 17.32

Found: C, 39.08; H, 1.16; Cl, 38.32; S, 17.42

The yield of purified material was 7.0 g. (0.019 mole, 68%) of 2,3,7,8-tetrachlorothianthrene-5-oxide. This material had not previously been described in the literature so that it was further characterized by oxidation, with chromic acid in glacial acetic acid, to the tetroxide which melted at 314-314.5°C. This agreed with the melting point of the tetroxide prepared by direct oxidation of 2,3,7,8-tetrachlorothianthrene.

2,7-Dichlorothianthrene-5,5,10,10-Tetroxide

This material was prepared in the usual manner by the oxidation of 2,7-dichlorothianthrene with chromium trioxide in glacial acetic acid as a solvent to obtain an 85% yield of the tetroxide. The oxide melted at 289-290°C. after recrystallization from acetone.

Anal. Calc'd for $C_{12}H_6Cl_2O_4S_2$: C, 41.26; H, 1.73; Cl, 20.30;
S, 18.36

Found: C, 41.15; H, 1.74; Cl, 19.88; S, 17.80

Baw, Bennet and Dearns[4] prepared this compound by an identical procedure and reported the melting point as 293°C. (305°C. Corr.). An infra-red spectrum of the 2,7-dichlorothianthrene-5,5-10,10-tetroxide was made using the potassium bromide pellet technique[169,170,171,189] (0.35% solid). Absorption peaks in the substitution region (11-15 microns) were found at 11.00, 11.28 (weak), 11.84, 12.32 and 13.95 microns. An extended discussion of the comparison of this spectrum with that obtained from the 2,8-dichlorothianthrene-5,5-10,1)-tetroxide appears in the appendix of this thesis.

The Preparation of 10-Thiaxanthenone-5,5-Dioxide

The quantity, 1.0 g. (0.0048 mole), of thiaxanthene was placed in a 100 ml. round-bottom flask with 25 ml. of glacial acetic acid and the solution was heated to its reflux temperature using a straight tube condenser. The thiaxanthene was oxidized with 2.4 g. (0.024 mole, 5 equivalents) of chromium trioxide by dropping a few crystals of the oxide at a time down the condenser tube and washing any oxidizing agent which adhered to the walls of the condenser into the reaction mixture with an additional 25 ml. of glacial acetic acid. This procedure has been described in previous oxidations of sulfides with this reagent. The oxidation mixture was heated at its reflux temperature for thirty minutes, then poured onto crushed ice, and stirred vigorously until solidification of the product took place. The quenched reaction mixture was set aside overnight to permit coagulation of the solid, filtered, and washed thoroughly to remove the green coloration. The product was recrystallized from ethanol to obtain an 81% yield of 10-thiaxanthenone-5,5-dioxide melting at 184.5-185.5°C. (Literature value[74,180] m.p. 184°C.)

Thiol Preparation

The Preparation of 2-Chlorobenzenethiol

CAUTION: This experiment should be performed in back of a shield and should not be carried out on a large scale.

The diazonium salt was formed by the procedure outlined by Tarbell and Fukushima[128] for obtaining meta-thiocresol. A one-liter three-neck flask was equipped with a stirrer, thermometer and dropping funnel. The quantities, 150 ml. of concentrated hydrochloric acid and 150 g. of crushed ice were placed in it and 95.5 g. (0.75 mole) of 2-chloroaniline was added slowly to the chilled acid solution while the flask was cooled in an ice-salt bath. A solution containing 55 g. (0.80 mole) of sodium nitrite dissolved in 125 ml. of water was prepared and chilled below 4°C. in an ice-calcium chloride bath. The nitrite solution was added to the aniline hydrochloride solution at a rate slow enough to keep the reaction temperature below 4°C. A solution of 140 g. (0.85 mole) of potassium ethyl xanthate (preparation described elsewhere) dissolved in 180 ml. of water was then prepared in a two-liter three-neck flask and placed in a water bath at 40-50°C. (Note--higher reaction temperatures lead to the formation of 2-chlorophenol as an impurity). The diazonium solution was added slowly behind a shield[128] to the potassium ethyl xanthate solution to form the 2-chlorophenyl ethyl xanthate. Vigorous stirring during the addition of the diazonium chloride is essential and it should be continued uninterrupted. A sudden gas evolution was noted in one instance when making a stirrer adjustment. After the addition of the diazonium chloride had been completed the reaction mixture was allowed to stir overnight. The following day the oily layer was extracted with ether and the ether layer was washed with dilute sodium carbonate (to remove acidic material) and then with water. The ether solution was dried over anhydrous sodium sulfate for 24 hours, the dessicant was removed by filtration and the ether solution was divided into two equal volumes for ease of handling during the metal hydride reduction of the xanthate. The method of Campaigne and Osborn[18] was used for the reduction and this is believed to be the first use of this method on an aryl chlorinated xanthate. For the reduction a two-liter, three-neck, round-bottom flask was equipped with a stirrer, condenser, dropping funnel and a nitrogen purge line. One liter of absolute ether (dried over sodium) was placed in the flask with 30 g. of lithium aluminum hydride. One-half of the ether solution containing 2-chlorophenyl ethyl xanthate was then added slowly from a dropping funnel into the flask at a rate sufficient to maintain a gentle reflux of the ether solution. The addition of the xanthate required an hour and a half after which the reaction mixture was stirred two hours and then set aside overnight. The following morning 100 ml. of water was carefully added to the reaction mixture to destroy excess hydride but there was very little reaction. This was followed by the addition of 500 ml. of 10% sulfuric acid. An insoluble complex precipitated and then redissolved during the addition of the acid except for a small amount of

solid. Gas continued to be evolved during the acidification and it was concluded that this was due to the effect of the acid on the solid material and a filtration was made to remove it from the mixture. The ether layer was separated, washed with water, dried over anhydrous sodium sulfate, filtered and the ether evaporated on a steam bath. The other half of the ether solution of 2-chlorophenyl ethyl xanthate was similarly reduced in a separate reduction and the oily product from this was combined with that obtained in the other reduction reaction for distillation. Fractionation of the combined oily products yielded 74 g. (0.52 mole, 70% yield) of 2-chlorobenzenethiol (b.p. 93°C./5 mm.). An infra-red spectrum of the material showed a thiol peak at 3.9 microns and an ortho substitution peak at 13.5 microns. There was a higher boiling residue remaining in the distillation flask and no attempt was made to distill this material but it was again submitted to the reduction treatment since it was thought that it could be unreduced ester or disulfide. However, only a small amount of thiol was obtained from this additional reduction.

The Attempted Preparation of 3,4-Dichlorobenzenethiol

Marvel and Caesar[134] claim the first reduction of a sulfonyl chloride to a thiol with lithium aluminum hydride. Since then several workers have reported similar reductions[135,136,137] with varying results. As no record of this method having been used on a chlorinated benzene sulfonyl chloride was found in the literature an attempt was made to use this procedure to prepare 3,4-dichlorobenzenethiol.

One liter of anhydrous ether was placed in a three-liter, three-neck, round-bottom flask equipped with a stirrer, dropping funnel, condenser, and apparatus for introducing a nitrogen atmosphere. The quantity, 43 g. (1.13 moles) of lithium aluminum hydride was placed in the flask and 100 g. (0.408 mole) of 3,4-dichlorobenzenesulfonyl chloride dissolved in 500 ml. of anhydrous ether was added from a dropping funnel as rapidly as the refluxing ether would allow. It required an hour and a half to add the sulfonyl chloride after which the reaction mixture was kept at its reflux temperature with a steam bath for a period of four hours. Water (100 ml.) was added cautiously and then 800 ml. of 10% sulfuric acid to dissolve the lithium salts. The mixture was filtered to remove insolubles and the ether layer was separated, washed with water, and dried overnight with anhydrous sodium sulfate. After filtration of the drying agent the ether was evaporated on a steam bath and the residue solidified on cooling. The melting point of the crude material was 87.5-88.5°C. The solid was recrystallized from ethanol to obtain 41 g. of a yellowish solid melting at 88.5-90°C. Two additional crystallizations from ethanol raised the melting point to 90-91.5°C.

Strating and Backer,[137] Schlesinger and Finholt,[139] and Field and Grunwald[136] report the formation of disulfides as by products in the lithium aluminum hydride reduction of benzenesulfonyl chlorides. The material was assumed to be bis(3,4-dichlorophenyl) disulfide.

Anal. Calc'd for $C_{12}H_6Cl_4S_2$: C, 40.46; H, 1.69; Cl, 39.82; S, 18.00

Found: C, 40.76; H, 1.87; Cl, 39.30; S, 17.68

The infra-red spectrum of the material shows a typical 1,2,4 substitution pattern and is almost identical with the spectrum from bis(3,4-dichlorophenyl) sulfide (see Figure 32) which is to be expected as the sulfur-sulfur bond has no characteristic absorption in the 2-14 micron region. Azouz, Parker, and Williams[190] who isolated the dichloromercapturic acid chromatographically after feeding o-dichlorobenzene to rabbits, hydrolyzed this to the thiol and then oxidized the latter to the disulfide, reported bis(3,4-dichlorophenyl) disulfide melted at 83-4°C.

Upon concentrating the mother liquor from the recrystallization of the disulfide a quantity of crystals was obtained which melted at 83-111°C. The infra-red spectrum of this material showed a new peak at 7.45 microns which is typical for a sulfone. Fractional crystallization of the material raised the melting point to 127.5-128°C. Synthesis of bis(3,4-dichlorophenyl) thiosulfonate by the method of Vinkler and Klivenyi[191] (zinc reduction of 3,4-dichlorobenzenesulfonyl chloride) produced a material melting at 127.5-128°C. A mixed melting point of this material with that described above showed no depression and the infra-red spectra of the two materials were identical. The production of thiosulfonates in lithium aluminum hydride reductions of benzenesulfonyl chlorides has recently been reported by Lehto and Shirley[135] for the first time.

The fractional crystallization yielded 2.0 g. (0.0151 mole, 2.56% yield) of bis(3,4-dichlorophenyl) thiosulfonate and an additional 6.0 g.

of the disulfide. The total yield of bis(3,4-dichlorophenyl) disulfide was 47 g. (0.132 mole, 65% yield). Examination of the residues from this reaction by means of infra-red gave no evidence of any absorption at 3.9 microns which is characteristic of a thiol.

It was rather obvious that insufficient lithium aluminum hydride had been used in the reduction. Further experience with the particular sample of hydride showed that it was of poor quality and also that the ether used was not absolutely dry. However, the amount of hydride which is necessary for these reductions seems to be unsettled as Field and Grunwald[192] using a mole ratio of 2.44 (hydride to sulfonyl chloride) obtained an 89% yield of para-toluenethiol while Marvel and Caesar[134] employing a ratio of 3.8 reported only a 50% yield of the same thiol.

Miscellaneous Preparations

The Preparation of 1-Chloro-2,4-Dibromobenzene

This material was prepared as an intermediate for the synthesis of 1-bromo-2-chlorobenzene since it is unavailable commercially. Chlorobenzene (790 g., 7.0 moles), ferric chloride (30 g.), and carbon tetrachloride (one and one-half liters) were placed in a five-liter, three-neck, round-bottom flask suitably equipped. The mixture was heated to its reflux temperature and 1383 g. (8.62 moles) of bromine were added over an eight hour period. The reaction proceeded readily, as evidenced by hydrogen bromide evolution, until approximately 900 g. of bromine had been added. The reaction rate slowed down appreciably at that point and a fair amount of bromine distilled over with the hydrogen bromide into the scrubber. Originally it had been planned to add more bromine, but a small crack was discovered in the condenser which allowed traces of moisture to enter the reaction vessel which destroyed the catalyst activity. The reaction mixture was treated with aqueous sodium thiosulfate to remove unreacted bromine, washed with 6N hydrochloric acid to remove the iron and then washed with water. The solvent was removed by distillation under vacuum and the oily residue was distilled into three fractions. The first consisted of 1226 g. of chlorobenzene, bromochlorobenzene, and the forecut from the dibromochlorobenzene, the second fraction consisted of 268 g. of dibromochlorobenzene in a nearly pure state, and the third fraction (15 g.) was solid tribromochlorobenzene, slightly contaminated with dibromochlorobenzene. The first fraction was placed in a clean reaction vessel with one and one-half liters of carbon tetrachloride and 30 g. of anhydrous ferric chloride and the mixture was heated to its reflux temperature. Bromine (464 g., 2.89 moles) was then added over a period of ten hours. After the first 200 g. of halogen had been added the reaction rate dropped sharply and an additional 30 g. of ferric chloride was added without a significant increase in the reaction rate. The reaction mixture was kept at its reflux temperature for an additional five hours following the complete addition of bromine, after which the mixture was worked up in the manner described above. Following the removal of the solvent the residue was distilled under vacuum and the following fractions were obtained:

monobromochlorobenzene (b.p. 90°C./25 mm.), mixed monobromochlorobenzene and dibromochlorobenzene, dibromochlorobenzene (b.p. 144°C./25 mm.), mixed dibromochlorobenzene and tribromochlorobenzene, and tribromochlorobenzene (b.p. 225°C./10 mm.). The solid tribromochlorobenzene which precipitated, on standing for several hours, from the mixed fractions was filtered and added to the tribromochlorobenzene and the combined material was recrystallized from chlorobenzene to give white crystalline solid melting at 155-7°C. This was recrystallized twice from ethylene dichloride to obtain 151 g. (0.432 mole) of tribromochlorobenzene melting at 161.5-162.5°C.

Anal. Calc'd for $C_6H_3Br_3Cl_1$: C, 20.63; H, 0.577; Br, 68.64; Cl, 10.15

Found: C, 20.69; H, 0.76; total halogen, 78.62

There are six possible isomers of this compound and the only one recorded in the literature is the 1,3,5-tribromo-2-chlorobenzene which melts at 90-1°C.[193] The infra-red spectrum of the unknown material in carbon disulfide solution was taken (Figure 60) and a single substitution peak appeared at 11.45 microns. The spectrum of 1,2,3,4-tetrachlorobenzene (Figure 10) had three peaks in the substitution region at 12.60, 13.05, and 13.55 microns. Since the unknown does not exhibit a pattern at all similar to this spectrum it is possible to eliminate two additional isomers, namely, 1,2,3-tribromo-4-chlorobenzene and 1,2,4-tribromo-3-chlorobenzene. The infra-red spectrum of 1,2,3,5-tetrachlorobenzene (Figure 9) likewise shows a complex substitution pattern with peaks at

11.70, 12.00, 12.25, and 12.50 microns. The absence of a similar pattern in the spectrum of the unknown eliminates the possibility of the 1,2,3-tribromo-5-chlorobenzene and the 1,2,5-tribromo-3-chlorobenzene. The spectrum is essentially identical with that exhibited by 1,2,4,5-tetrachlorobenzene (Figure 8) and it must be concluded that the compound is 1,2,4-tribromo-5-chlorobenzene.

The solid monobromochlorobenzene, which precipitated from the mixed fractions on standing, was filtered and added to the monobromochlorobenzene fraction and the combined material was recrystallized from ethanol to obtain 761 g. (4.0 moles) of 1-bromo-4-chlorobenzene melting at 67-8°C. (Literature[194] m.p. 67.4°C.). This material was subsequently used for condensations with thiophenols to prepare para-chlorodiphenyl sulfides. The mother liquors from the recrystallizations of the tribromochlorobenzene and the monobromochlorobenzene were subjected to vacuum distillation to remove the solvent and the oily residue was combined with the mixed cuts from the previous fractionation. The combined residues were fractionally distilled under vacuum primarily to remove the remaining dibromochlorobenzene. This fraction was then added to the two previous dibromochlorobenzene fractions and the material was subjected to a final purification distillation using a 40 cm. vigreux column to obtain 464 g. (1.71 moles) of dibromochlorobenzene, (b.p. 144°C./25 mm., $n_D^{25} = 1.6235$). Supercooling of the liquid lead to a solid which melted at 24°C. The infra-red spectrum of this material (not included in the appendix) exhibits peaks at 11.55, 12.40, 12.85, and 13.05 microns. The first two peaks are stronger and are typical of 1,2,4 substitution while the latter two are weaker peaks of a doublet which seem to be typical of the carbon-bromine bond absorption in this type of substitution.

The bromination of 1-bromo-4-chlorobenzene, the isomer formed in bromination under these conditions, can lead to two possible isomers, 1,3-dibromo-4-chlorobenzene and 1,2-dibromo-4-chlorobenzene. The constitution of the product can be shown to be predominantly 1,3-dibromo-4-chlorobenzene since reduction of this material with hydrogen using 5% palladium on charcoal as the catalyst in the presence of a base such as sodium acetate leads selectively to 1-bromo-2-chlorobenzene.[195] Quantitative infra-red shows this material to be contaminated with less than a 5% of 1-bromo-3-chlorobenzene which would be formed by the selective reduction of the 1,2-dibromo-4-chlorobenzene which is the other possible isomer formed in the bromination. The predominance of the 1,3-dibromo-4-chlorobenzene would be expected as this compound has one chlorine and one bromine atom ortho to each other while the other isomer had two adjacent bromine atoms and due to the smaller covalent radius of the chlorine atom the former arrangement would be preferred on a steric basis. There is no previous record of the preparation of this compound by direct bromination in the literature although Hurtley[196] prepared both of the isomers mentioned above from suitable anilines by diazotization processes. The physical constants recorded in his article for

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*This material can best be obtained from the mother liquors from the commercial preparation of 1-bromo-4-chlorobenzene.

1,3-dibromo-4-chlorobenzene were: m.p. 27°C., b.p. 139°/41 mm. The recorded boiling point does not agree with that found, but it is inconsistent with that given by Hurtley for the other isomer so that it is probably in error. The constants given[196] for 1,2-dibromo-4-chlorobenzene were: m.p. 35.5°C., b.p. 121°C./19 mm.

The total moles of bromine used in both brominations was 11.51 moles. The yield of 4.0 moles of 1-bromo-4-chlorobenzene accounted for 4.0 moles of bromine while the 1.71 moles of 1,3-dibromo-4-chlorobenzene required 3.42 moles of bromine for its formation and the 0.432 mole of 1,2,4-tribromo-5-chlorobenzene isolated consumed 1.296 moles of bromine. Thus, 8.72 moles of bromine can be accounted for in purified products and the balance (2.79 moles) can be attributed to handling losses such as sublimation and the rest was unpurified mixed fractions from the final fractional distillations.

The Preparation of 1-Bromo-2-Chlorobenzene

This material was prepared as an intermediate, for condensation with thiophenols, by the process of selective debromination.[195] Six separate reductinns were made and the crude products from all the reductions were combined and processed in a single distillation.

A typical reduction consisted of 137 g. (0.506 mole) of 1,3-dibromo-4-chlorobenzene (prepared by the direct bromination of chlorobenzene), 46 g. (0.56 mole) of sodium acetate, 1 g. of 5% palladium on charcoal, and 85 ml. of 95% ethanol. This mixture was placed in a Parr hydrogenator bottle and shaken under hydrogen pressure. A pressure drop of 37 pounds of hydrogen pressure was required for the reduction. The catalyst was removed by filtration on a sintered glass suction funnel and after six of these reductions were carried out the filtrates were combined and the solvent removed by distillation at atmospheric pressure. The residue was fractionated under vacuum to obtain 58 g. (0.52 mole) of chlorobenzene, 302 g. (1.60 moles) of 1-bromo-2-chlorobenzene and 146 g. (0.54 mole) of recovered 1,3-dibromo-4-chlorobenzene. The product had a refractive index (n_D^{25}) of 1.5784 and Philip[197] records that of 1-bromo-2-chlorobenzene as 1.5786. The yield of 1-bromo-2-chlorobenzene was 64% based on the amount of starting material which was consumed in the reaction. Examination of the infra-red spectrum of the product showed a strong ortho band at 13.35 microns with a trace of meta substitution at 12.95 microns and a carbon-bromine peak at 13.95 microns. This material was subsequently interracted with potassium thiophenate to give 2-chlorophenyl phenyl sulfide which on oxidation gave a solid sulfone. This material had the same melting point as 2-chlorophenyl phenyl sulfone prepared by another method described in the literature.[8]

The Preparation of 1-Bromo-2,5-Dichlorobenzene

This material was synthesized for condensation and coupling reactions since it is not readily available commercially. A five-liter, three-neck, round-bottom flask was equipped for the bromination and charged with two liters of carbon tetrachloride, 738 g. (5.0 moles) of 1,4-dichlorobenzene, and 10 g. of sublimed ferric chloride. The reaction mixture was warmed to 60°C. and bromine addition was started. Since the rate of hydrogen bromide evolution was very slow an additional 20 g. of ferric chloride was added with negligible results and the subsequent addition of 5 g. of iodine likewise had no effect. At this point 200 g. (1.25 moles) of bromine had been added and still the rate of hydrogen bromide evolution was very slow. At this juncture 10 g. of anhydrous aluminum chloride was added and rapid hydrogen bromide evolution was achieved. It had been hoped to avoid the use of such a vigorous catalyst since it was known that it favored poly substitution. A total of 800 g. (5.0 moles) of bromine was added over a period of five hours after which the reaction mixture was stirred for five hours at 60°C. and then at its reflux temperature for another hour. The mixture was cooled and the unreacted bromine was destroyed with aqueous sodium thiosulfate. The solvent layer was separated and washed consecutively with bicarbonate solution and water and the solvent removed by distillation at atmospheric pressure. The unreacted para-dichlorobenzene was removed using a distillation set up with a large bore vacuum take off, in order to avoid plugging of the vacuum line due to sublimation. Then a crude cut of the monobromodichlorobenzene was made (b.p. 60-70°C./1.5 mm.) after which the column was removed and the dibromocompound was sublimed over at 30 mm. pressure using a distillation head as a short path column. The dibromodichlorobenzene was recrystallized from ehtanol to obtain 193 g. (0.734 mole) of a white crystalline solid melting at 149-150°C. The infra-red spectrum of this material (see Figure 59) showed a single substitution peak at 11.43 microns which is characteristic of 1,2,4,5 substitution. The material therefore must be 1,4-dibromo-2,5-dichlorobenzene since the two chlorines were originally para to each other. This compound had previously been prepared by Wheeler and MacFarland[198] who characterized it as the dibromo compound melting at 148°C. but they were unable to assign its structure definitely. There was a 35 g. residue in the distillation flask which did not sublime which probably contained tribromodichlorobenzene but no effort was made to isolate this material.

The crude monobromo compound was redistilled to obtain 450 g. (1.97 moles, 39.6% yield) of purified product boiling at 64°C./1.5 mm. or 121°C./26 mm. (n_D^{25} = 1.5968 on supercooled liquid). On standing at room temperature, overnight, the oil crystallized to a solid melting at 34-6°C. Recrystallization from ethanol gave a white crystalline solid melting at 35.5-6°C. (Literature[199] m.p. 35°C.). No previous record was found of the preparation of this compound by direct bromination although there were several preparations in the literature[199,196] from aniline derivatives.

Bis(3,4-Dichlorophenyl) Thiosulfonate

This compound was prepared according to the method of Vinkler and Klivenyi[191] for the purpose of checking the structure of a by-product obtained in the lithium aluminum hydride reduction of 3,4-dichlorobenzenesulfonyl chloride. This type of intermediate has recently been reported by Lehto and Shirley for the first time[135] in a metal hydride reduction although it had previously been postulated by Field and Grunwald[132] as an intermediate in sulfonyl chloride reductions.

The quantity, 24.5 g. (0.1 mole) of 3,4-dichlorobenzenesulfonyl chloride, 300 ml. of dry ether, and 9.8 g. of zinc dust were placed in a one-liter flask equipped with a good stirrer and a reflux condenser. A 64 ml. quantity of concentrated hydrochloric acid was then added dropwise to the refluxing reaction mixture over a two hour period. Stirring was continued overnight and still a little zinc remained which necessitated heating the reaction mixture at its reflux temperature an additional two hours. The solids were removed by filtration and the ether layer separated and washed successively with sodium carbonate solution and water. The ether layer was dried in contact with anhydrous sodium sulfate, filtered, and the ether removed by evaporation. The solid residue was recrystallized from methanol to give 10.5 g. (0.027 moles, 55.5% of theory) of white solid melting at 125-6°C. A second recrystallization from absolute ethanol raised the melting point of the product to 126.5-127°C.

Anal. Calc'd for $C_{12}H_6Cl_4O_2S_2$: C, 37.13; H, 1.55; Cl, 36.54;
S, 16.52

Found: C, 37.04; H, 1.62; Cl, 36.32; S, 16.26

This compound has not previously been recorded in the literature.

2,4,5-Trichlorophenyl-3',4'-Dichlorophenyl Sulfide

Since the chlorination of bis(3,4-dichlorophenyl) sulfide had been achieved accidentally when attempting a ring closure reaction with sulfuryl chloride (SO_2Cl_2) it was desirable to study this reaction further as a preparative reaction since one can visualize the potential preparation of many symmetrical and unsymmetrical diphenyl sulfide isomers starting with a known sulfide. The unsymmetrical isomers in particular are not available by other methods.

A one liter flask was equipped with a stirrer, thermometer, dropping funnel and condenser exit, and 49 g. (0.15 mole) of bis(3,4-dichlorophenyl) sulfide, 15.0 g. (0.11 mole) of anhydrous aluminum chloride and 300 ml. of ethylene dichloride were placed in it. Sulfuryl chloride (20.5 g., 0.15 mole) was added to the reaction mixture without cooling over a two hour period. The reaction mixture was then refluxed for one hour and quenched in cold dilute hydrochloric acid. The ethylene dichloride layer was separated and washed and 250 ml. of solvent were removed by vacuum distillation. The residual material was chilled and a solid precipitated. This was filtered and washed with methanol to obtain solid melting at 135-140°C. It was recrystallized from methyl ethyl ketone to obtain 6 g. (0.015 mole) of bis(2,4-5-trichlorophenyl) sulfide melting at 148-150°C. (Highly purified material melts at 149-150°C.). The residues were collected and the solvents were removed by vacuum distillation. The residual material was then carefully distilled through a 20 cm. vigreux column to obtain four fractions. Fraction I consisted of 4 g. of crude bis(3,4-dichlorophenyl) sulfide (b.p. 210-230°C./6 mm.) Fraction II contained 30 g. of crude pentachlorodiphenyl sulfide which was recrystallized from acetone to obtain 23 g. (0.065 mole, 43% yield) of 2,4,5-trichlorophenyl-3',4'-dichlorophenyl sulfide melting at 84-5°C. (Highly purified material melts at 85-85.5°C.) Fraction III was dissolved in hot methyl ethyl ketone and upon cooling to room temperature precipitated a very small crop of material melting at 197-215°C. There was possibly the ring closure product but the amount of the material was so small that it could not be purified and an infra-red spectra was not obtained. Fraction IV was shown to be impure bis(2,4,5-trichlorophenyl) sulfide by the usual procedure.

2-Thienyl-2,4-Dinitrophenyl Sulfide

The initial attempt to prepare this sulfide resulted in failure due to the use of excess caustic. A review of the earlier work of Turner, Bost and Norton[34] employing 2,4-dinitrochlorobenzene as a characterizing agent indicated that this error resulted in the formation of brown colored insoluble materials instead of the desired product. This error was corrected and an excess of the thiol was used as they had directed and no further difficulty was experienced. The quantity, 1.75 g. (0.086 mole) of 2,4-dinitrochlorobenzene was placed in a 200 ml. round bottom flask with 20 ml. of ethanol. A solution containing 0.34 g. (0.086 mole) of sodium hydroxide dissolved in 3 ml. of water was prepared and added to 2.0 g. (0.172 mole) of 2-thiophenethiol (obtained as a decomposition product in the condensation of thiophene with sulfur dichloride) dissolved in 30 ml. of ethanol. The latter ethanol solution was added to the ethanol solution of the dinitro compound while shaking the reaction flask.

There was no evident heat of reaction and although the solid dinitrochlorobenzene oiled out of solution there was no formation of a precipitate. The flask contents were then warmed gradually and at 40°C. it was evident that sulfide formation was taking place since a bright yellow precipitate commenced to separate from solution. The solution was heated to it's reflux temperature using a total reflux condenser and the addition of 60 ml. of ethanol was necessary to effect solution of the sulfide. The reaction mixture was then treated with Darco, filtered and the solution set aside overnight. Bright yellow crystals formed which were filtered and dried in a drying pistol under vacuum. The sulfide weighed 1.9 g. (0.067 mole, 79% yield based on the dinitrochloro benzene) and melted at 118-119°C. An additional recrystallization of the sulfide from ethanol raised the melting point to 119-119.5°C. Bost, Turner and Norton[34] reported 119°C. for 2-thienyl-2,4-dinitrophenyl sulfide. The sulfide was then oxidized by their procedure using potassium permanganate in acetic acid to obtain 2-thienyl-2,4-dinitrophenyl sulfone in 75% yield melting at 142-3°C. Literature value[34] m.p. 143°C.

1,1-Bis(p-Chlorophenyl) Ethylene

Method A. The quantities, 450 g. (4.0 moles) of chlorobenzene and 80 g. (0.60 mole) of anhydrous aluminum chloride, were placed in a two-liter three-neck round-bottom flask suitably equipped for the condensation reaction. The reaction flask was placed in a cold water bath and 48.5 g. (0.50 mole) of vinylidene chloride (previously chilled in a dry ice-acetone bath to prevent evaporation) was added to the reaction flask during a two hour period while holding the temperature of the flask at 25°C. Hydrogen chloride evolution was a little slow when the reaction temperature was lowered further and higher temperatures caused excessive decomposition with attendent tar formation. The reaction mixture was stirred for fifteen minutes and then quenched by pouring it into cold dilute hydrochloric acid. The oily layer was separated after the metal complex had been completely hydrolyzed and was washed consecutively with dilute hydrochloric and water. It was then distilled under vacuum to remove the unreacted chlorobenzene. The residue was vacuum distilled to obtain 92 g. (0.37 mole, 75% yield) of mixed isomers (b.p. 150-153°C./10 mm.) and 46 g. of a black tarry residue. The oil was chilled by overnight storage in a refrigerator to crystallize the 1,1-bis(p-chlorophenyl) ethylene. This was recovered by filtration from the oil on a Buchner funnel and recrystallized from 95% ethanol to obtain 48.5 g. (0.19 mole, 53% yield) of 1,1-bis(p-chlorophenyl) ethylene melting at 85-6°C. (Literature value[200] m.p. 84-5°C.). No attempt was made to isolate and identify the other isomers in the oil since the di-para isomer was the most suitable case to employ in the ring closure experiments.

Method B. The method of Barry and Boyer[201] was also employed for the preparation of 1,1-bis(p-chlorophenyl) ethylene since 1,1,1-trichloroethane was more readily available than the low boiling vinylidene chloride. A two-liter, three-neck, round-bottom flask was equipped with a stirrer, thermometer, dropping funnel and a hydrogen chloride scrubber. A 225.0 g. (2.0 mole) quantity of chlorobenzene and 66.5 g. (0.5 mole) of anhydrous aluminum chloride were added to the reaction flask. The quantity, 53.0 g. (0.4 mole) of 1,1,1-trichloroethane, was added to the halobenzene-aluminum halide mixture during a two hour period and copius evolution of hydrogen chloride occurred. The reaction was initiated at room temperature and then cooled to 5°C. The reaction mixture was stirred for two hours following the final addition of the trichloroethane and then it was hydrolyzed by pouring it into cold dilute hydrochloric acid and stirring it vigorously. The product isolation procedure used was the same as that employed in Method A above to obtain 59.5 g. (0.24 mole, 62% yield) of an oil which partially crystallized on chilling to obtain 35.0 g. (0.14 mole, 59% yield) of 1,1-bis(p-chlorophenyl) ethylene melting at 85-6°C. (Literature value[201] m.p. 86°C.

1,1-Bis(p-Chlorophenyl) Ethane

This compound had previously been prepared[200] in a 62% yield by the reduction of the corresponding ethylene derivative using platinum black as a hydrogenation catalyst.

The quantities, 50.0 g. (0.20 mole) of 1,1-bis(p-chlorophenyl) ethylene and 200 ml. of acetone were placed in a Parr hydrogenator bottle and 2.0 g. of moist commercial Rainey nickel (Davidson or Girdler) was added. The hydrogenation bottle was placed in the Parr shaker, saturated with hydrogen (4 atms.) and shaken until a 15 pound pressure drop (0.20 mole) had occurred. The nickel catalyst was removed by filtration taking great care to keep the catalyst wet as it is extremely pyrophoric. The acetone was removed in vacuo and the oil which remained slowly solidified at room temperature. It was recrystallized from ethanol to obtain 44.0 g. (0.17 mole, 88% yield) of 1,1-bis(p-chlorophenyl) ethane melting at 54.5-55.5°C. (Literature value[200] m.p. 54-55°C.).

Potassium Ethyl Xanthate

A solution of potassium ethoxide was prepared by adding 600 g. (9.2 moles, 85%) potassium hydroxide pellets to 2500 ml. of absolute ethanol and heating the mixture at its reflux temperature for an hour. It was then cooled to room temperature, filtered to remove insoluble material, and the filtrate transferred to a five-liter, three-neck, round-bottom flask, equipped with a stirred, thermometer, and a dropping funnel. Carbon disulfide (700 g., 9.2 moles) was added dropwise to the vigorously stirred potassium ethoxide solution. The reaction mixture was stirred for an hour following the addition of the disulfide, cooled to room temperature in an ice water bath, and filtered on a Buchner to recover the potassium ethyl xanthate. The solid xanthate was slurried in ether to remove the orange coloration, vacuum filtered as dry as possible, and finally dried thoroughly in a vacuum dessicator. The yield, as a creamy yellow solid, was 1,056 g. (6.6 moles) a 71.7% yield.

This material was used for the preparation of substituted benzenethiols by reaction with substituted benzenediazonium chlorides and subsequent reduction of that product to the thiol.

3,4-Dichlorobenzenesulfonyl Chloride

Chlorosulfonic acid (962 g., 8.25 moles) was placed in a three-liter, three-neck, round-bottom flask suitably equipped and 588 g. (4.0 moles, 99+% purity) o-dichlorobenzene was added portionwise to the stirred acid over a period of four hours while holding the reaction temperature at 30°C. with a water bath. Stirring was continued four hours after the complete addition of o-dichlorobenzene and then the reaction mixture poured onto ice. A liter of carbon tetrachloride was added and the mixture was filtered to remove the insoluble sulfone. The carbon tetrachloride layer was separated, washed with dilute sodium carbonate solution, then with water, after which it was dried overnight in contact with anhydrous sodium sulfate, and the carbon tetrachloride removed under reduced pressure. The residue was fractionated to give 365 g. (1.49 moles, 37% yield based on o-dichlorobenzene) of the 3,4-dichlorobenzenesulfonyl chloride boiling at $125\text{-}7^{\circ}$C./1 mm. The boiling point of this material has not previously been reported in the literature although its melting point of $22\text{-}3^{\circ}$C. has been recorded. An infra-red spectrum determined on the purified liquid indicated exclusive 1,2,4 substitution. Only 30 ml. of o-dichlorobenzene was recovered indicating that the major product, lost in the water solution during the washing process, was 3,4-dichlorobenzenesulfonic acid. Since a 2:1 ratio of chlorosulfonic acid was used it would seem that 30°C. was not high enough to convert the sulfonic acid to the sulfonyl chloride. The literature shows a 58% yield[101] of 4-chlorobenzenesulfonyl chloride at 25°C., a 75% yield[130] of benzenesulfonyl chloride at 25°C, and an 85% crude yield of 2,5-dichlorobenzenesulfonyl chloride at 150°C. Quite possibly a longer contact time at 30°C., a larger excess of chlorosulfonic acid, or an increase in reaction temperature with possible sacrifice in exclusive orientation would increase the yield.

The carbon tetrachloride insoluble material and the higher boiling fraction from the distillation were recrystallized from ethylene dichloride to give 42 g. (0.118 mole) of bis(3,4-dichlorophenyl) sulfone melting at 174-5°C. Literature value,[8] m.p. 173-4°C.

SUMMARY

1. A large number of aromatic sulfides have been prepared by the Friedel Crafts condensation of aromatic compounds with sulfur dichloride. The structures of these compounds have been established by synthesis, preparation of oxidation derivatives and by a novel substitution identification system based on a comparison of the infra-red spectra of the sulfides and their oxidation products.

2. The Friedel Crafts condensation of thionyl chloride with benzene derivatives has been studied and it was found to be a superior preparative method for the formation of the sulfoxide (by direct condensation) and the sulfide (via reduction) linkage although it has limitations when applied to deactivated compounds.

3. A comparison of the usefulness of sulfur dichloride and sulfur monochloride in the Friedel Crafts condensations of aromatics has been made.

4. Ring closure experiments utilizing the various sulfur chlorides and oxychlorides have been studied. Various derivatives of thianthrene as well as phenoxathiin and thiaxanthene have been prepared.

5. A method for the preparation of diphenyl sulfides by fusion condensation of alkali thiophenates with "psuedo activated" halobenzenes has been studied.

6. The preparation of aromatic thiols via a recently published method consisting of the lithium aluminum hydride reduction method of xanthate esters and benzene sulfonyl chlorides was made. Supporting evidence of the mechanism of sulfonyl chloride reduction was found.

APPENDIX

A. Reagents

Investigators interested in the chemistry of sulfur halides and oxyhalides will find the commercial literature on these reagents of great value. Notable among these are the Hooker Electrochemical Co. Data Sheets No. 718-C ($SOCl_2$), 760-A (S_2Cl_2), 759 (SCl_2), 717-B (SO_2Cl_2) and Bulletin 330 (SO_2Cl_2) and 328-A (Chlorinating agents) as well as Stauffer Chemical Co. Bulletin 7561950 (S_2Cl_2 and SCl_2).

An intimate working relation of reactions 1-6 is necessary to understand the interrelationships between the various sulfur compounds[202,172,203,27]

$$\mathrm{SOCl_2} \rightleftharpoons \mathrm{SCl_4} + \mathrm{SO_2} \tag{1}$$

$$\mathrm{SCl_4} \rightleftharpoons \mathrm{SCl_2} + \mathrm{Cl_2} \tag{2}$$

$$\mathrm{2SCl_2} \rightleftharpoons \mathrm{S_2Cl_2} + \mathrm{Cl_2} \tag{3}$$

$$\mathrm{S_2Cl_2} \rightleftharpoons \mathrm{SCl_2} + \mathrm{S^o} \tag{4}$$

$$\mathrm{S^o} + \mathrm{Cl_2} \rightleftharpoons \mathrm{S_2Cl_2} \tag{5}$$

$$\mathrm{SO_2Cl_2} \rightleftharpoons \mathrm{SO_2} + \mathrm{Cl_2} \tag{6}$$

Thionyl chloride via reactions 1,2,3 and 4 can act as a chlorinating agent for an aromatic nuclei such as phenoxathiin on refluxing.

Obviously both sulfur monochloride and dichloride can also act as chlorinating agents (reactions 3 and 5) and their catalytic activity in chlorinating mixture has been well established. Although sulfur monochloride is a rather stable compound (b.p. 138°C.), sulfur dichloride is essentially an equilibrium mixture whose composition is governed by reactions 2,3,4, and 5. The equilibrium mixture shows heavy decomposition at 54°C. but even at low temperatures there is a constant chlorine pressure in a closed system. Sulfur dichloride in an improperly closed system or container gradually builds up a fair concentration of sulfur monochloride due to the escape of gaseous chlorine from the system. It is inadvisable to fill a container of sulfur dichloride completely with the liquid dichloride since if the container becomes slightly warm it will erupt on opening due to supersaturation with chlorine. Caution should be exercised on warm days and care should be taken to keep containers of this reagent away from any heat source such as steam lines, etc.

B. A Discussion of Work-up Procedures

In condensation reactions using sulfur monochloride, sulfur dichloride and thionyl chloride it is a common occurrence to have "high melting" solids precipitate after the reaction mixture is quenched. Separation of the solid at this point frequently allows easy separation of a nearly pure isomer. In some cases (for example with p-dichlorobenzene) this solid is polymeric but this can usually be determined readily by its melting and solubility characteristics.

In most cases, however, it is necessary to remove the solvent and/or excess reactant and make a preliminary distillation of the residue using a "short path" column. This separates the polymeric and decomposable materials which interfere with the fractionation of products. The insertion into the vacuum line of a tower filled with alternate layers of sodium (or potassium) hydroxide pellets and anhydrous calcium chloride (to absorb the water formed and prevent caking of the caustic) is very effective in absorbing the gaseous decomposition products (HCl and H_2S) which are formed. Since decomposable intermediates appear to be present in almost all crude products, this step without this precaution, can be extremely frustrating to an investigator who is not experienced in this field. Once these unstable intermediates are removed one is amazed at the thermal stability of the products.

Due to the high boiling points (180-250°C./3 mm.) of aromatic sulfide and sulfoxide products it is usually necessary to use asbestos wrappings on the columns and asbestos cloth to cover the distillation flask since otherwise heat losses would make distillation of these products impossible without this aid. Resistance wiring may also be used to compensate for heat losses and to keep solids from freezing and plugging the fraction cutter. The use of a flame to warm the equipment prior to thermal equilibrium is necessary in the absence of wiring. The use of a thermometer in the distillation flask is almost mandatory since the internal temperature toward the last of these distillations comes close to the softening point of the glass.

C. Infra-red Spectra Interpretation

I. Introduction

A large section of 62 infra-red spectra has been included in this appendix for the purpose of exhibiting some of the spectral evidence cited for structure proof and as an aid to future investigators in this area. The first two Sections (I and II) are spectra of reference compounds, namely, the chlorinated benzenes and the dichlorotoluenes. The former were included since their spectra are the most analogous to that of the chlorinated diphenyl sulfides, sulfoxides and sulfones which were the types of products obtained in the present study. The dichlorotoluenes were included since they illustrate the variation of spectra when the same groups occupy different positions in the same substitution type. Section III contains the spectra of the various diphenyl sulfides, sulfoxides and sulfones arranged in the order of increasing degree of substitution for easy comparison of the oxidation states. The section on thianthrenes (IV) is also arranged in an analogous manner. The miscellaneous section (V) contains spectra of compounds not directly classifyable in the above arrangement. Most of the spectra were made at the standard concentration of 0.065 molar in order to facilitate comparison of the spectra. These spectra were scanned using a "Perkin Elmer (Model 21) Recording Infra-red Spectrophotometer" with a 0.5 mm. thickness solution cell. Some of the more insoluble materials were scanned using saturated solutions at concentrations lower than

0.065 molar. All of the spectra in the appendix section were made using carbon disulfide solutions with carbon disulfide in the reference cell. In the early part of the spectra work two solvents were used in order to obtain a complete spectrum as is done in most commercial laboratories today. Carbon tetrachloride was used from 2-715 microns and carbon disulfide from 7.5-14.5 microns and the pertinent solvent was used in the reference cell. The two halves were matched into a continuous spectrum by a slight adjustment of the balance knob. However, since this technique required the preparation of two solutions it was abandoned as soon as it was apparent that the region from 6-7 microns (which is lost in the carbon disulfide spectrum due to total absorption by the solvent) was not pertinent to the problem at hand.

An attempt was made to prepare spectra of many of the more insoluble compounds (sulfone analogs) using the nujol mull technique[204] but poor spectra resulted due to low concentrations and light scattering. However, in the last phases of the work equipment for the potassium bromide pellet technique[169,170,171,189,6] became available and it was found that this technique was highly satisfactory for work with solid material and is particularly well suited for very insoluble crystalline and amorphous materials. None of the spectra from the last two techniques appear in this appendix section, however, due to space limitations.

II. Hydrogen Out of Plane Bending Vibrations and Their Relation to Aromatic Substitution

Infra-red spectroscopy has become a vital tool to the organic chemist. Inexpensive laboratory instruments have recently become available and the technique of using the instrument can be readily mastered under the guidance of a fellow chemist who is familiar with the instrument. Many readable references[204,205,206,207,208,209,210,211,212,213] are available to explain the origin of spectra, sample preparation and interpretation. A summary of all current infra-red work may be found in the bi-annual review by Gore in "Analytical Chemistry." Probably the most helpful item to the novice and the professional are the simplified interpretation charts showing the range usually exhibited by the various types of absorption. The most frequent uses of the infra-red absorption spectra are in the identification of functional groups and compounds by the so-called "finger print method." Although these techniques were useful in this investigation for the identification of the thiol grouping and for the comparison of identical samples the IR method was much more valuable in the location of compounds during fractional crystallizations and as a means of detecting aromatic substitution. The method of locating isomers or other mixed materials has been used by Bard, Perro and Rees[214] and its use is discussed in a number of the experimental sections.

The basis for the detection of aromatic substitution is discussed by Bellamy,[205] Colthup[215] and Randle and Whiffen.[216] The method is based upon the characteristic vibrations of the carbon hydrogen bond. These vibrations have been classified into hydrogen stretching, hydrogen in-plane bending and hydrogen out of plane deformation vibrations. Hydrogen stretching vibrations occur along the axis of the C-H bond and the amplitude of the absorption peak (3.25 microns) for aromatic ring hydrogens is an indication of the degree of substitution on the nucleus but shows nothing of the position of that substitution. Hydrogen (in plane) bending vibrations show absorption in the 6-7.5 micron region and although these are useful for the identification of aliphatic compounds or side chains they are of no use in identifying aromatic substitution. The out of plane hydrogen bending vibrations (i.e., hydrogen wagging, twisting and rocking) show characteristic absorption depending upon how many hydrogens appear adjacent to each other on an aromatic ring. Overtones from these vibrations appear in the 5-6 micron range. Bellamy[205] gives a chart on page 90 showing the characteristic patterns for each type of substitution in that region. Although this is a useful region, if the sample concentration is high enough, it did not find much use in this investigation since the saturation level of many of the compounds was too low. The main absorption peaks from the hydrogen out of plane bending vibrations occur in the 8-15 micron region. Early investigators have shown[205] that aromatic substitution can be characterized by absorption in the 8-9 and 11-15 micron region although the patterns exhibited in the 8-9 micron region show more variation and are not as characteristic as those in the 11-15 micron region. Compared to the absorptions in 5-6 micron region these bands are very strong and have been used for quantitative work.[205] The 11-15 micron region was used exclusively in this investigation and the others will not be referred to again in this discussion. The absorption peaks in this region are essentially independent of the type of substitution and may be attributed to the number of hydrogens adjacent to each other on the aromatic ring. The various substitution types may exhibit one or more of these peaks depending upon the combinations of these hydrogens found on the ring. For example, in 1, 2,4 substitution there are two groups of hydrogens found on the ring, namely, one single and two adjacent hydrogens. The various hydrogen groups and the usual absorption wavelength of the hydrogen out of plane bending vibrations are as follows:

Type	Wavelength in Microns
Single hydrogen	11.3-12.2
Two adjacent hydrogens	12.0-12.5
Three adjacent hydrogens	12.7-13.2
Four adjacent hydrogens	13.3-13.5
Five adjacent hydrogens	13.2-13.5
Six adjacent hydrogens	14.9

When these combinations appear on the benzene ring we have the bands for the various substitution types as follows:

Type of Benzene Substitution	Wavelength in Microns
Benzene (6 adjacent)	14.9
Mono (5 adjacent)	13.2-13.5 and 14.5
Ortho (4 adjacent)	13.3-13.5
Meta (1 single and 3 adjacent)	11.4-11.7 and 12.7-13.0
Para (2 adjacent)	12.0-12.3
1,2,4 (1 single and 2 adjacent)	11.5 and 12.3-12.5
1,3,5 (3 single)	11.8-12.1
1,2,3 (3 adjacent)	12.7-13.2
1,2,3,4 (2 single)	11.3-12.2
1,2,3,5 (2 single)	11.8
1,2,4,5 (2 single)	11.4
Penta (1 single)	11.5-11.7

Examples of each of these substitution types are found in Section D of the appendix (Figures 1-12) for each of the chlorinated benzene isomers which were used for reference types in this investigation. Analogous substitution types as well as mixed types (unsymmetrical) are found in the section on chlorinated diphenyl sulfides. The same substitution patterns still hold for benzene like aromatics such as thianthrene, phenoxathiin and phenothiazine which show ortho type substitution (4 adjacent hydrogens) at 13.4, 13.35 and 13.50 microns respectively. These same patterns are also shown in linear sulfides such as are exhibited in Figures 61, 62, 63, and 64. Molecules which have multiple substitution are not as likely to be quite as consistent in their patterns as cases of lower substitution and this is particularly true in cases where the substituents consist of more than one type even when they have the same substitution (see Figures 13 and 14).

III. The Effect of Oxidation State on the Substitution Spectra of Aromatic Sulfides

The infra-red spectra in appendix D have been arranged so that the sulfur compounds appear in the order of increasing degree of substitution and oxidation state. Examination of the spectra which appear in Part III and IV of Section D shows that the bivalent diphenyl sulfides and thianthrenes exhibit normal substitution spectra as discussed in the previous section on hydrogen out of plane bending vibrations. There are minor differences in the absorption peaks of the sulfur compounds as compared to the reference chlorinated benzenes in Part I. A typical example of this is found in a comparison of the spectra of 1,2,4,5-tetrachlorobenzene (Figure 8) and bis(2,4,5-trichlorophenyl) sulfide (Figure 42). Both of these compounds are 1,2,4,5 tetrasubstituted and should show single hydrogen out of plane bending vibration peaks. In the case of the tetrasubstituted chlorobenzene a single absorption peak due to the two single hydrogens in the molecule is found at 11.38 microns. The sulfide exhibits two peaks at 11.25 and 11.47 microns respectively. These differences in the two substitution patterns may be readily explained by reference to the environment of the two single hydrogens on the ring. In the sulfide case there are indeed two single hydrogens the same as the tetrachlorobenzene but in the benzene case both hydrogens are adjacent to two chlorine groups. The fact that one of the hydrogens on the ring in the sulfide is adjacent to two chlorine groups and one by a chlorine and a sulfide link furnishes sufficiently different environment that each hydrogen in the sulfide case has a different frequency for its out of plane hydrogen bending vibrations leading to two separate absorption peaks in the same general region. Analogously any differences in the absorption peaks in the substitution region between the chlorinated benzenes and the bivalent chlorinated sulfur compounds may be explained by minor environmental effects.

A comparison of the oxides of these sulfur compounds with the analogous bivalent isomer shows that there is increasing complexities of the peaks (splitting) and changes in wavelength. The sulfones frequently showed broad splitting of the substitution peaks (in the 11-15 micron region) with as much as one micron between the divided absorption peaks. Carbon-chlorine peaks were frequently shifted into the substitution region and if they already appeared then their amplitude was increased.

The sulfoxides generally showed little or no peak splitting. Broadening of the peak was usually apparent with some splits as wide as 0.25 microns. Carbon-chlorine peaks when they were present were increased in amplitude.

These effects caused utter confusion in the early period of collecting spectra since it was virtually impossible to tell the substitution of the oxidation products. In unsymmetrical compounds with two substitution types all the absorption peaks were modified. After a sufficient number of the spectra had been collected it was apparent that the oxygens on the sulfur atoms were causing the effects which were noted. It was found in examining the spectra catalog that these shifts could be predicted for a given substitution type. Close examination of the sulfide spectra as compared to the analogous oxidation products (especially the sulfones) revealed that substitution of unknown isomers in which the substitution of the sulfide was not readily apparent could be predicted from a comparison of the spectra of the sulfide and its oxidation products.

The effects noted were particularly apparent where the single hydrogens were adjacent to the sulfide link. In bis(2,4,5-trichlorophenyl) sulfide (Figure 42) where there are two single hydrogens on the benzene ring interaction of the sulfone oxygen with the adjacent single hydrogen depressed the absorption for that hydrogen and shifted the wavelength from 11.25 to 11.10 microns. The other single hydrogen although not depressed at all shifted from 11.47 to 11.35 microns. Carbon-chlorine absorption was shifted into the substitution region as shown by a strong peak at 14.45 microns.

The 2,7-dichlorothianthrene (Figure 52) exhibited normal 1,2,4 type substitution whereas the monoxide (Figure 53) exhibits splitting of both substitution peaks. Examination of the structure shows that one of the single hydrogens and one pair of the two adjacent hydrogens interacts with the sulfoxide whereas the other hydrogens are strategically located so that there is no interaction. This gives separate vibration frequencies for each set of hydrogens leading to four peaks. The tetroxide of this material likewise showed splitting even though there was no difference in interaction of the hydrogens.

A typical example of these effects is found in bis(4-chlorophenyl) sulfide (Figure 25). A strong para substitution peak appears in the spectrum of this compound at 12.25 microns with a weak carbon-chlorine peak at 13.5 microns. The sulfoxide shows a broadening of the para peak and a large increase in the amplitude of the carbon-chlorine peak. The sulfone interaction splits the para peak completely giving two peaks at 12.15 and 13.15 microns respectively while retaining a strong carbon chlorine absorption at 13.45 microns.

The 3,4-dichlorophenyl phenyl sulfide (Figure 23) provides an example of the effect on two types of substitution. The 1,2,4 substitution shows a single hydrogen peak at 11.55 microns and a two adjacent hydrogen peak at 12.35 microns with monosubstitution absorption at 13.5 and 14.5 microns. Conversion to the sulfone (Figure 24) depresses the single hydrogen peak to a nub, leaves the two adjacent hydrogen peak unaffected and splits the monosubstitution peak at 13.30 and 13.00 microns. Unsymmetrical sulfides show less effect than the symmetrical sulfides. For example in bis(3,4-dichlorophenyl) sulfide (Figure 34) the two adjacent hydrogen peak at 12.35 is split at 12.00 and 12.25 microns when converted to the sulfone (Figure 34).

The spectra catalog shows variations of these effects in some degree in all the cases presented and many others were found. It is apparent that some effect between the oxygens on the sulfur linkage and the hydrogens adjacent to them cause modification of the hydrogen out of plane vibrations. Sterically the extra spatial requirements of the oxygen atoms would restrict the out of plane vibrations. Potts[217] found such effects with alkyl benzene. Since larger effects were noted in symmetrical compounds where spatial tolerances would be even closer this would seem to be logical. In addition there may be a form of hydrogen bonding between the oxygens and the adjacent hydrogens which is operative and one could expect that this would increase with increased symmetry and oxidation state if that is true.

These effects were particularly helpful in the examination of the 2,7 and 2,8 dichlorothianthrene. The 2,8 isomer had been questioned by Baw, Bennet and McDonald[4] and since the two materials gave essentially the same 1,2,4 trisubstitution spectra and their tetroxides had melting points within one degree of each other it was necessary to obtain further evidence to show their difference. A spectrum of the tetroxide of each of the materials showed that there was no question that they were different as would be predicted since two different types of hydrogen-oxygen interaction can be seen from their tetroxide structures.

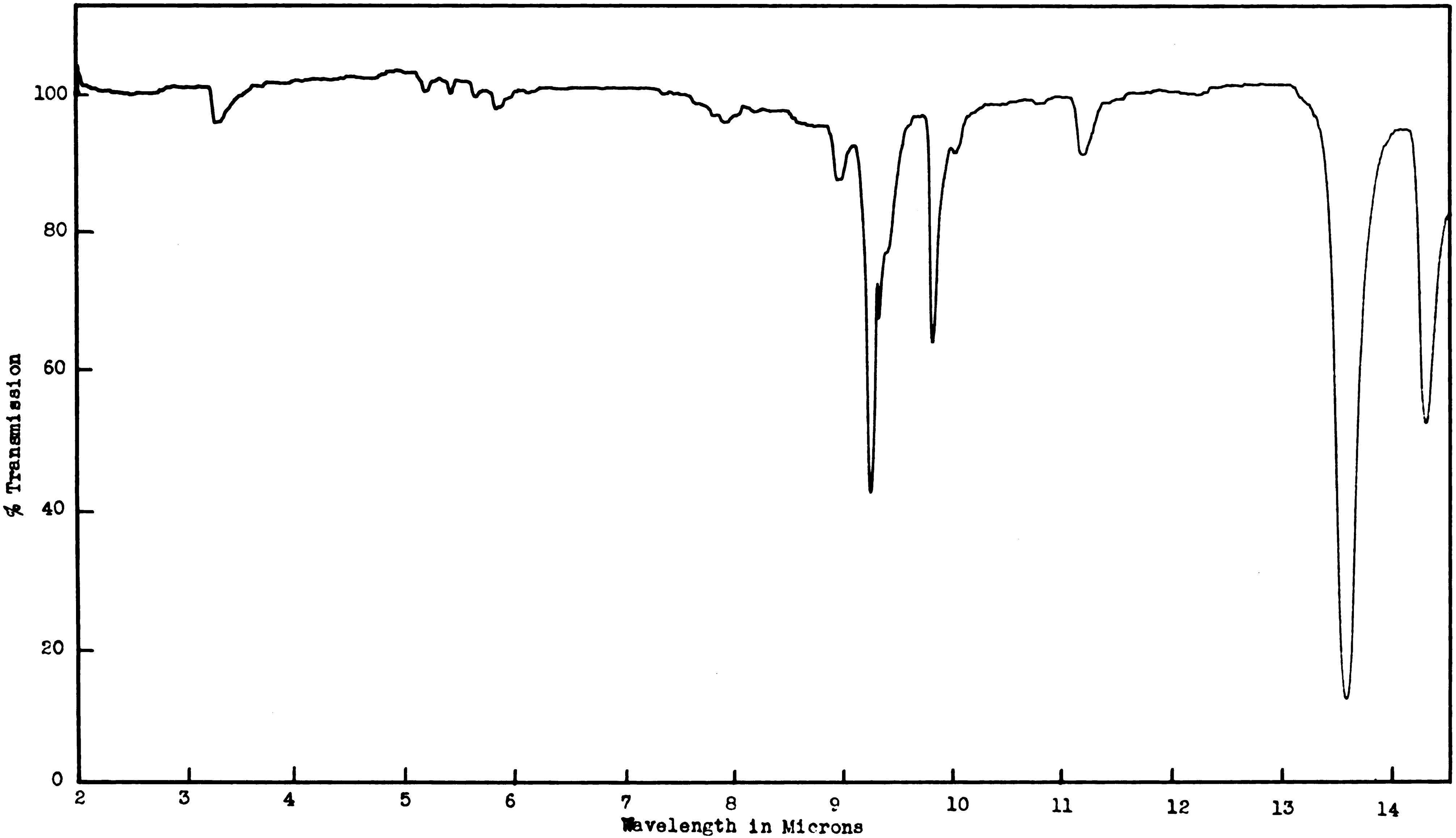

Figure 1. Infra-red Spectrum of Chlorobenzene (0.065 Molar in CS_2)

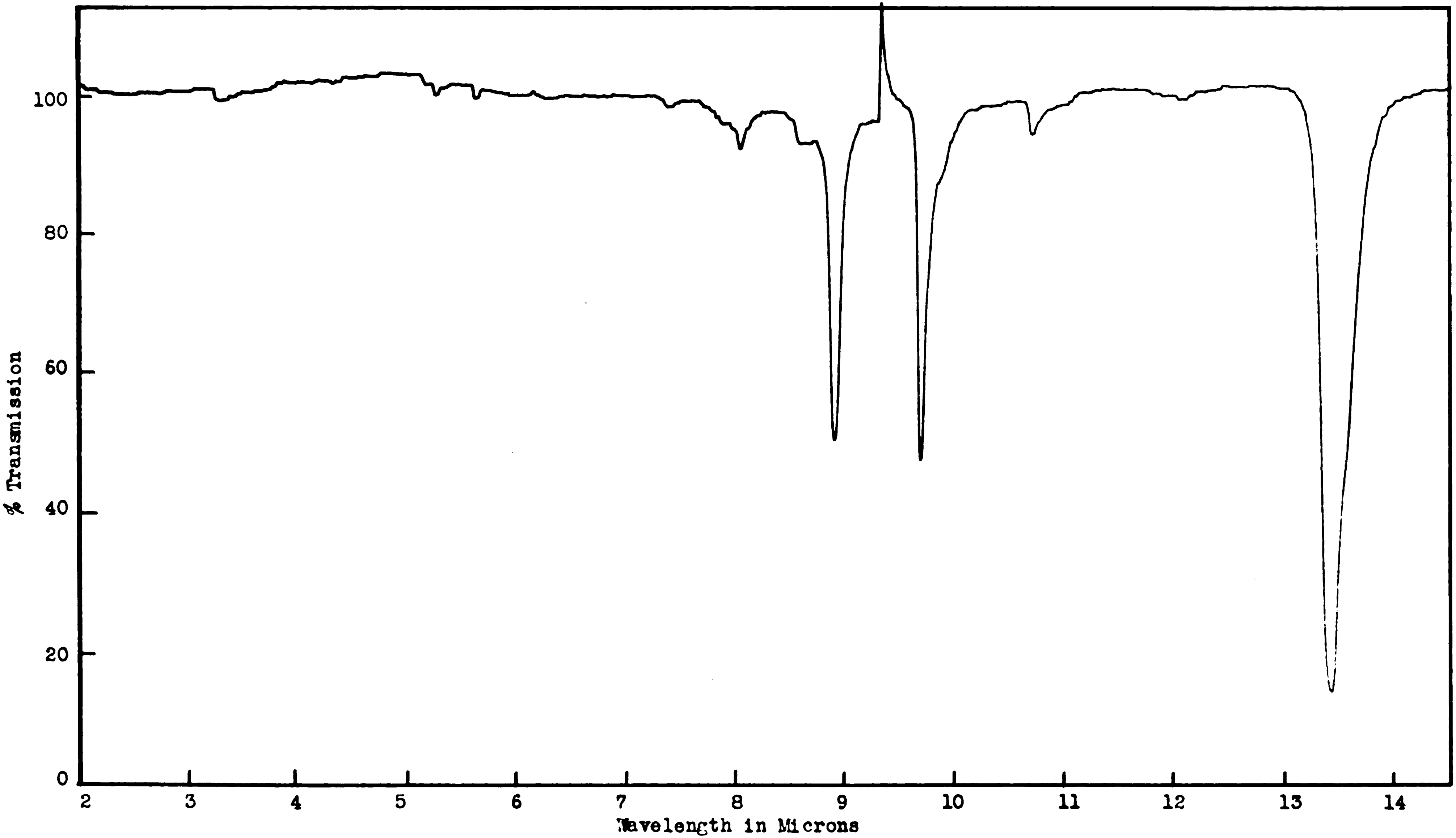

Figure 2. Infra-red Spectrum of o-Dichlorobenzene (0.065 Molar in CS_2)

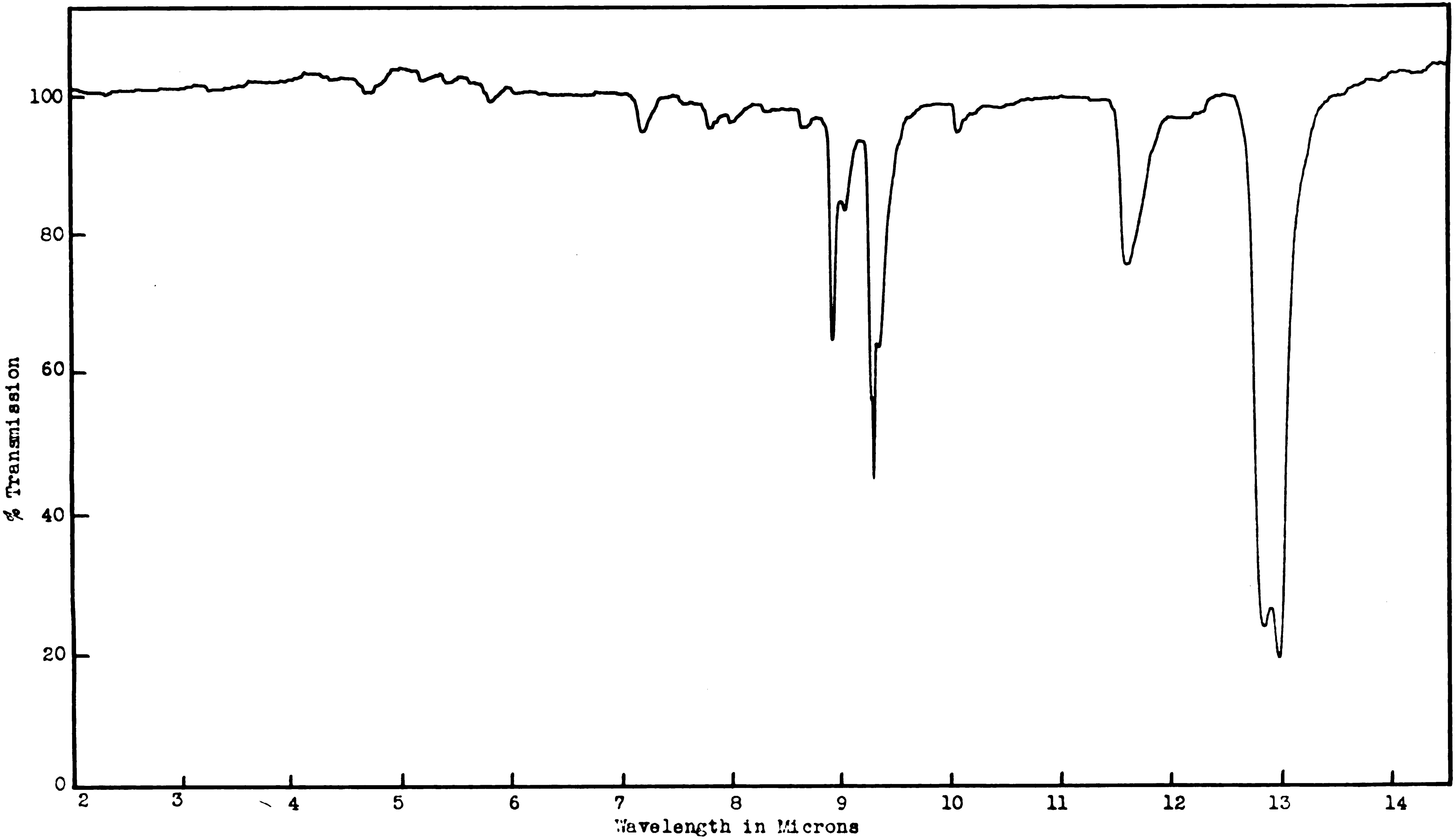

Figure 3. Infra-red Spectrum of m-Dichlorobenzene (0.065 Molar in CS_2)

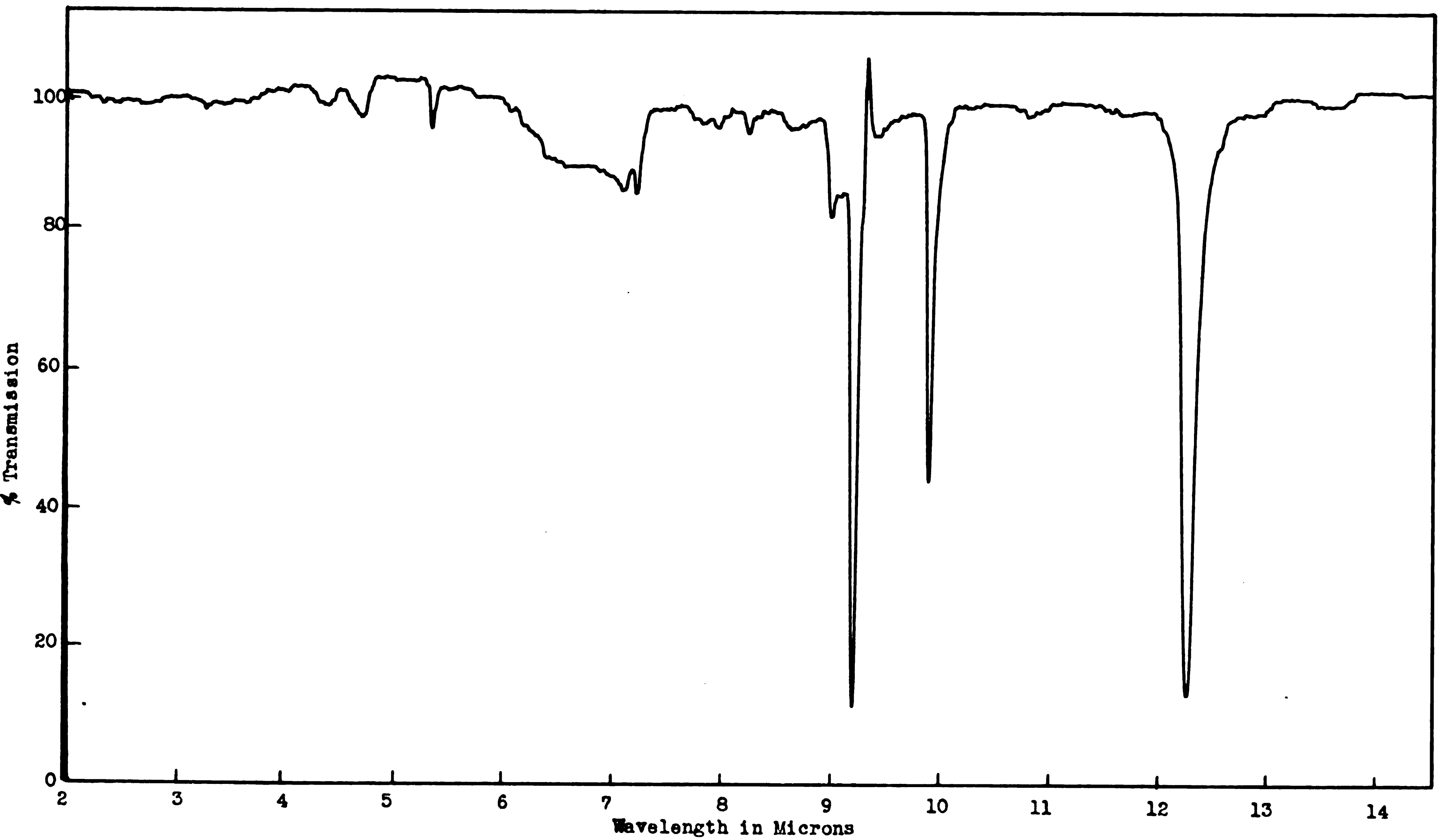

Figure 4. Infra-red Spectrum of 1,4-Dichlorobenzene (0.065 Molar in CS_2)

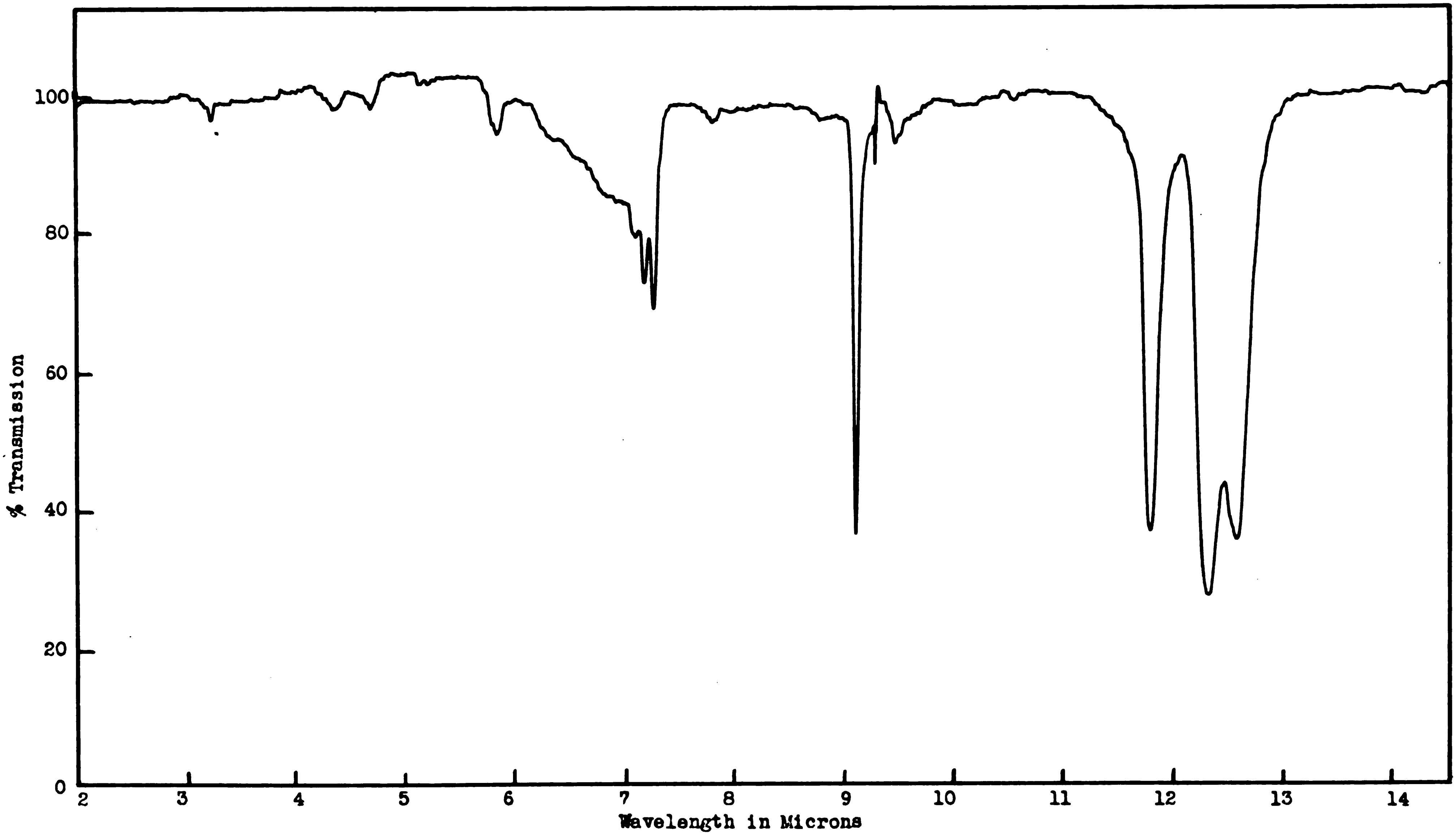

Figure 5. Infra-red Spectrum of 1,3,5-Trichlorobenzene (0.065 Molar in CS_2)

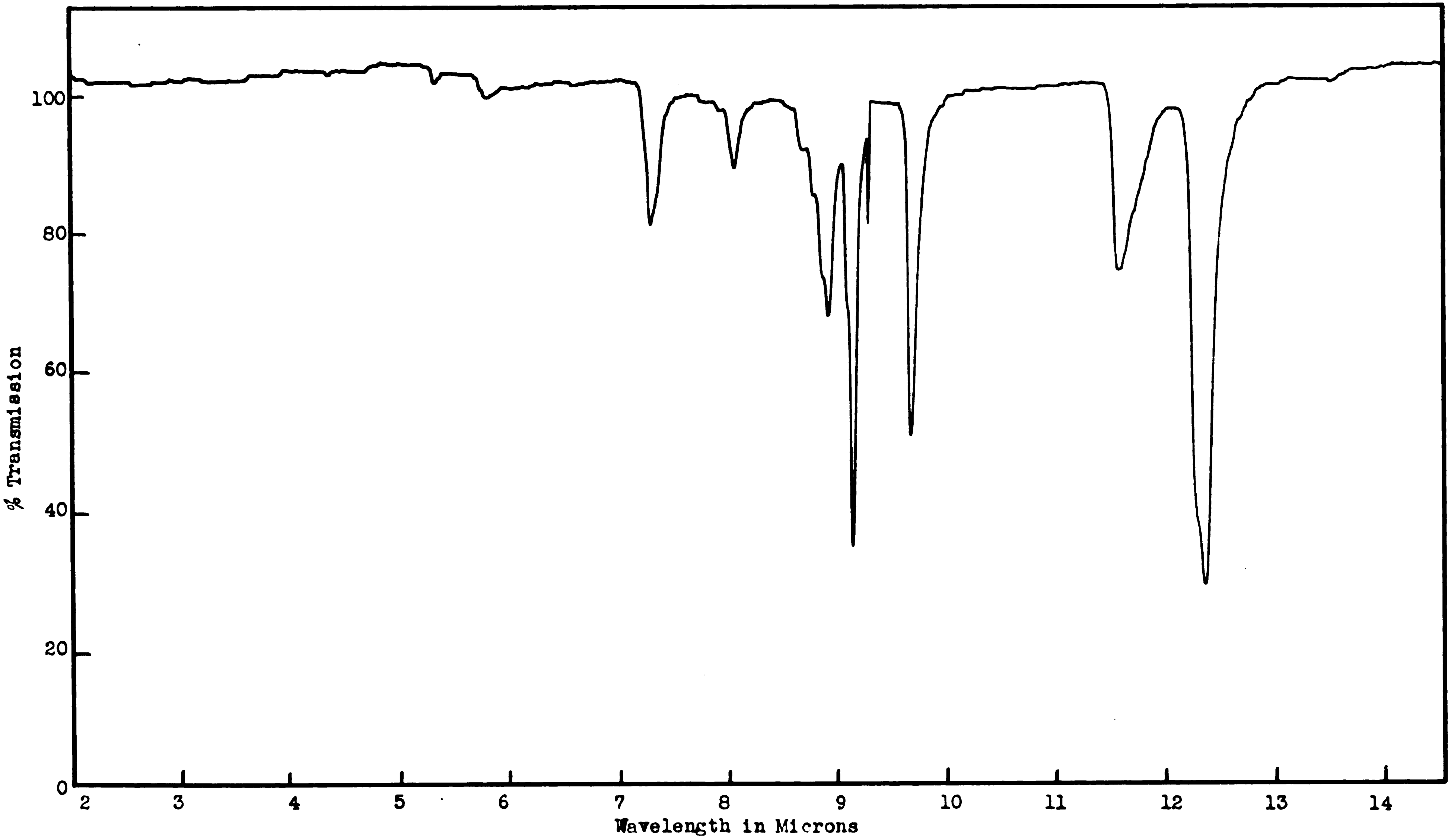

Figure 6. Infra-red Spectrum of 1,2,4-Trichlorobenzene (0.065 Molar in CS_2)

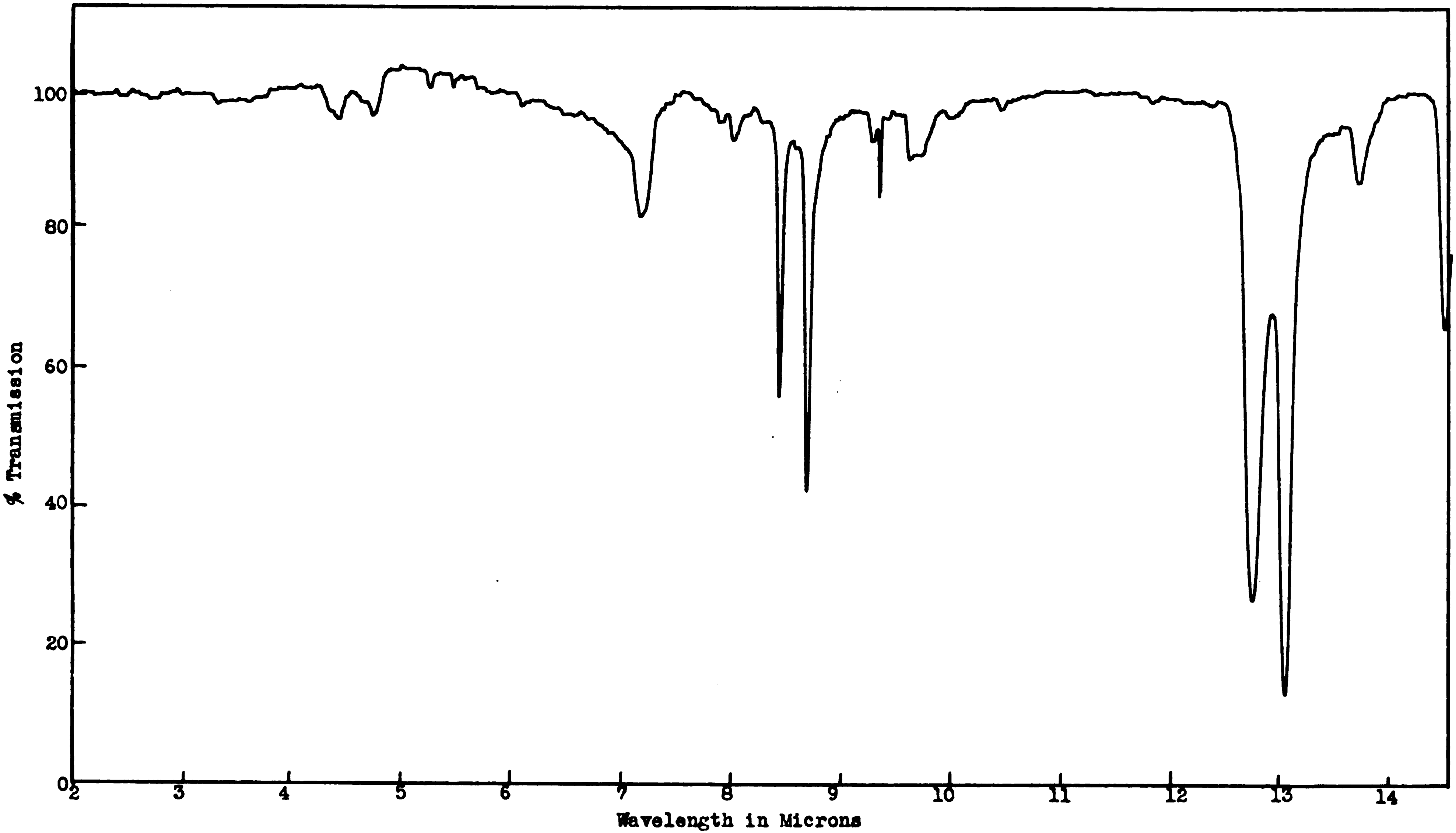

Figure 7. Infra-red Spectrum of 1,2,3-Trichlorobenzene (0.065 Molar in CS_2)

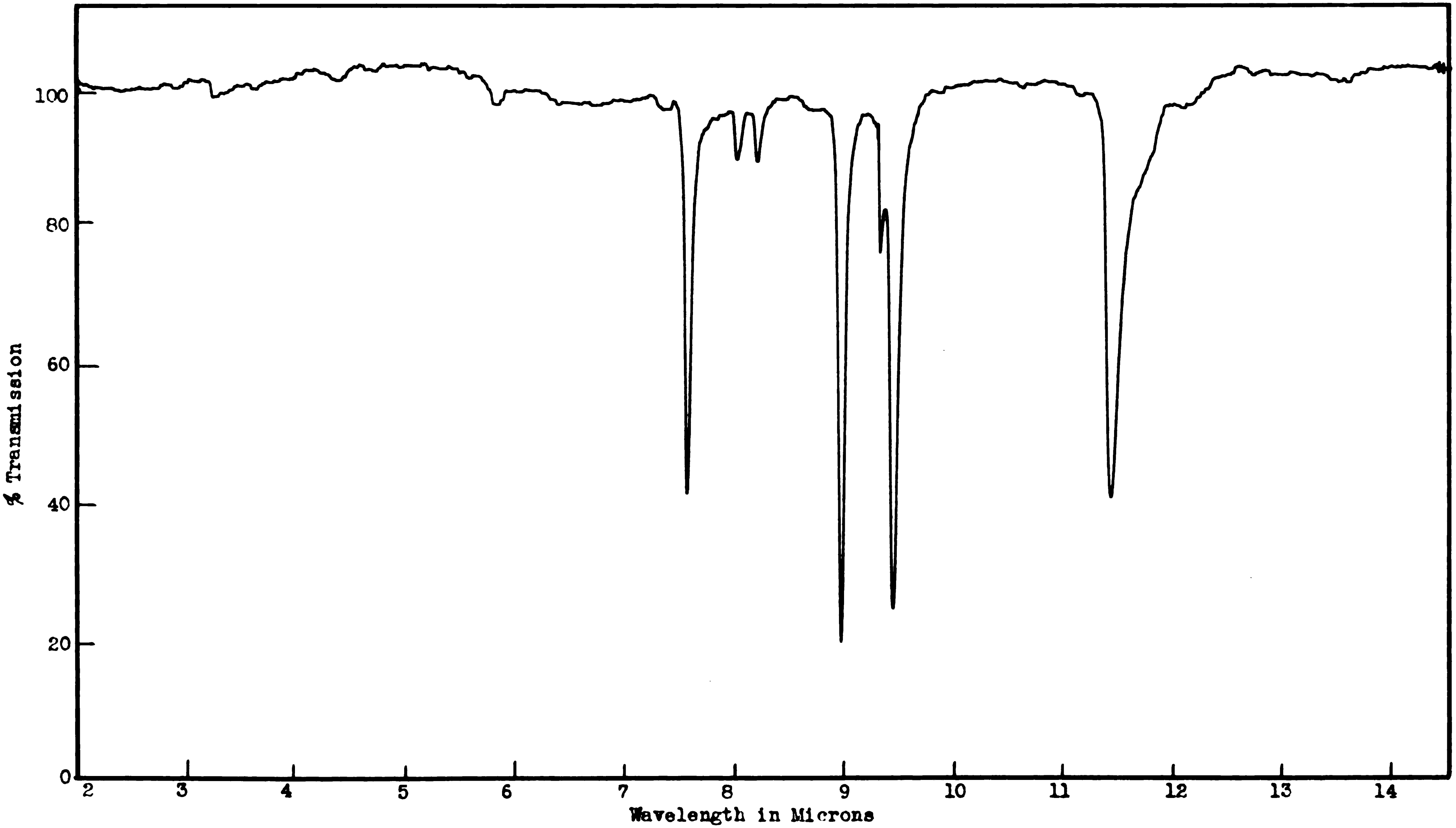

Figure 8. Infra-red Spectrum of 1,2,4,5-Tetrachlorobenzene (0.065 Molar in CS_2)

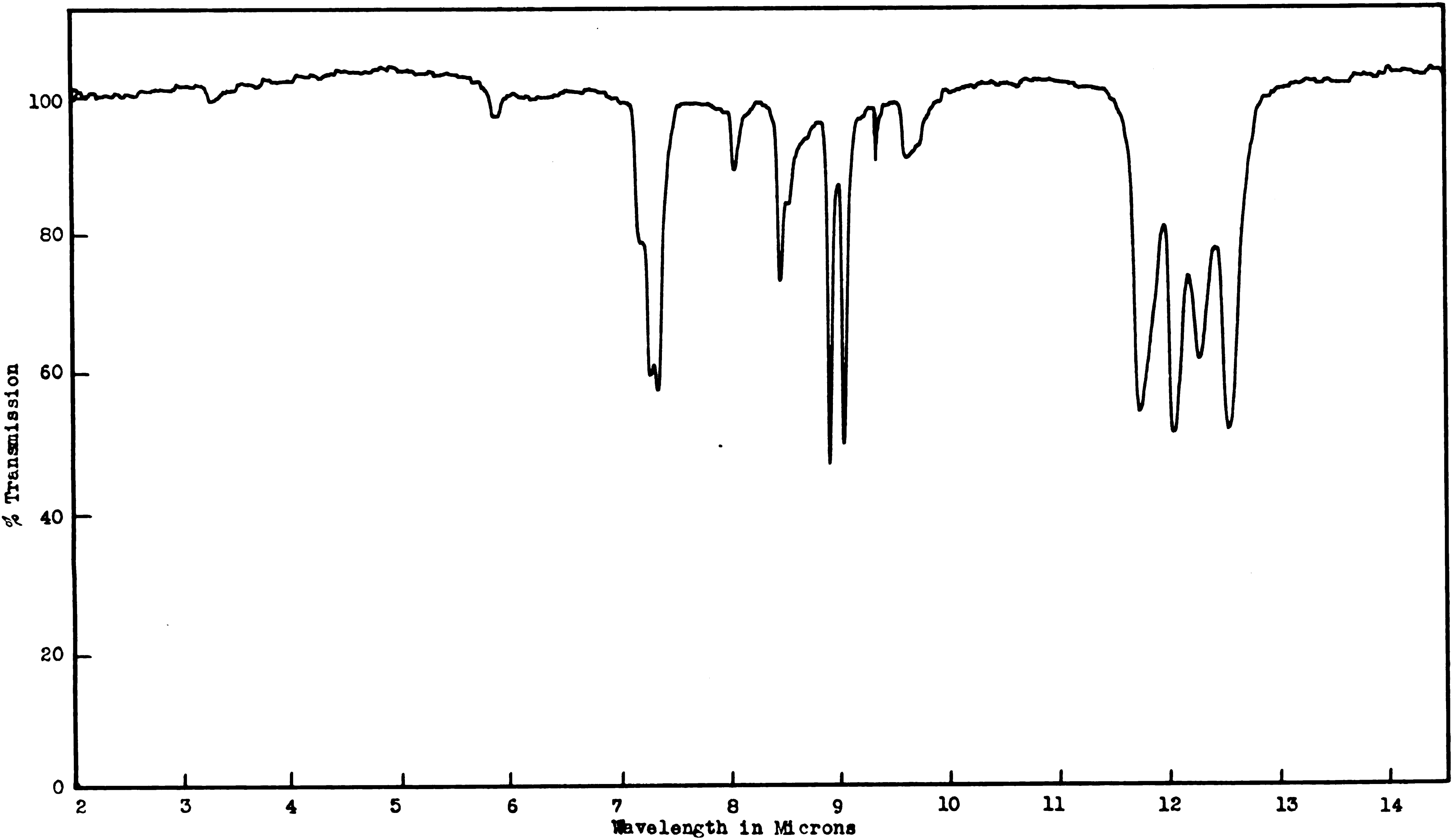

Figure 9. Infra-red Spectrum of 1,2,3,5-Tetrachlorobenzene (0.065 Molar in CS_2)

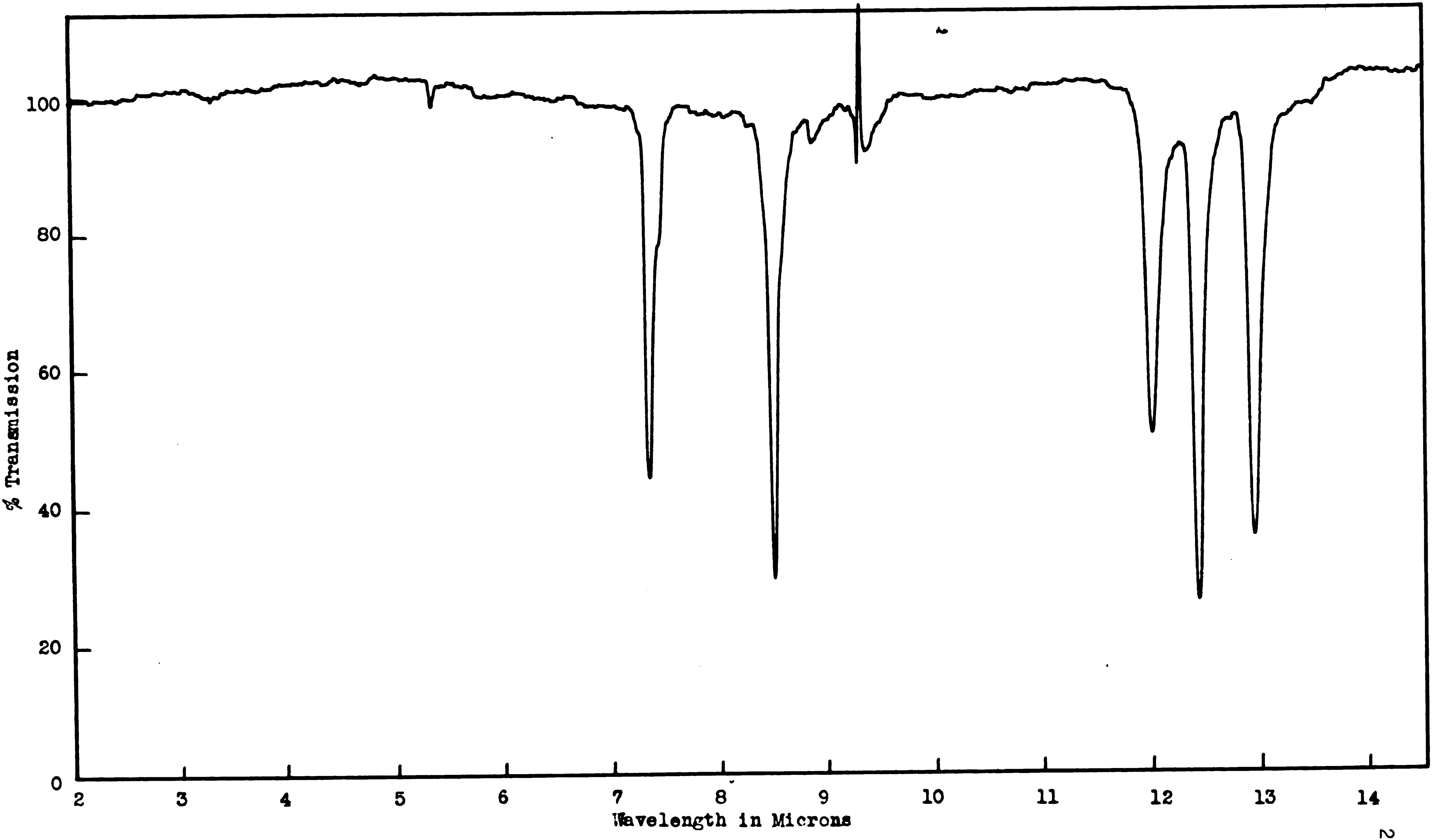

Figure 10. Infra-red Spectrum of 1,2,3,4-Tetrachlorobenzene (0.065 Molar in CS_2)

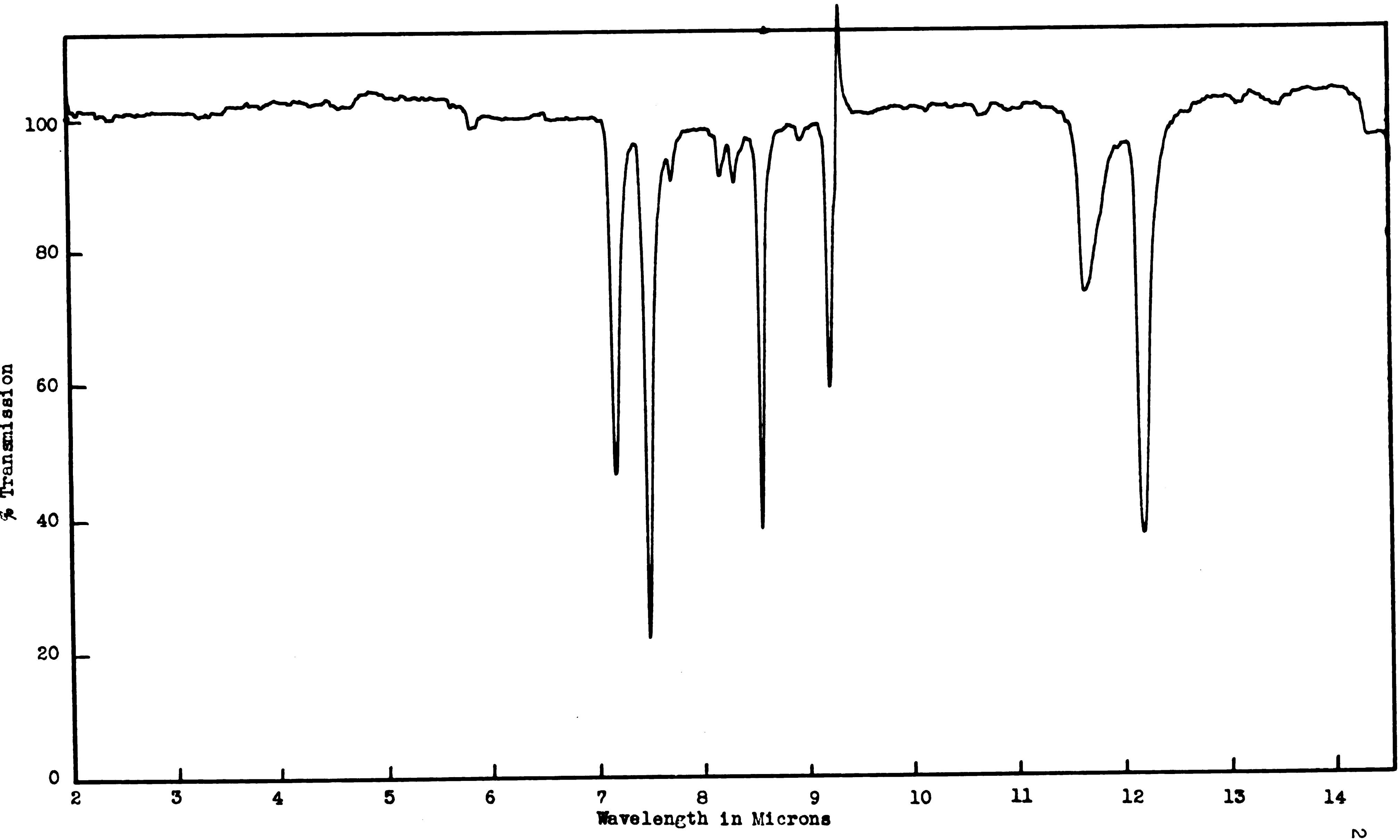

Figure 11. Infra-red Spectrum of Pentachlorobenzene (0.065 Molar in CS_2)

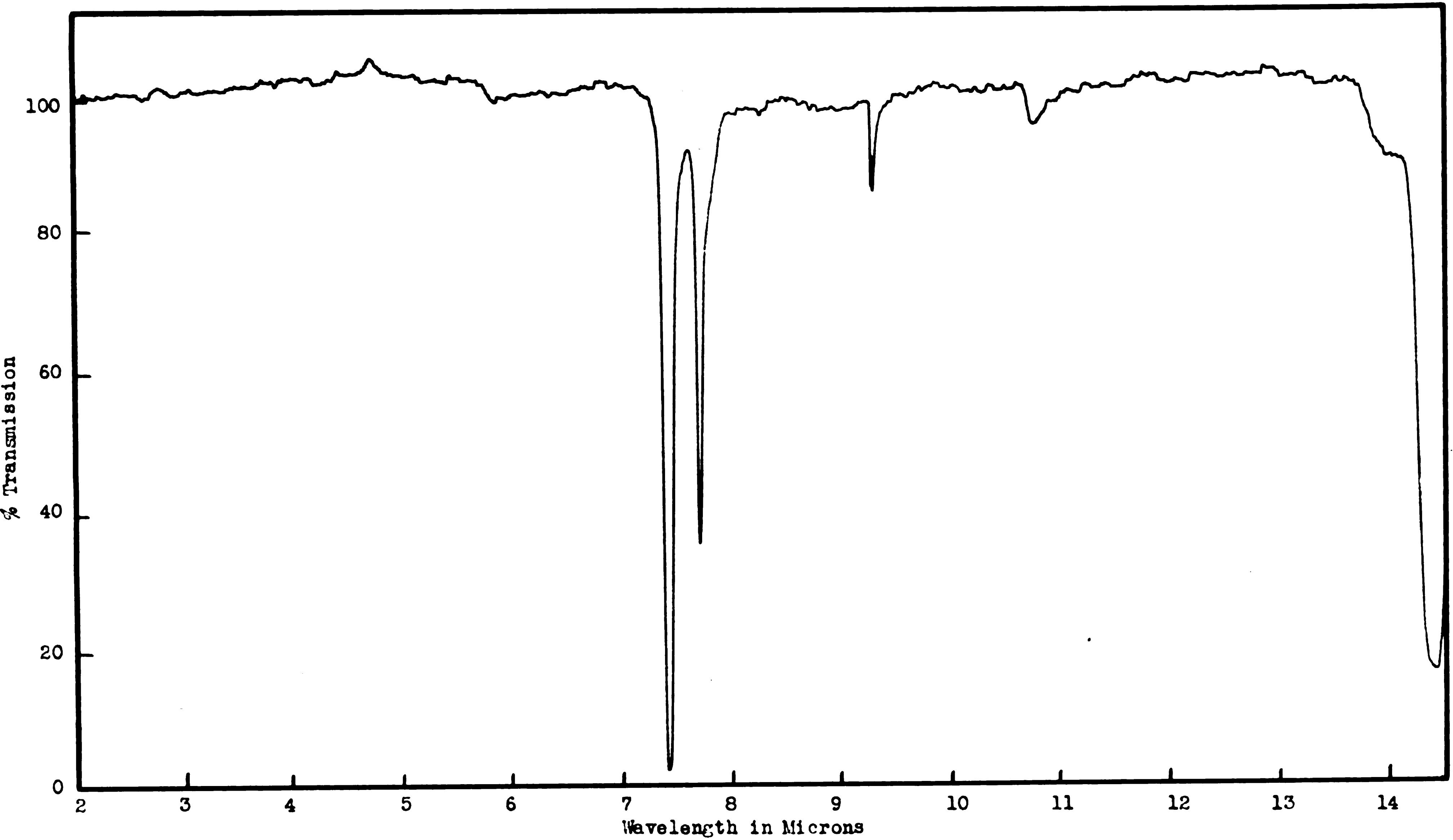

Figure 12. Infra-red Spectrum of Hexachlorobenzene (0.065 Molar in CS_2)

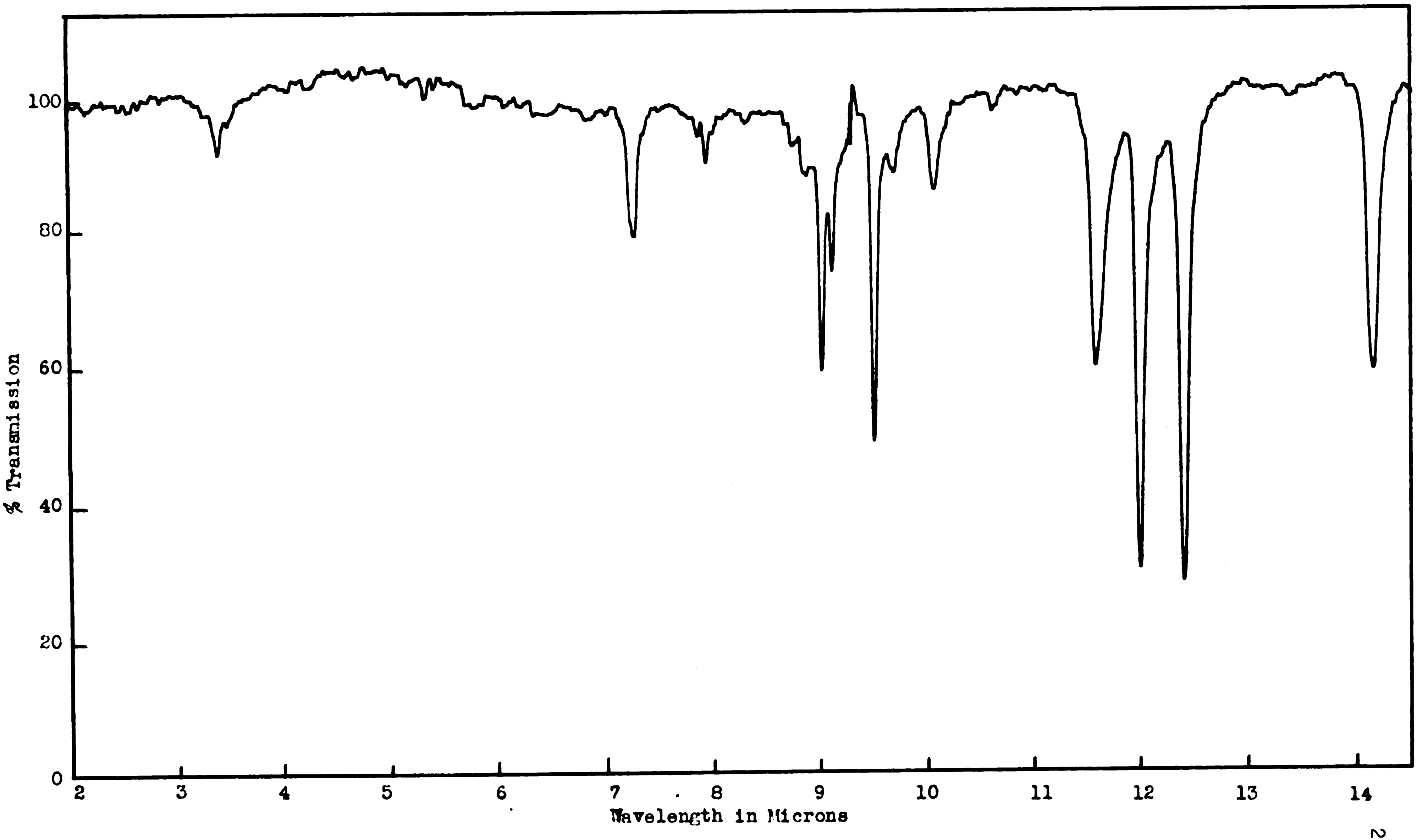

Figure 13. Infra-red Spectrum of 2,4-Dichlorotoluene (0.065 Molar in CS_2)

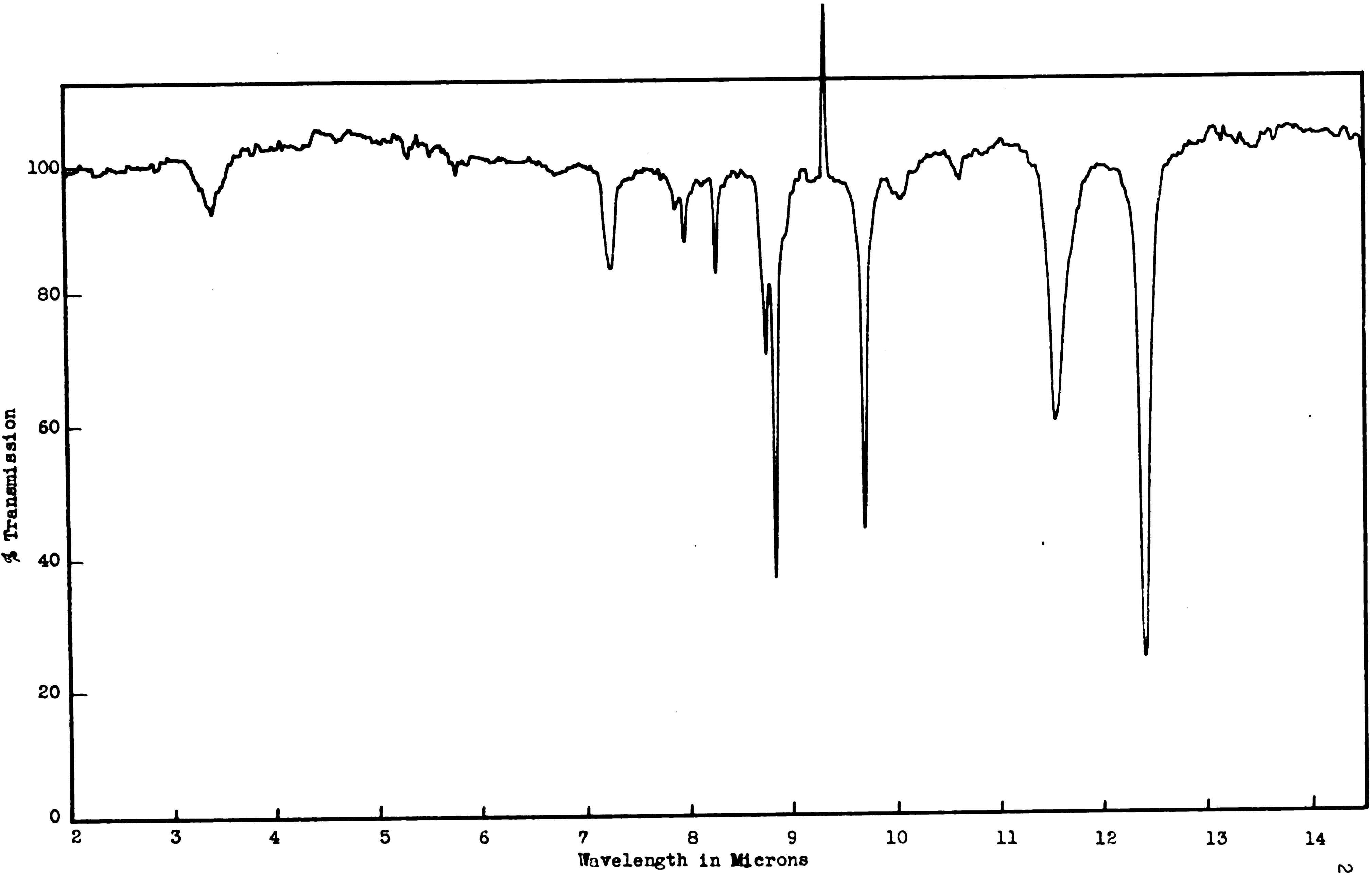

Figure 14. Infra-red Spectrum of 3,4-Dichlorotoluene (0.065 Molar in CS_2)

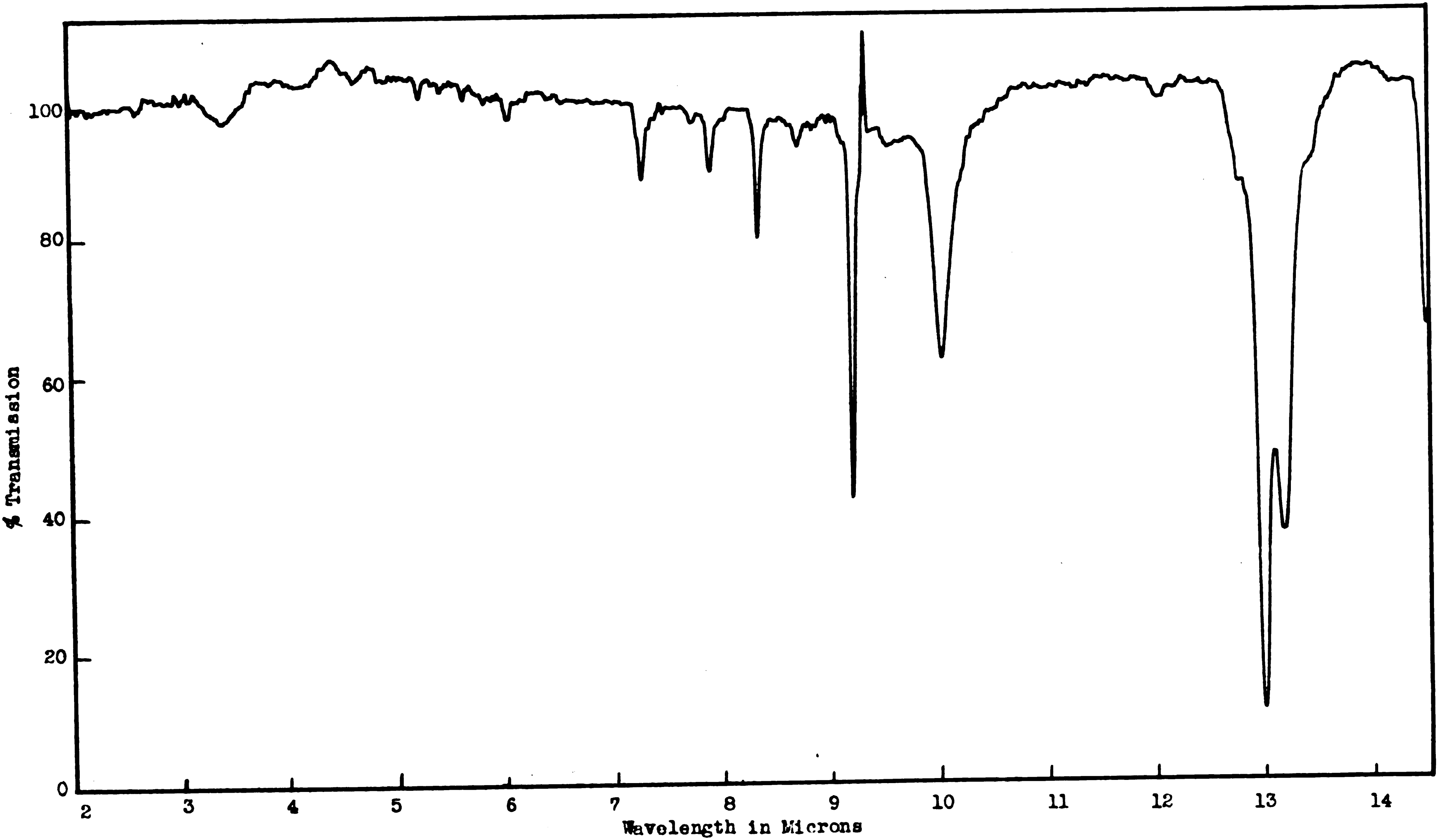

Figure 15. Infra-red Spectrum of 2,6-Dichlorotoluene (0.065 Molar in CS_2)

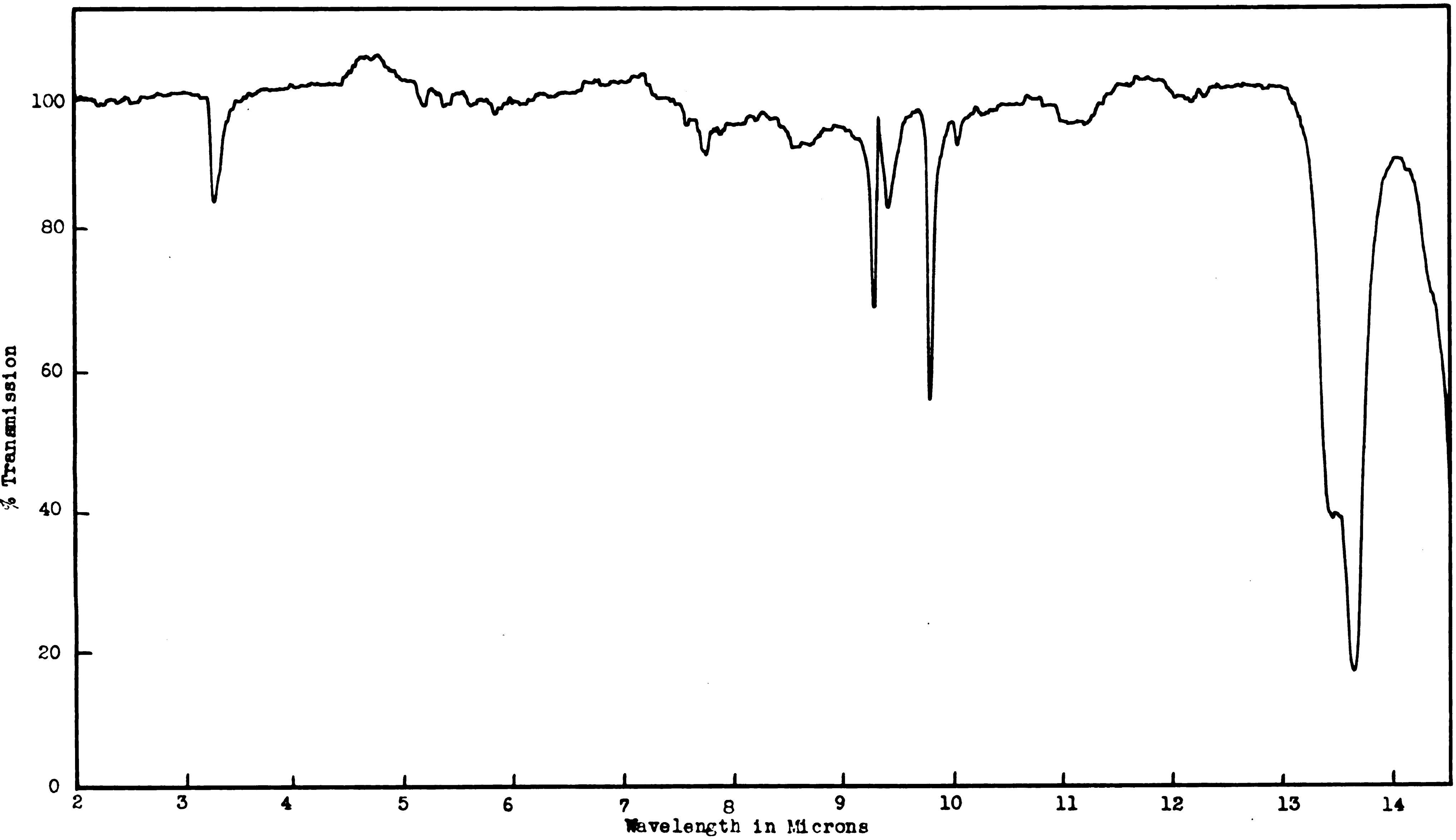

Figure 16. Infra-red Spectrum of Diphenyl Sulfide (0.065 Molar in CS_2)

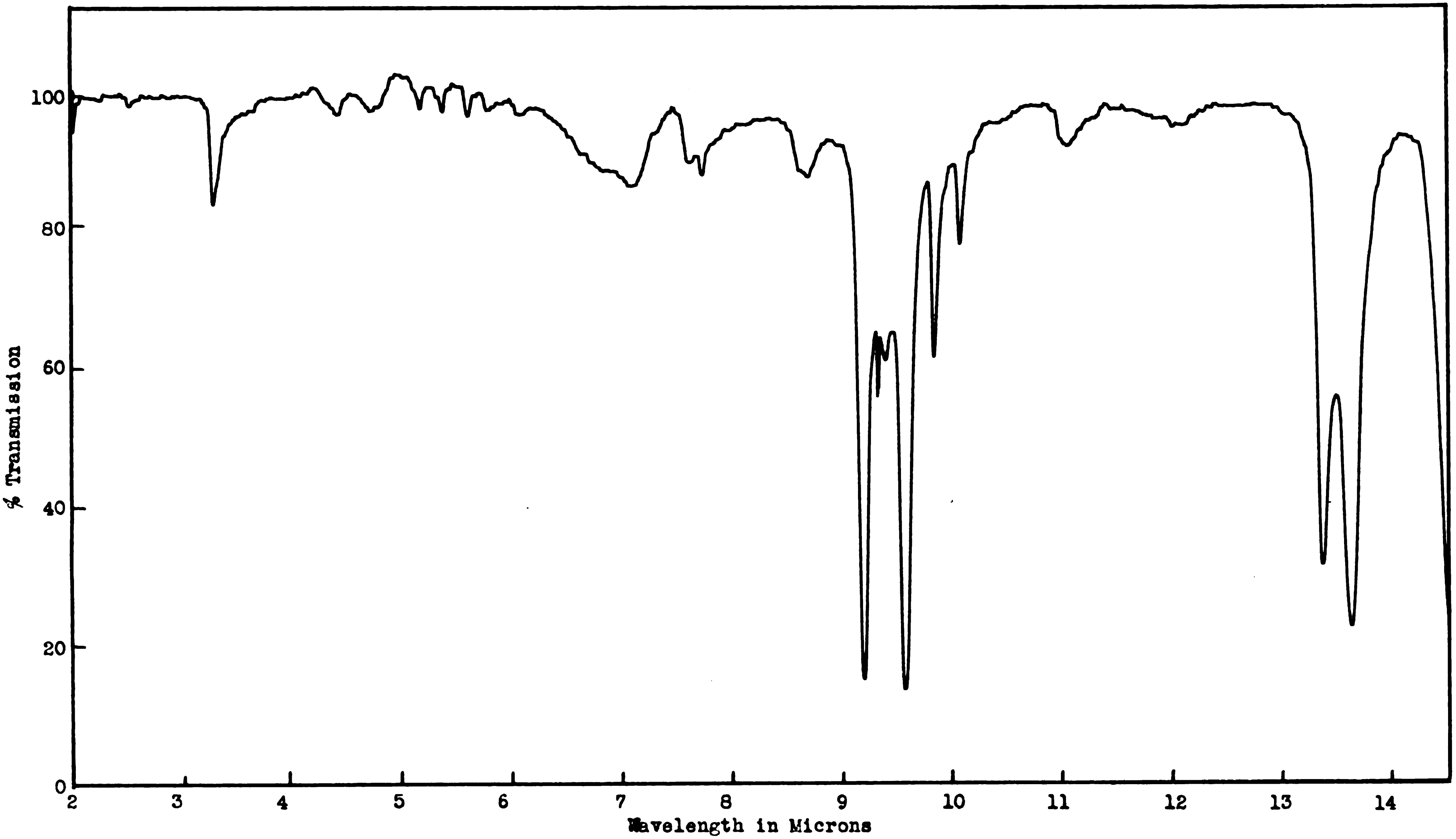

Figure 17. Infra-red Spectrum of Diphenyl Sulfoxide (0.065 Molar in CS_2)

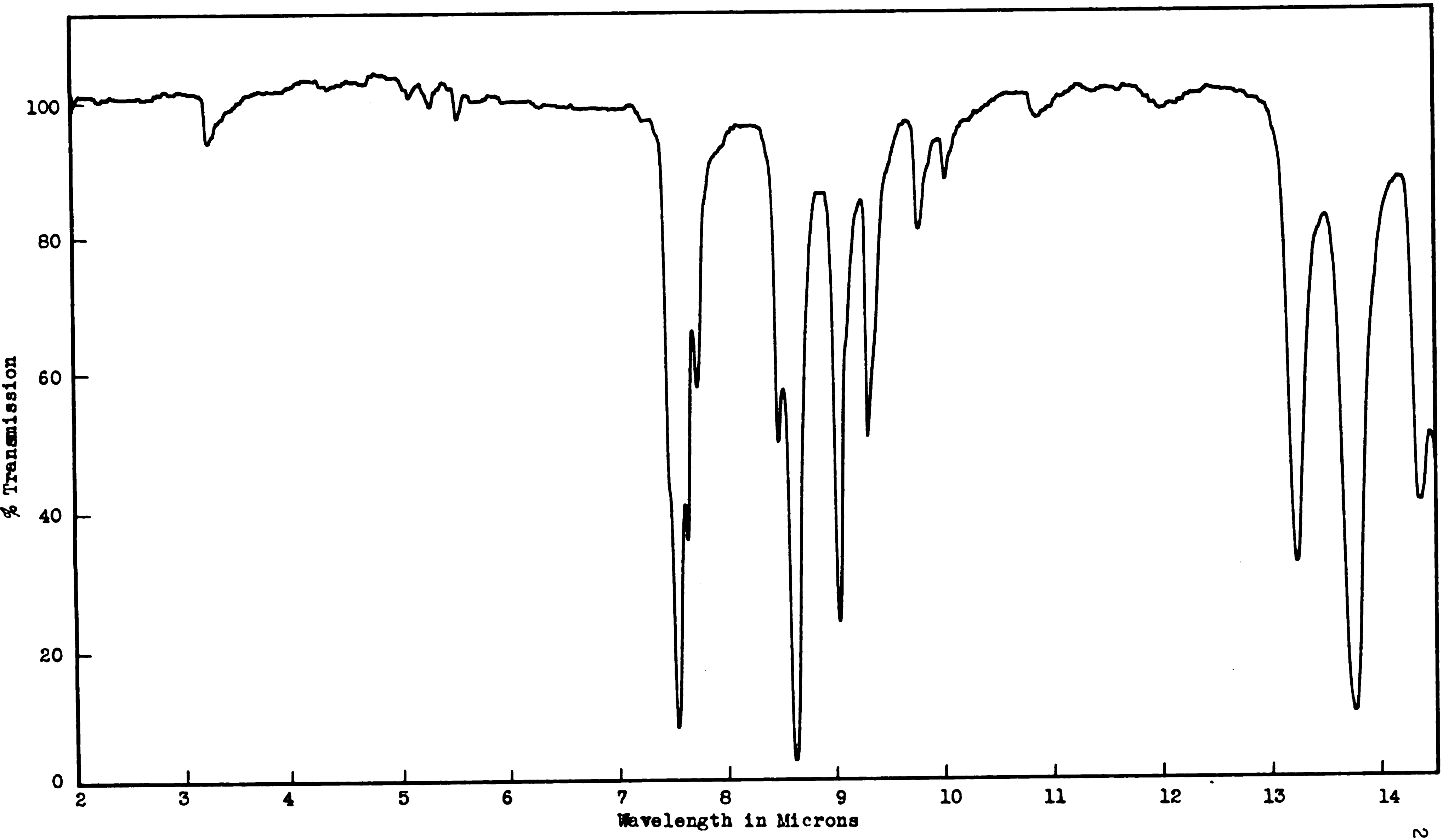

Figure 18. Infra-red Spectrum of Diphenyl Sulfone (0.065 Molar in CS_2)

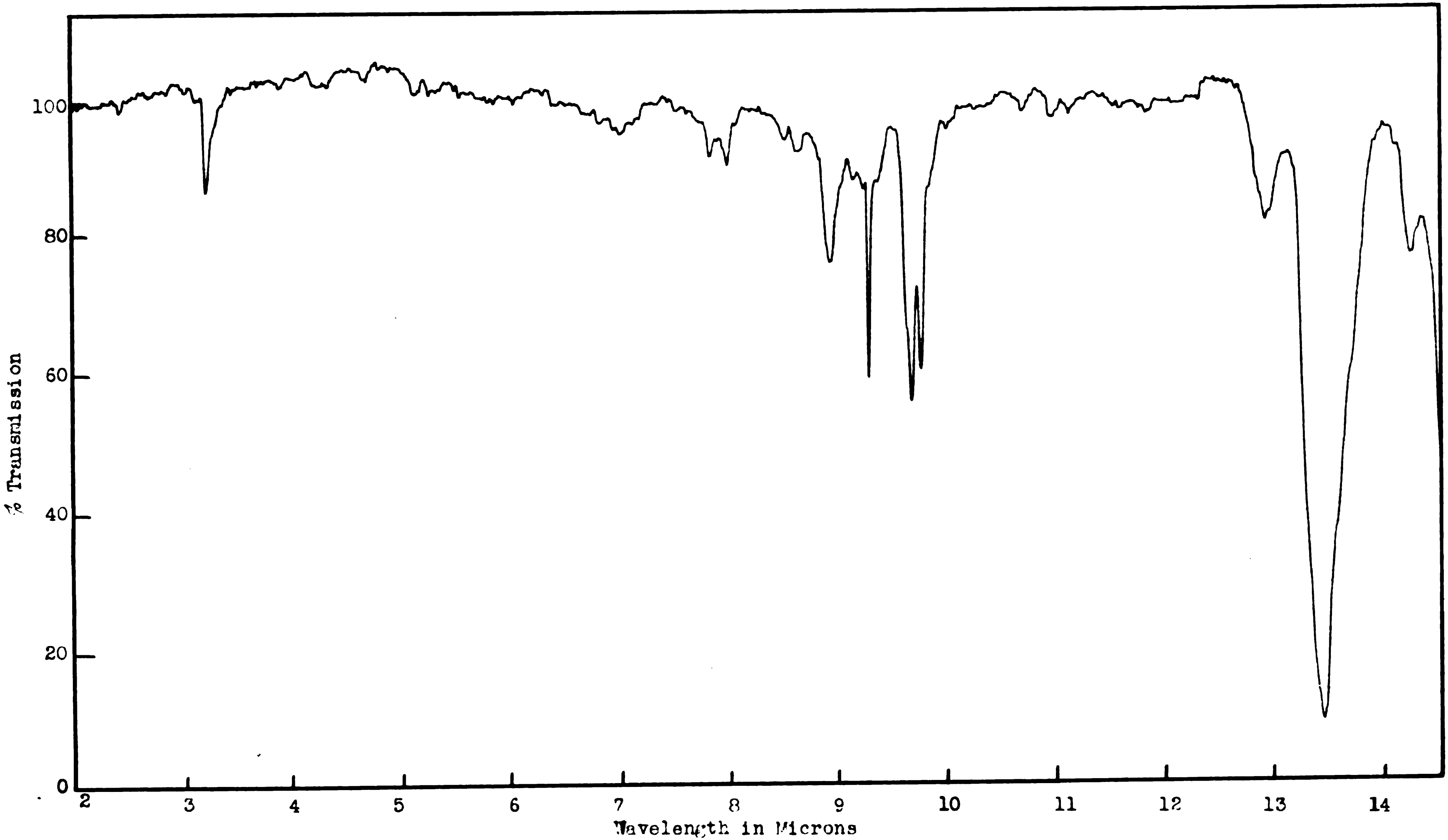

Figure 19. Infra-red Spectrum of 2-Chlorophenyl Phenyl Sulfide (0.065 Molar in CS_2)

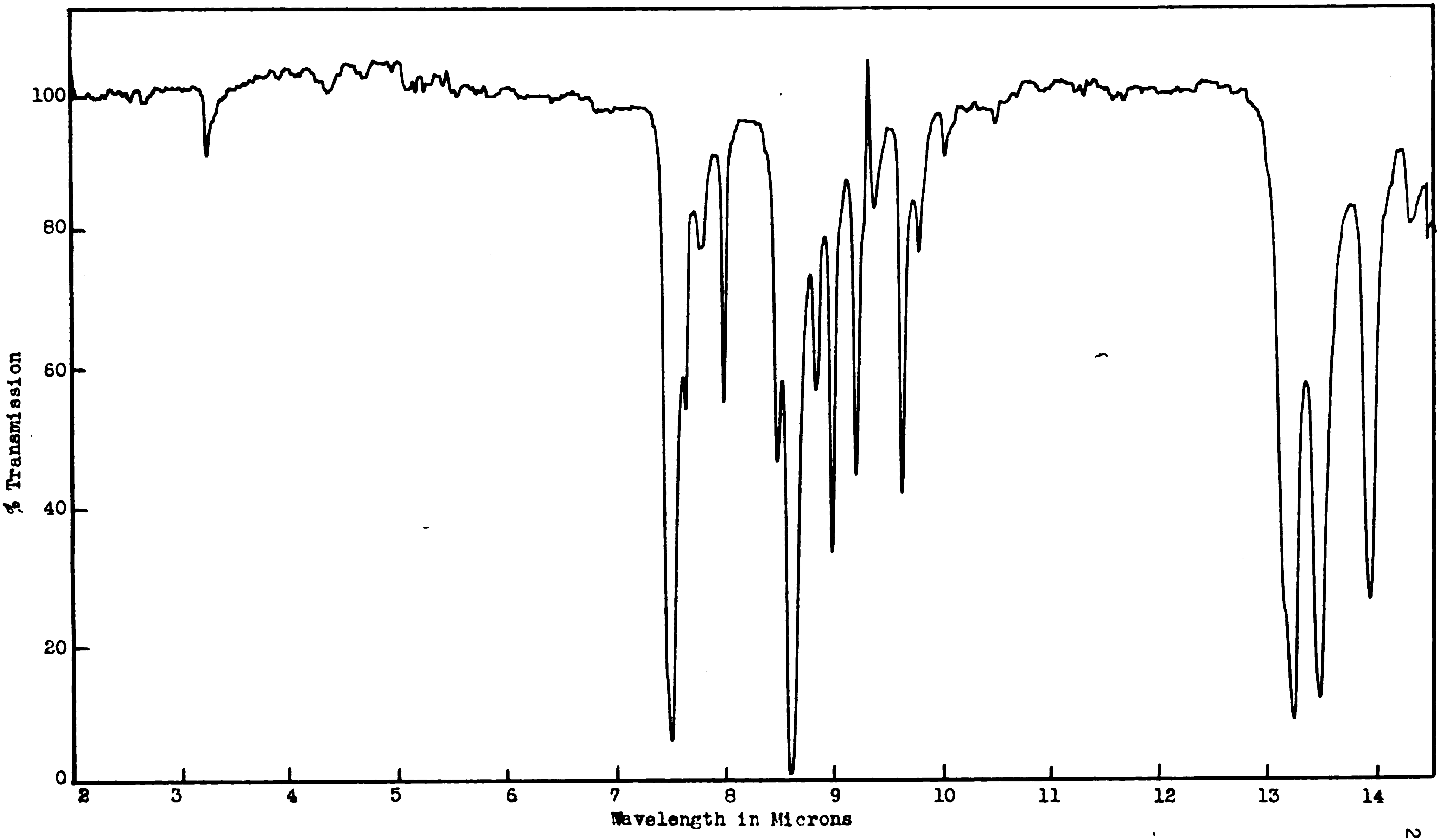

Figure 20. Infra-red Spectrum of 2-Chlorophenyl Phenyl Sulfone (0.065 Molar in CS_2)

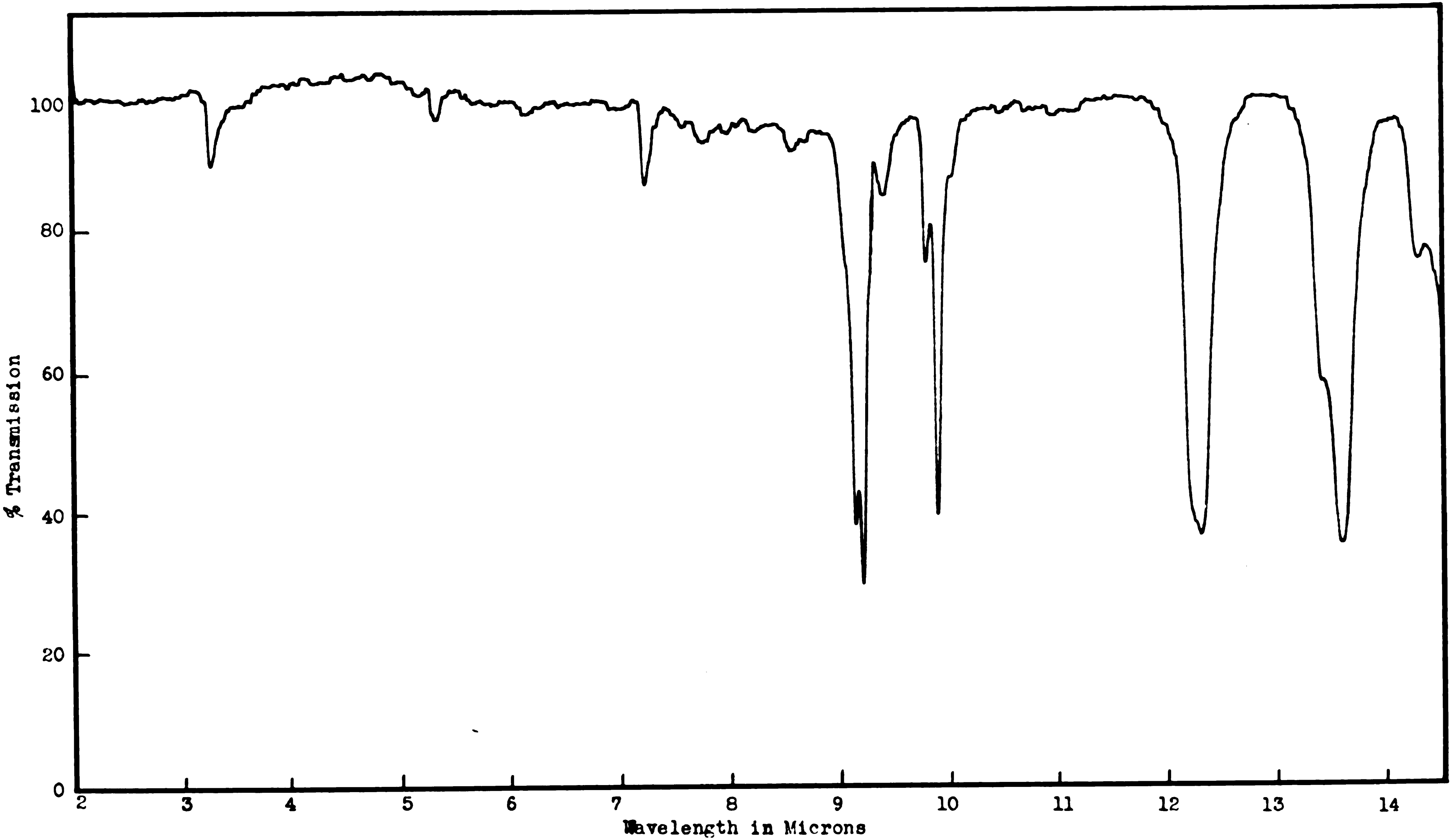

Figure 21. Infra-red Spectrum of 4-Chlorophenyl Phenyl Sulfide (0.065 Molar in CS_2)

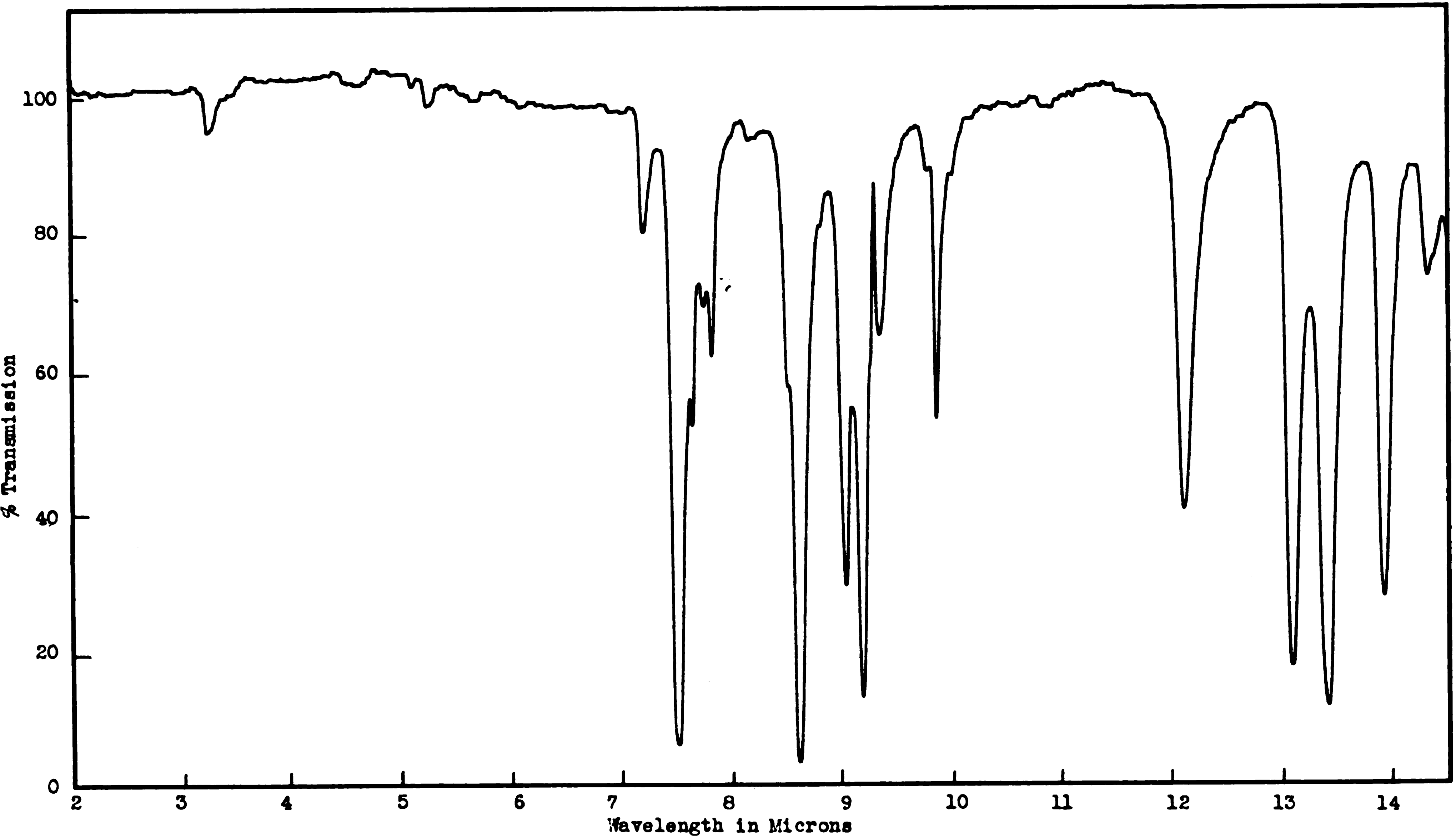

Figure 22. Infra-red Spectrum of 4-Chlorophenyl Phenyl Sulfone (0.065 Molar in CS_2)

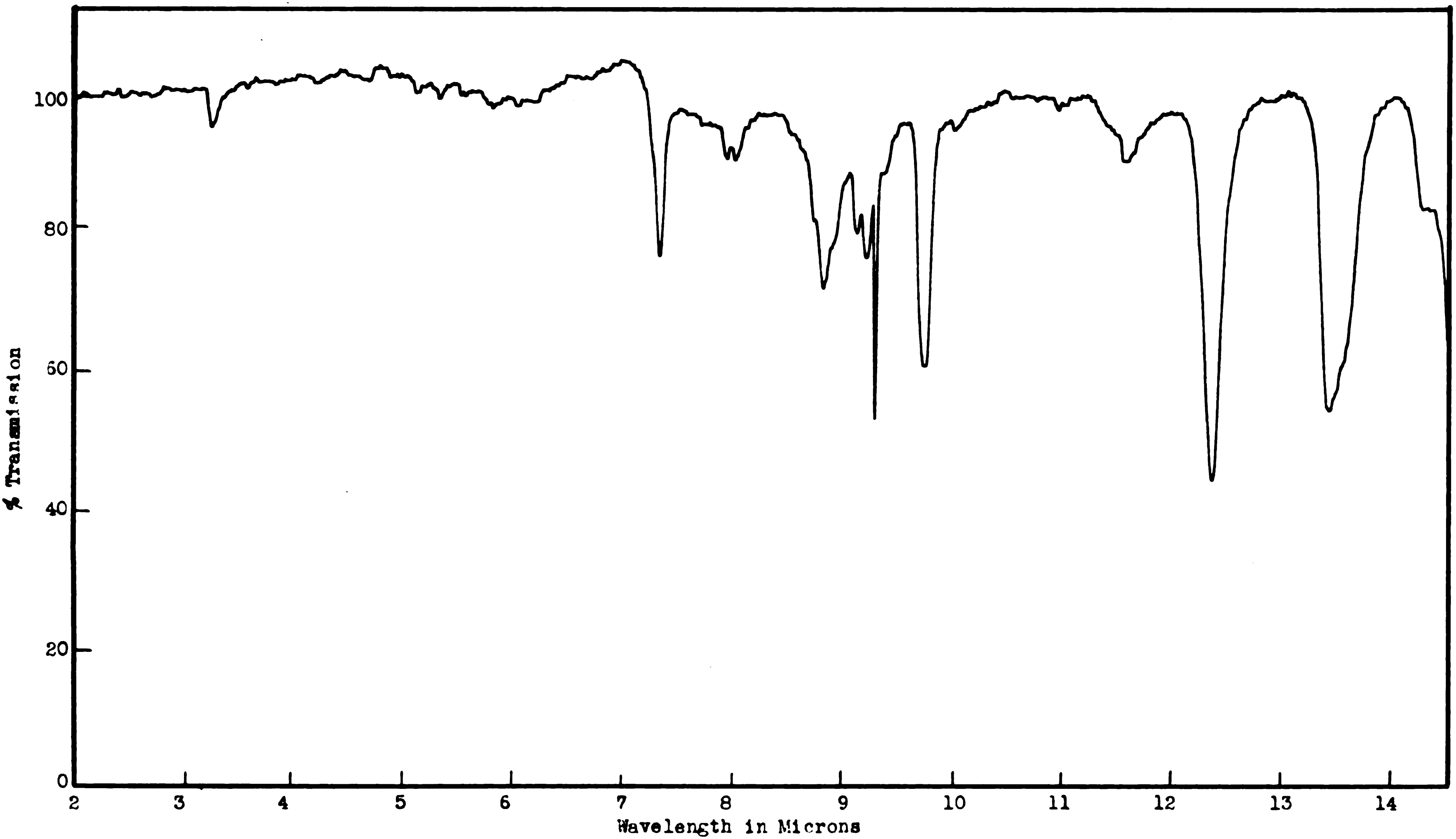

Figure 23. Infra-red Spectrum of 3,4-Dichlorophenyl Phenyl Sulfide (0.065 Molar in CS_2)

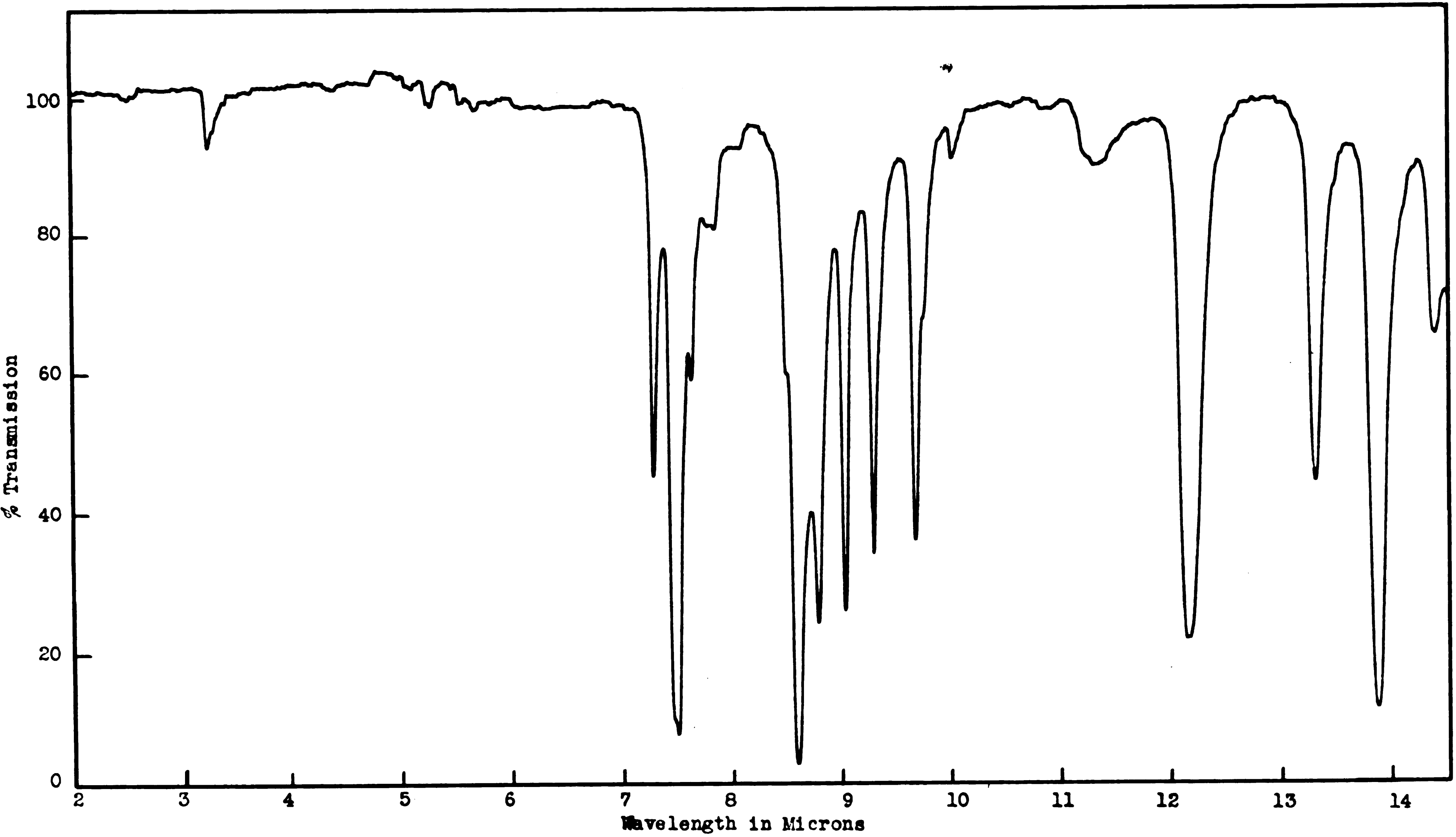

Figure 24. Infra-red Spectrum of 3,4-Dichlorophenyl Phenyl Sulfone (0.065 Molar in CS_2)

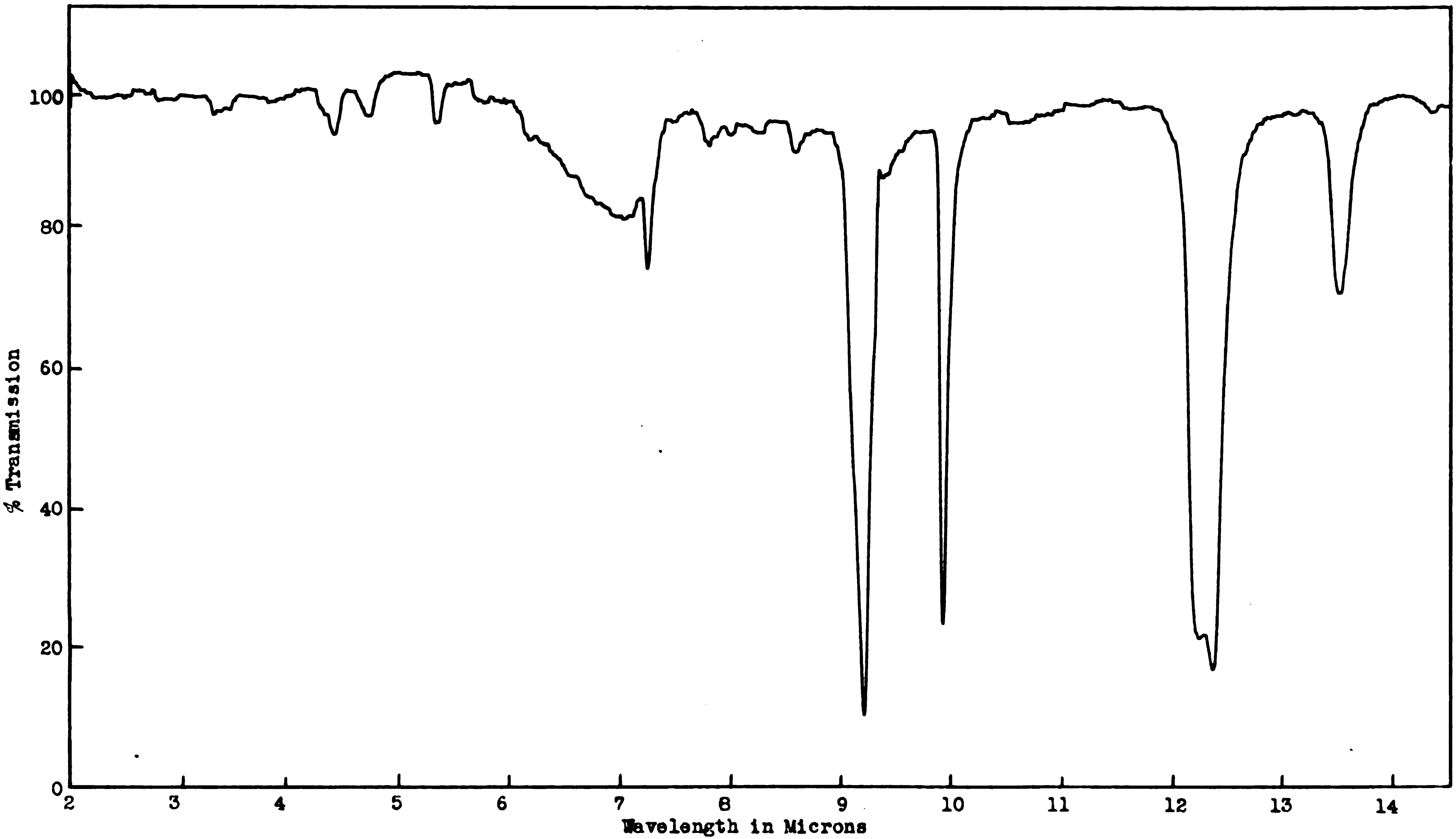

Figure 25. Infra-red Spectrum of Bis(4-Chlorophenyl) Sulfide (0.065 Molar in CS_2)

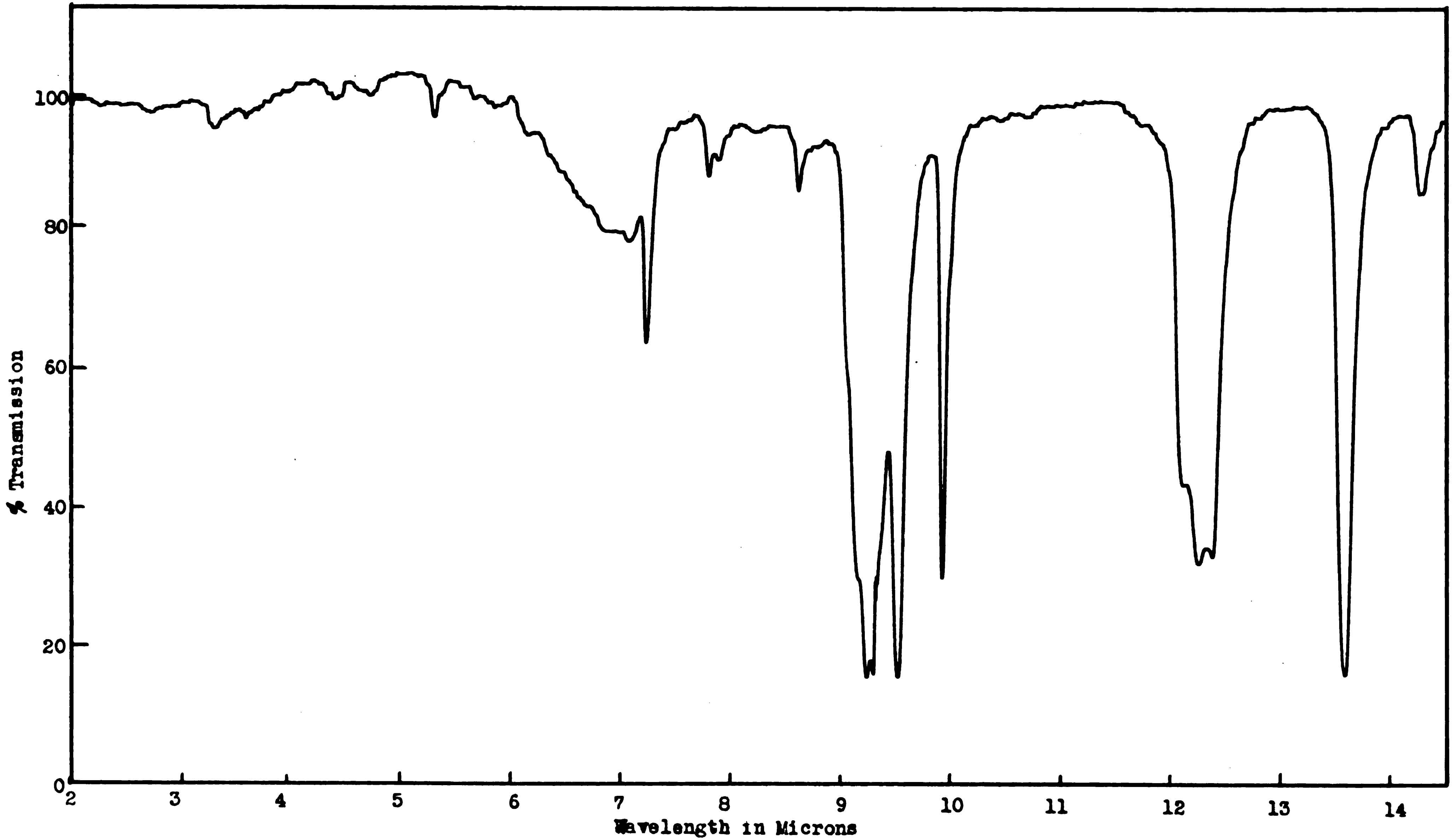

Figure 26. Infra-red Spectrum of Bis(4-Chlorophenyl) Sulfoxide (0.065 Molar in CS_2)

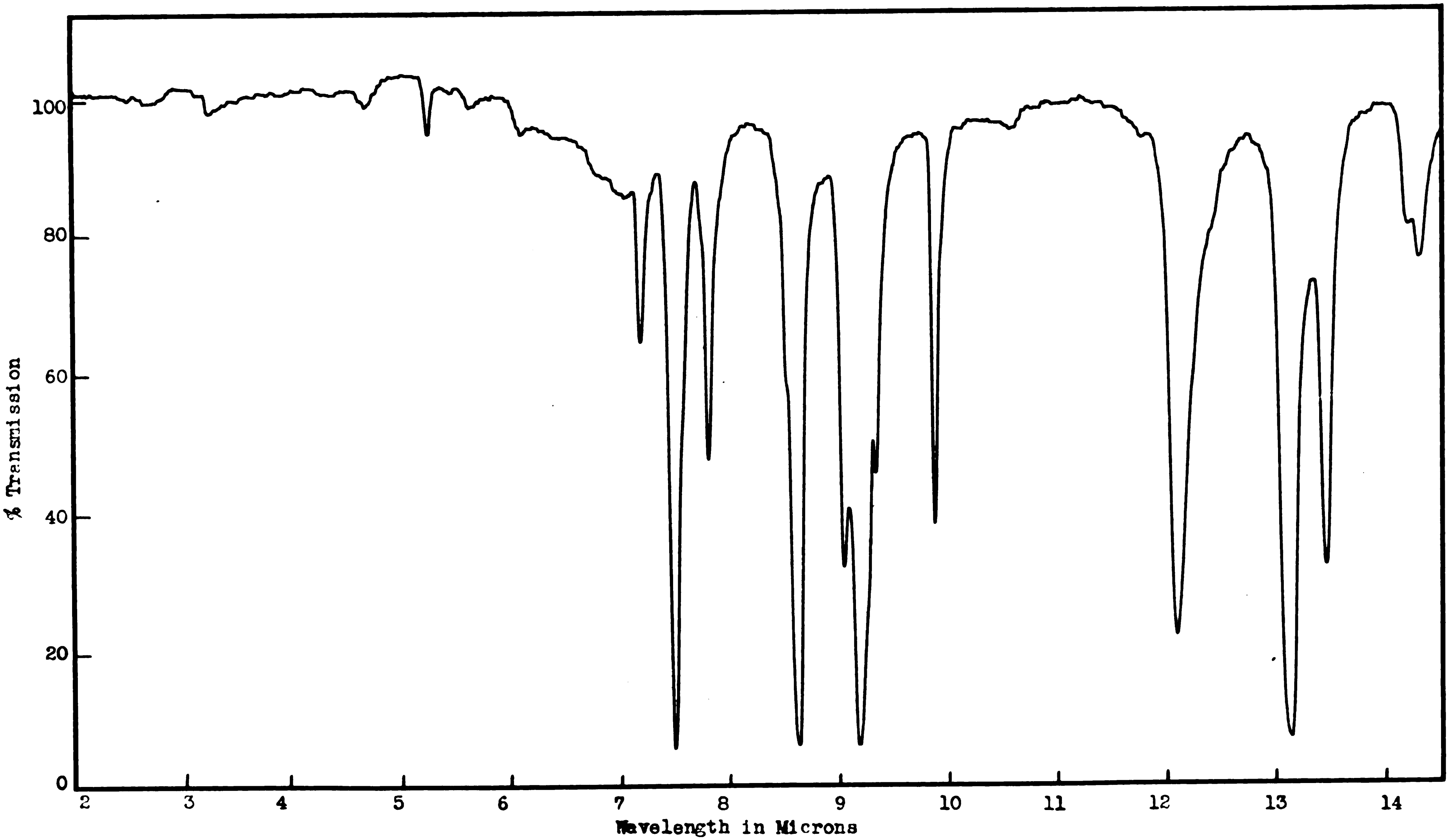

Figure 27. Infra-red Spectrum of Bis(4-Chlorophenyl) Sulfone (0.065 Molar in CS_2)

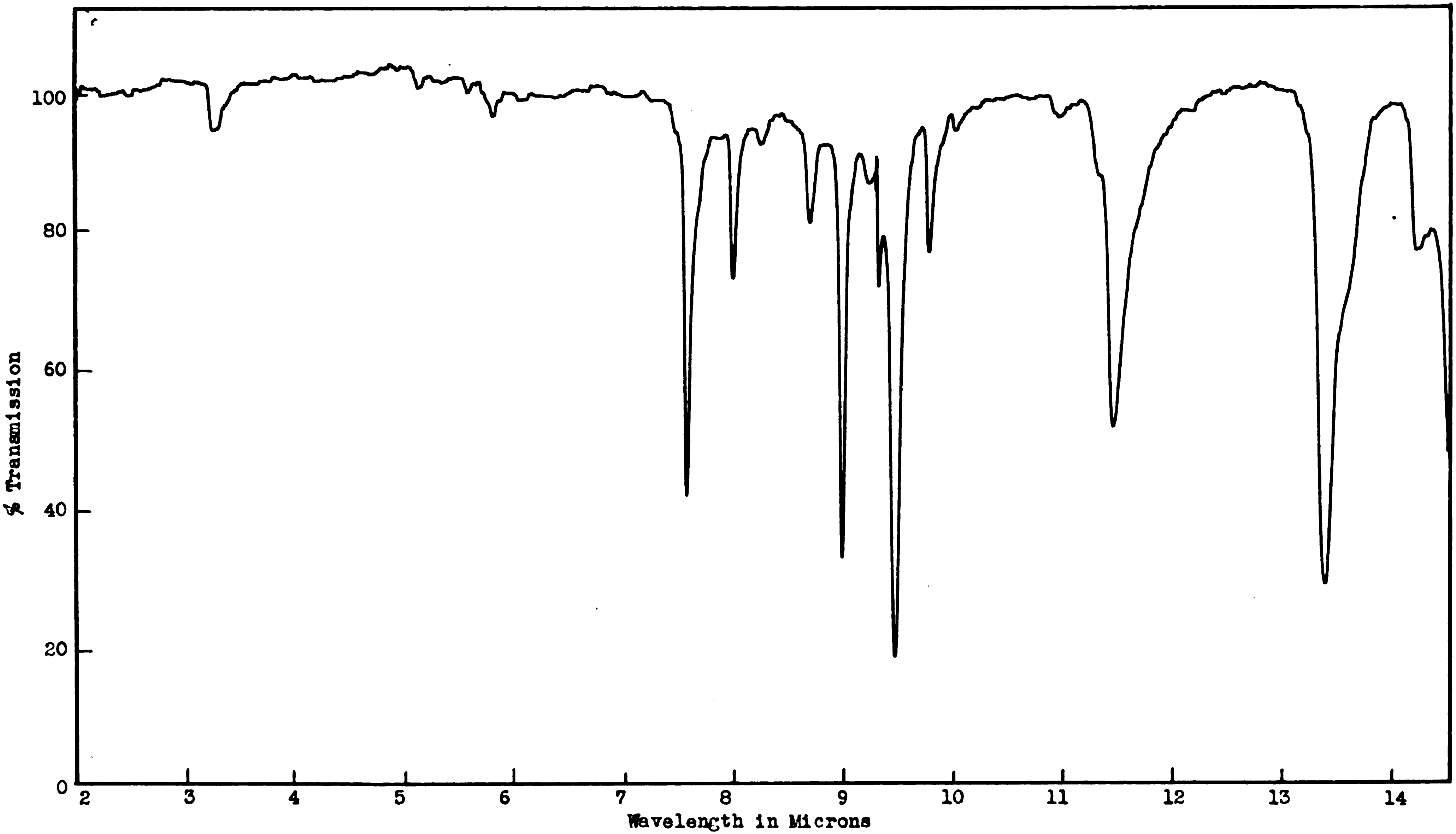

Figure 28. Infra-red Spectrum of 2,4,5-Trichlorophenyl Phenyl Sulfide (0.065 Molar in CS_2)

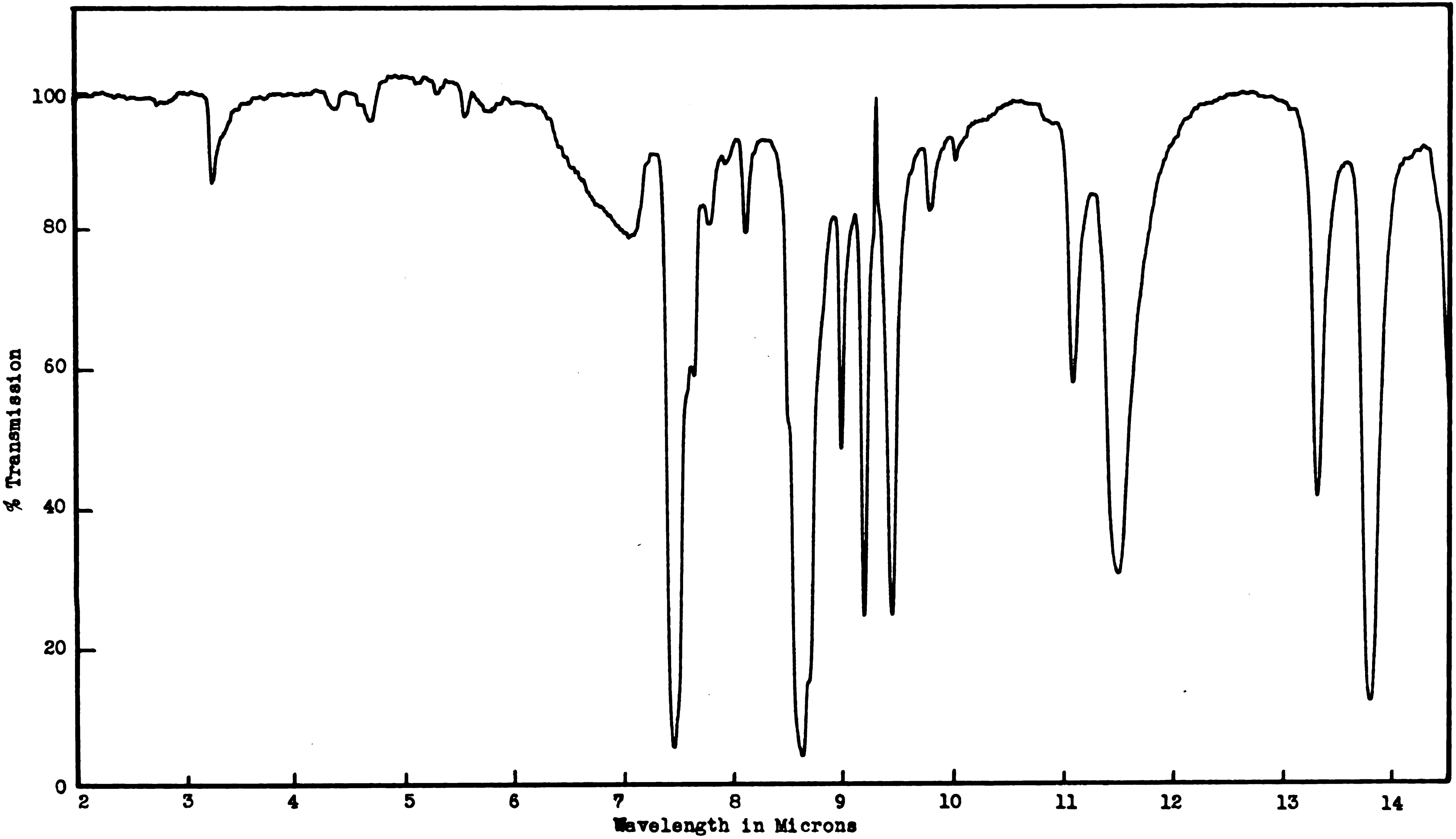

Figure 29. Infra-red Spectrum of 2,4,5-Trichlorophenyl Phenyl Sulfone (0.065 Molar in CS_2)

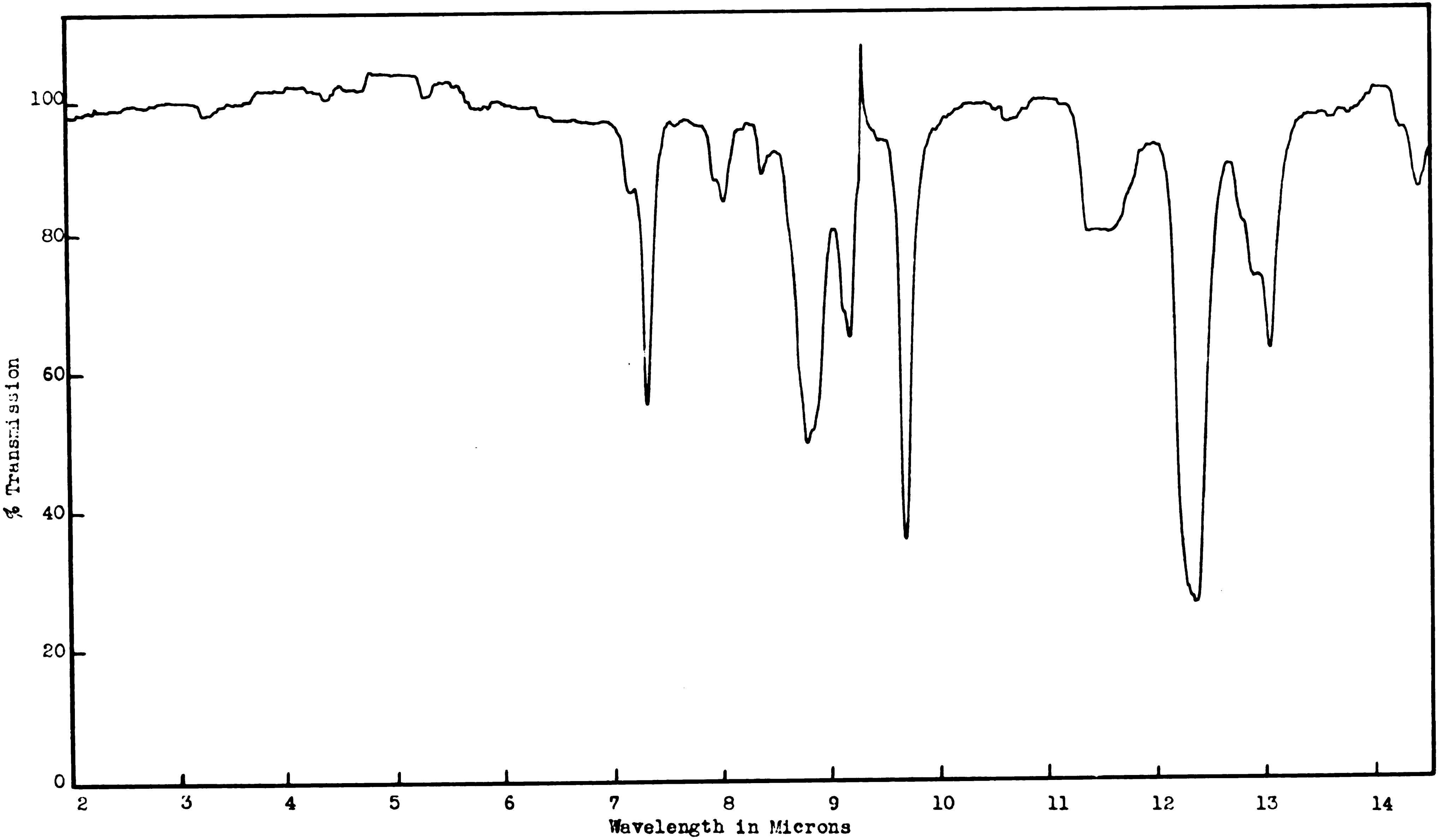

Figure 30. Infra-red Spectrum of 2,3,3',4'-Tetrachlorodiphenyl Sulfide (0.065 Molar in CS_2)

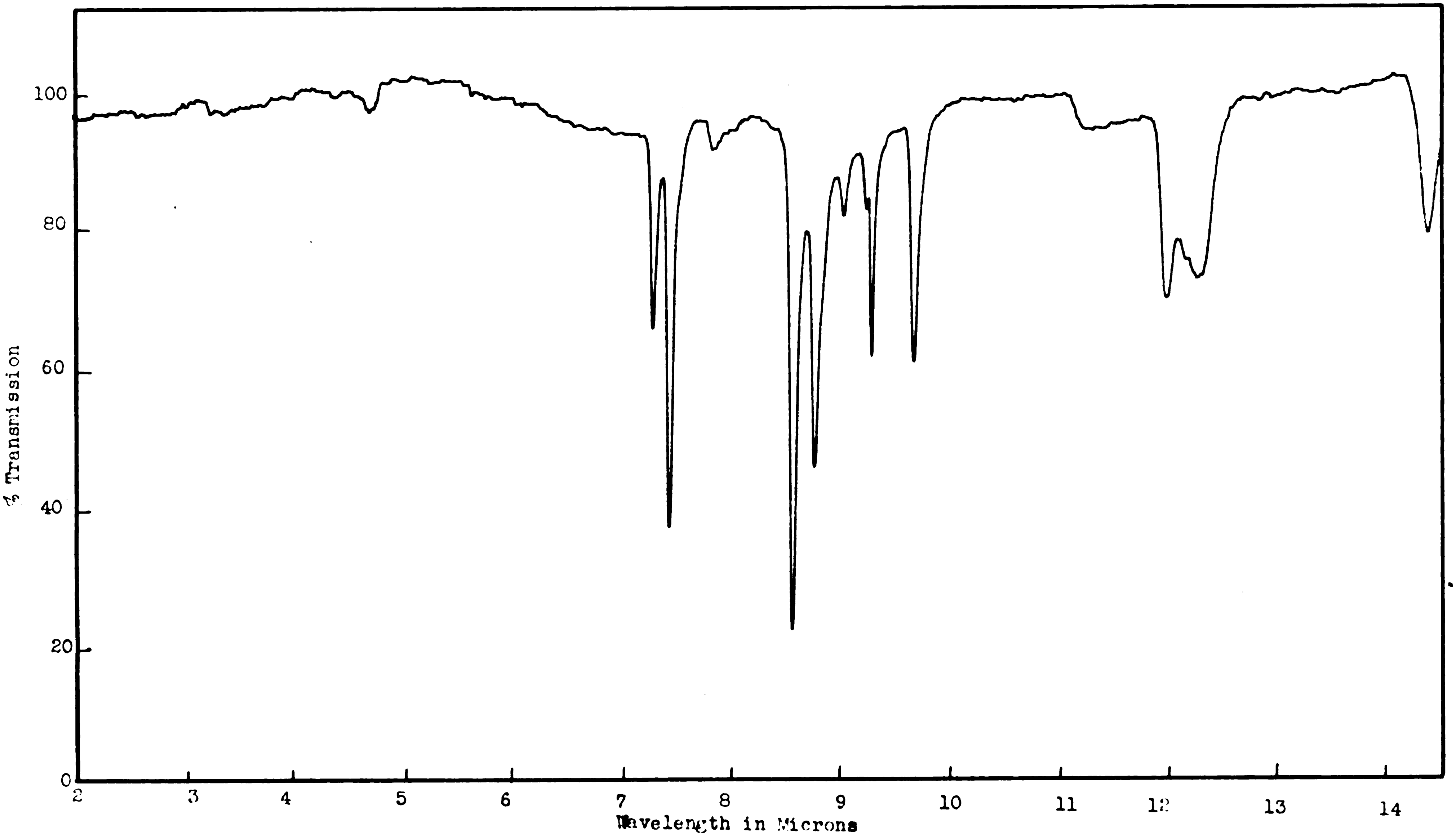

Figure 31. Infra-red Spectrum of 2,3,3',4'-Tetrachlorodiphenyl Sulfone (0.016 Molar in CS_2)

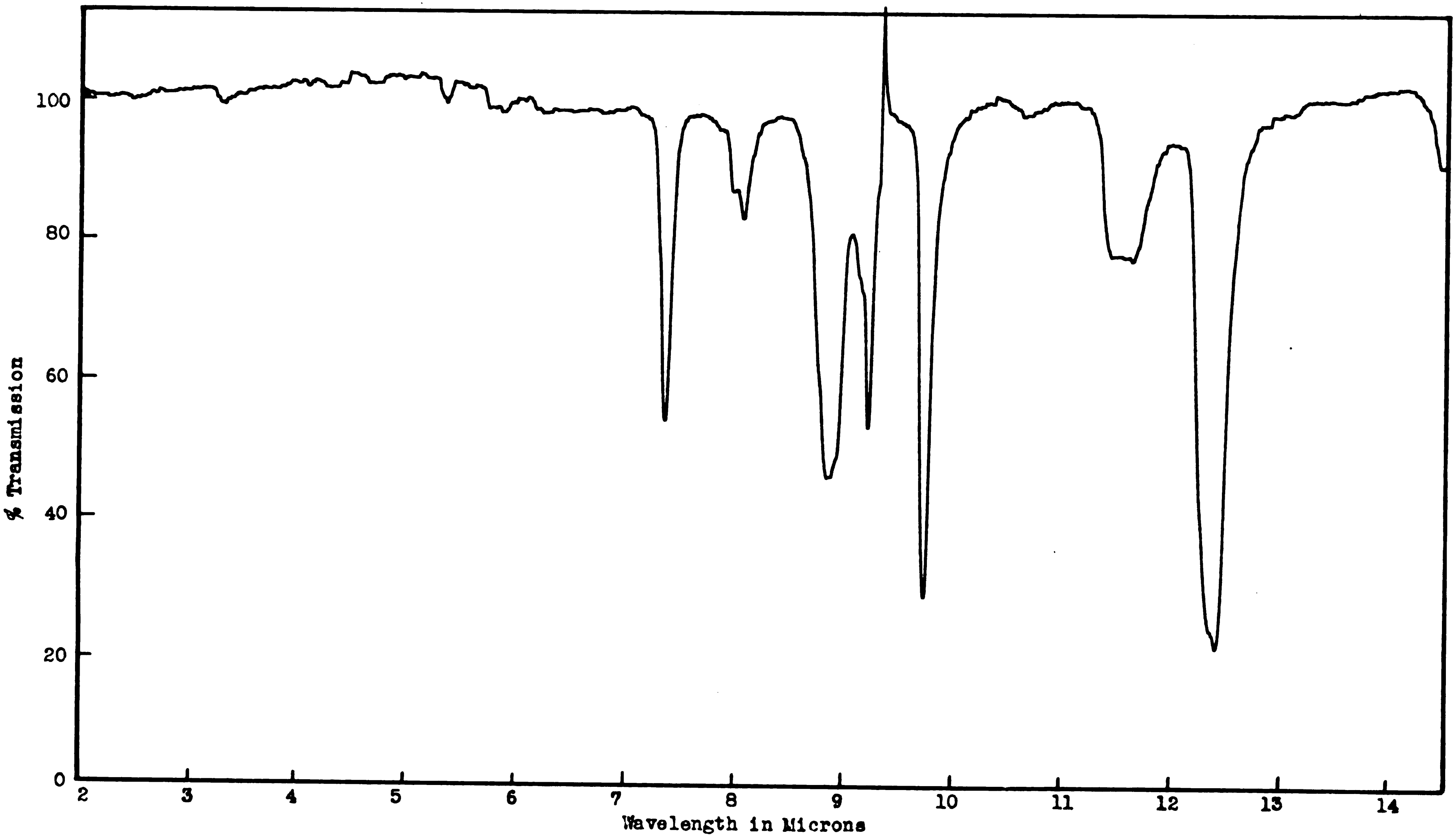

Figure 32. Infra-red Spectrum of Bis(3,4-Dichlorophenyl) Sulfide (0.065 Molar in CS_2)

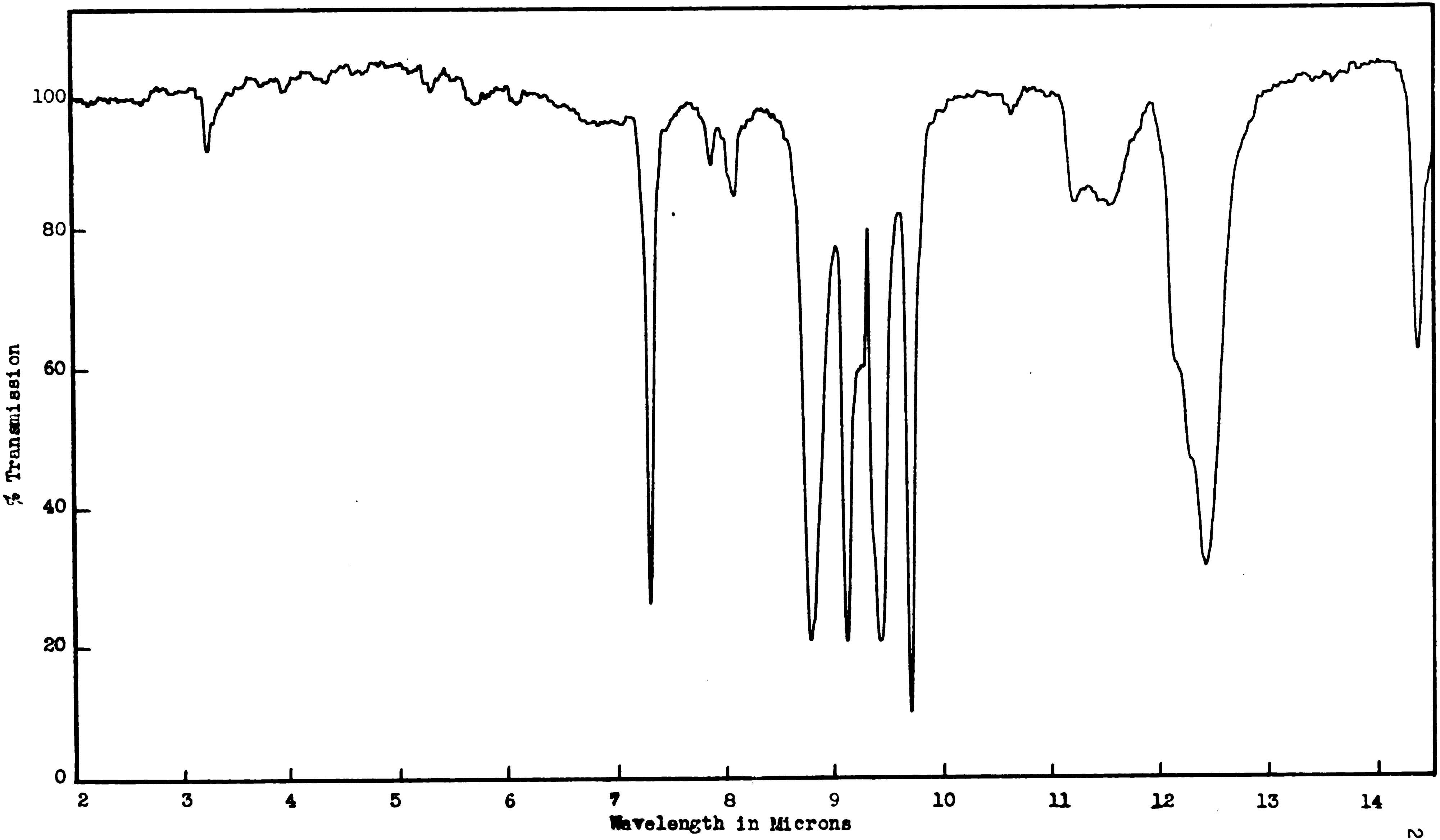

Figure 33. Infra-red Spectrum of Bis(3,4-Dichlorophenyl) Sulfoxide (0.065 Molar in CS_2)

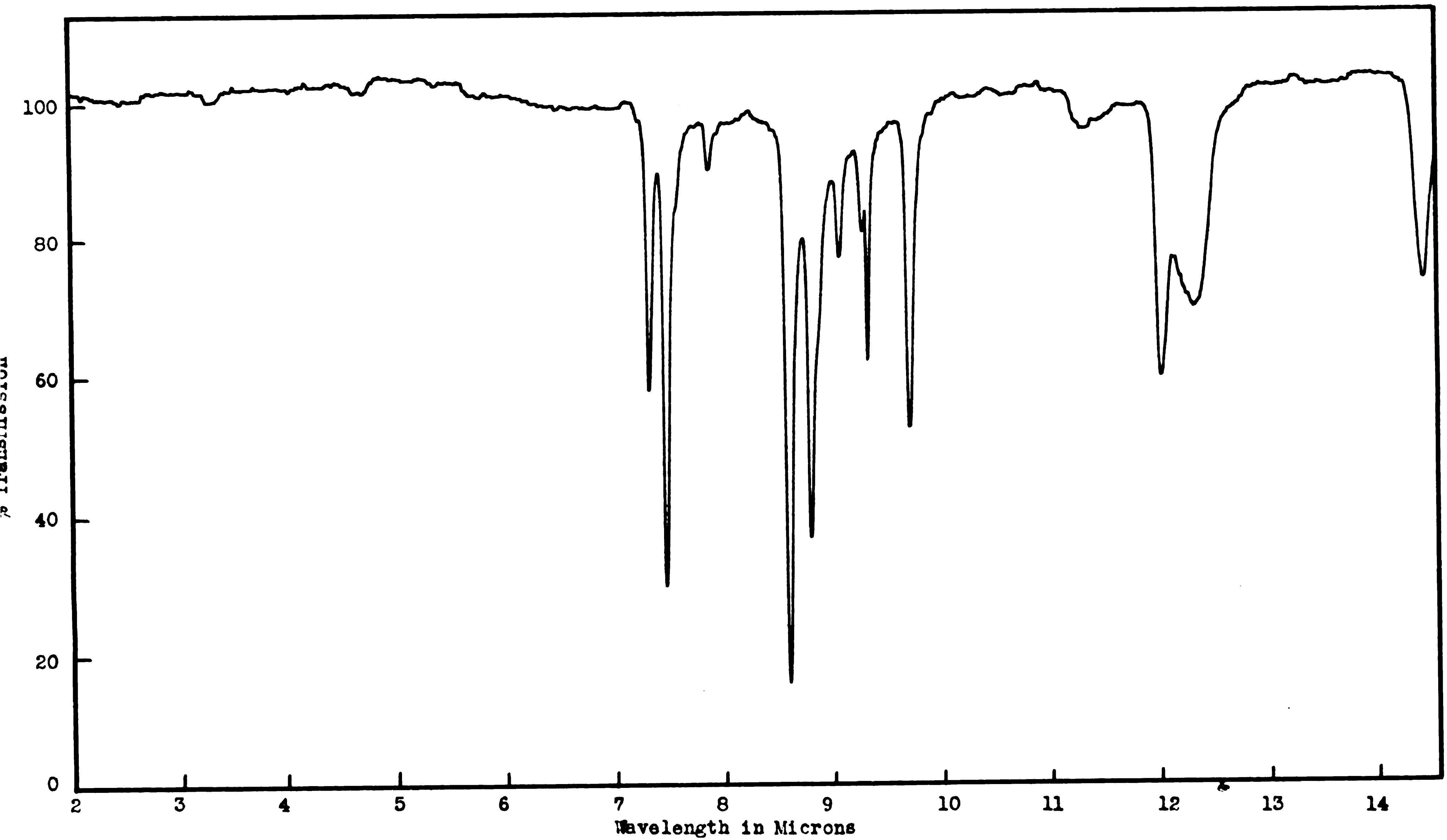

Figure 34. Infra-red Spectrum of Bis(3,4-Dichlorophenyl) Sulfone (0.022 Molar in CS_2)

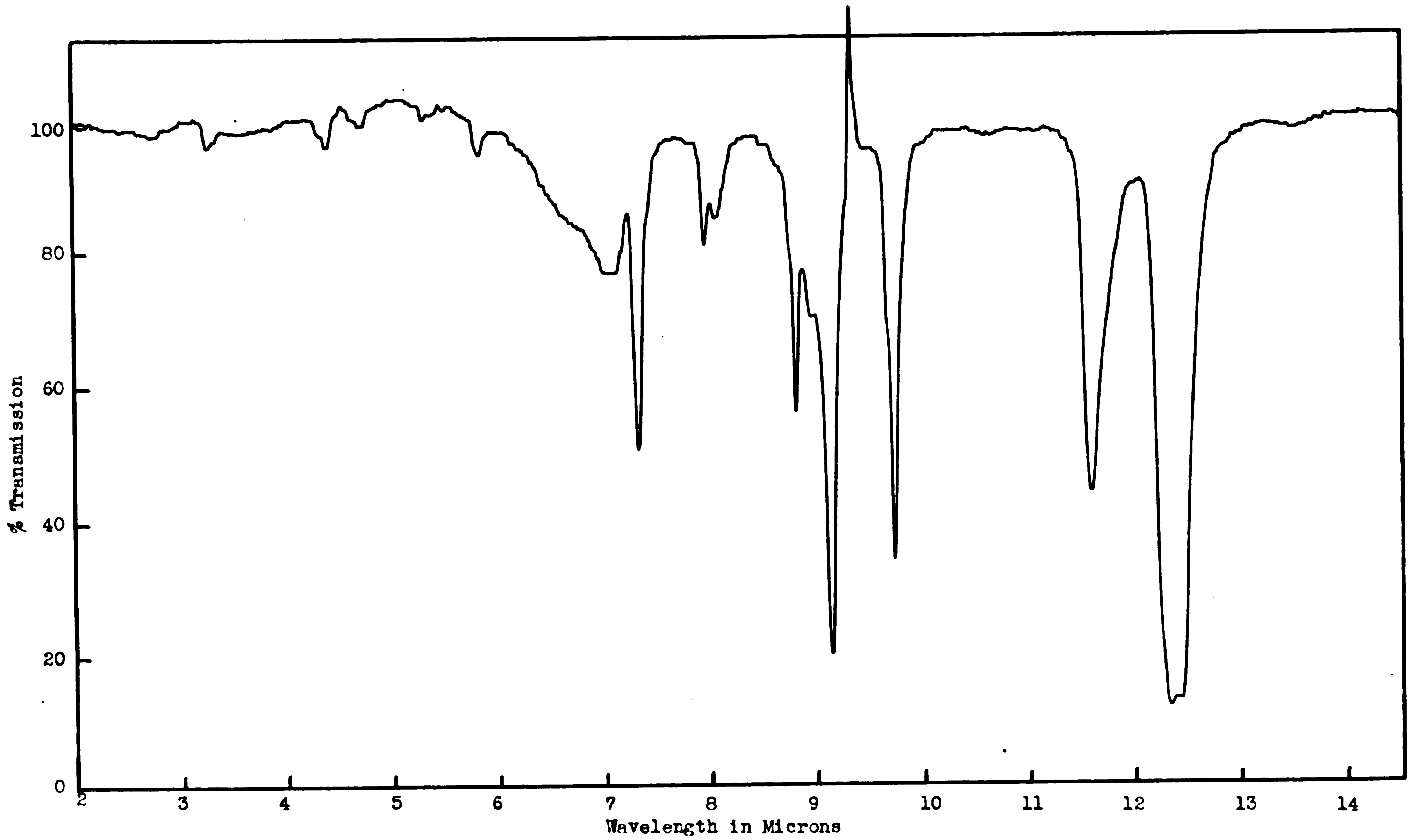

Figure 35. Infra-red Spectrum of Bis(2,4-Dichlorophenyl) Sulfide (0.065 Molar in CS_2)

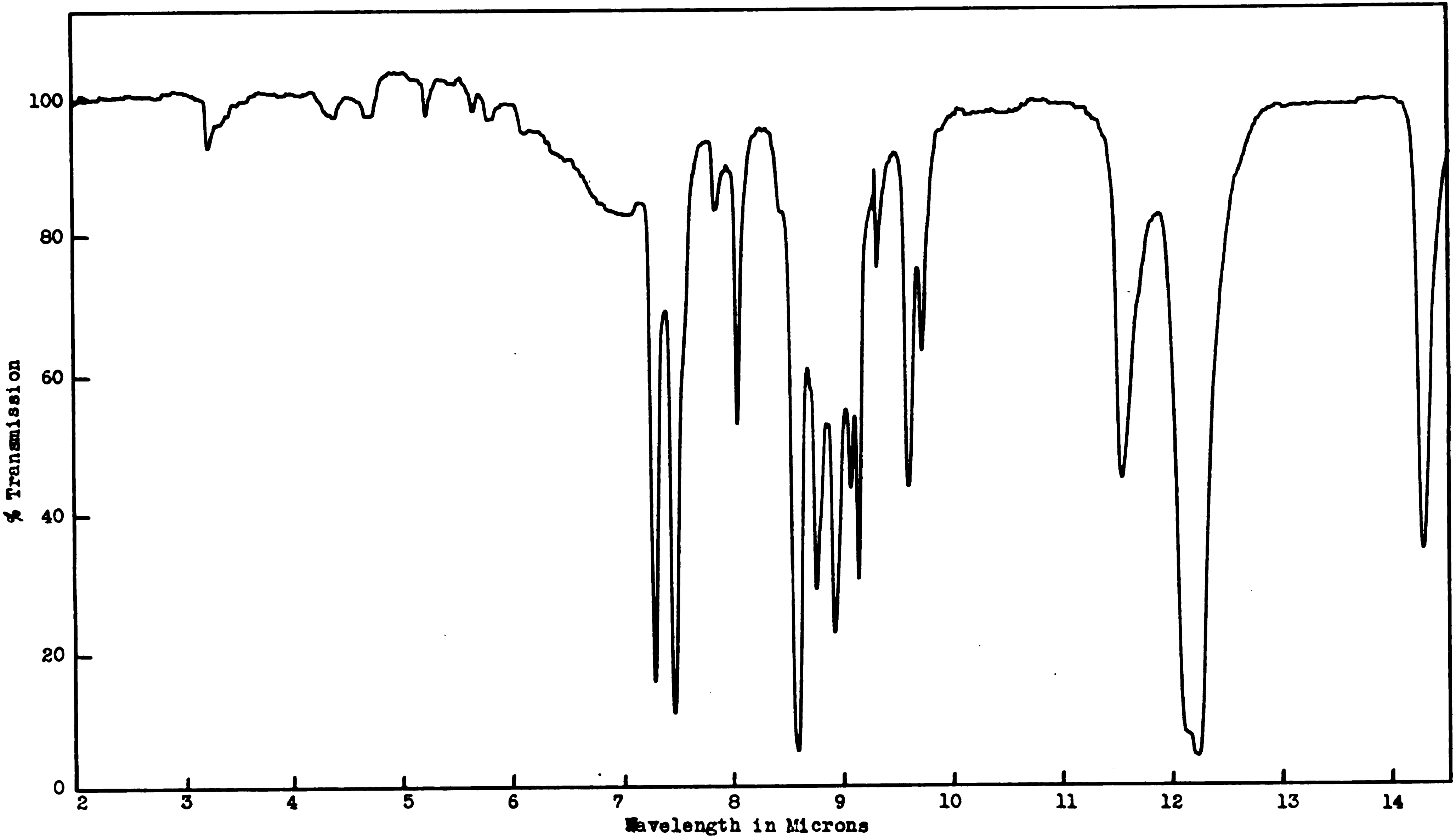

Figure 36. Infra-red Spectrum of Bis(2,4-Dichlorophenyl) Sulfone (0.065 Molar in CS_2)

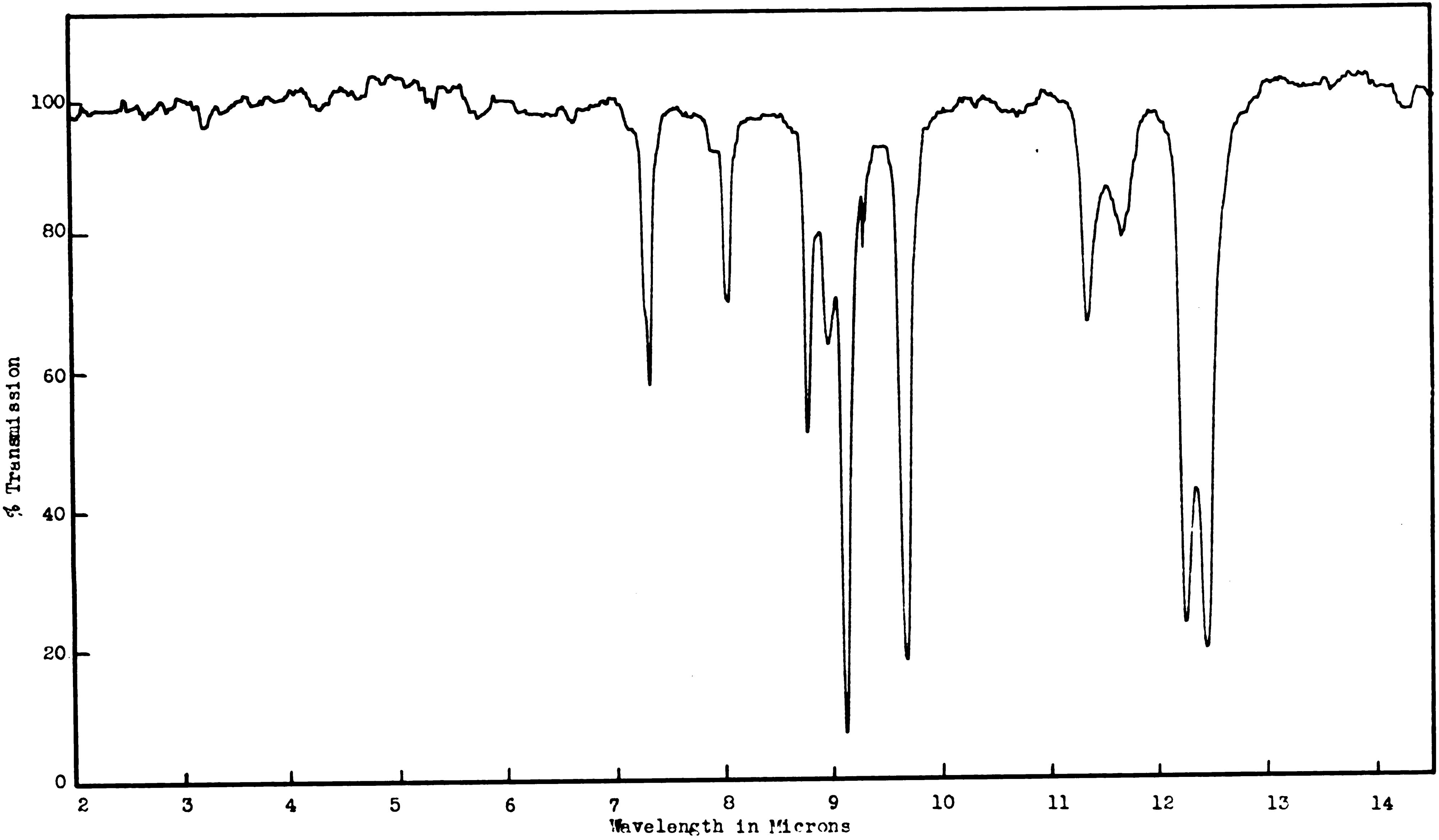

Figure 37. Infra-red Spectrum of Bis(2,5-Dichlorophenyl) Sulfide (0.065 Molar in CS_2)

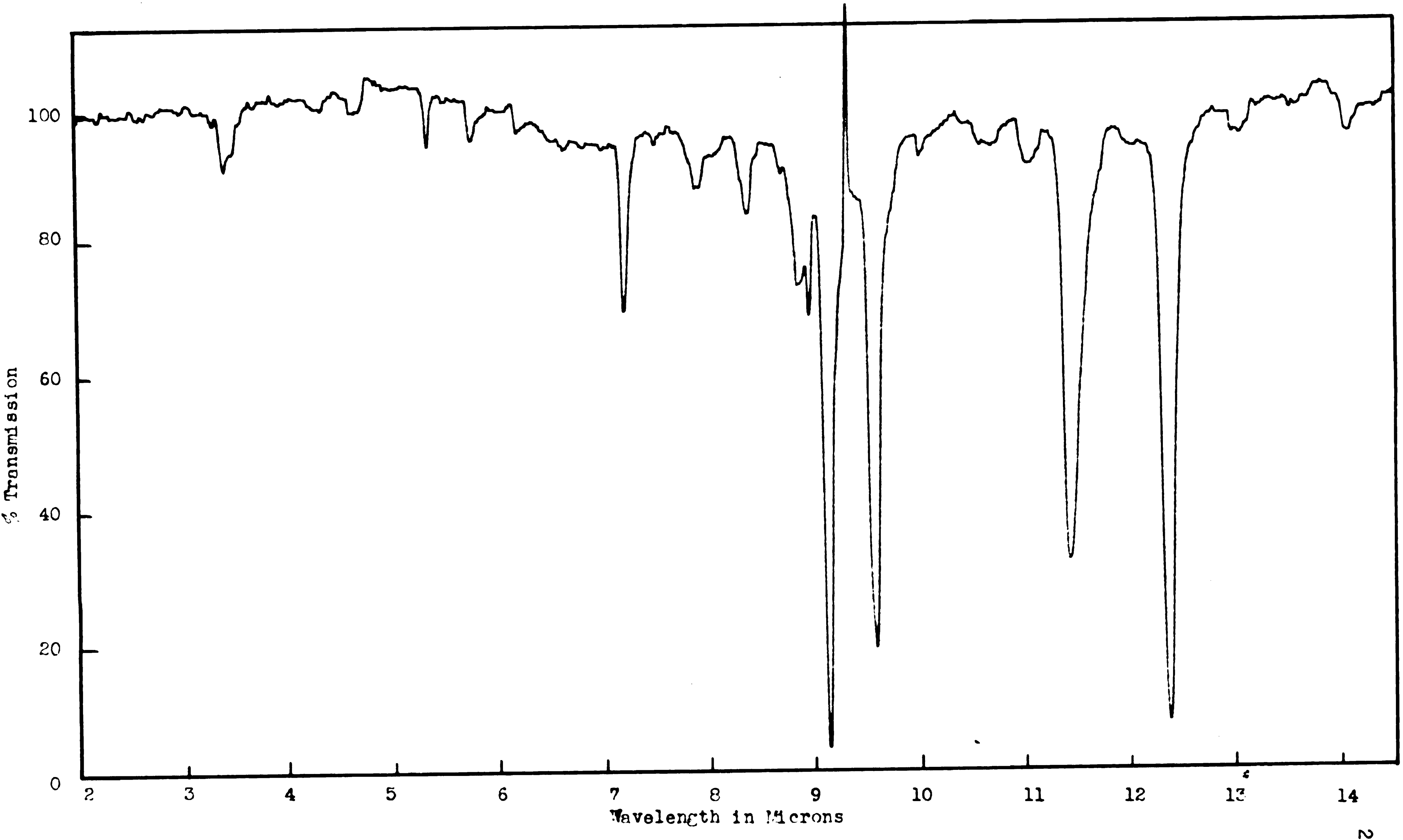

Figure 38. Infra-red Spectrum of Bis(2,5-Dichlorophenyl) Sulfoxide (0.065 Molar in CS_2)

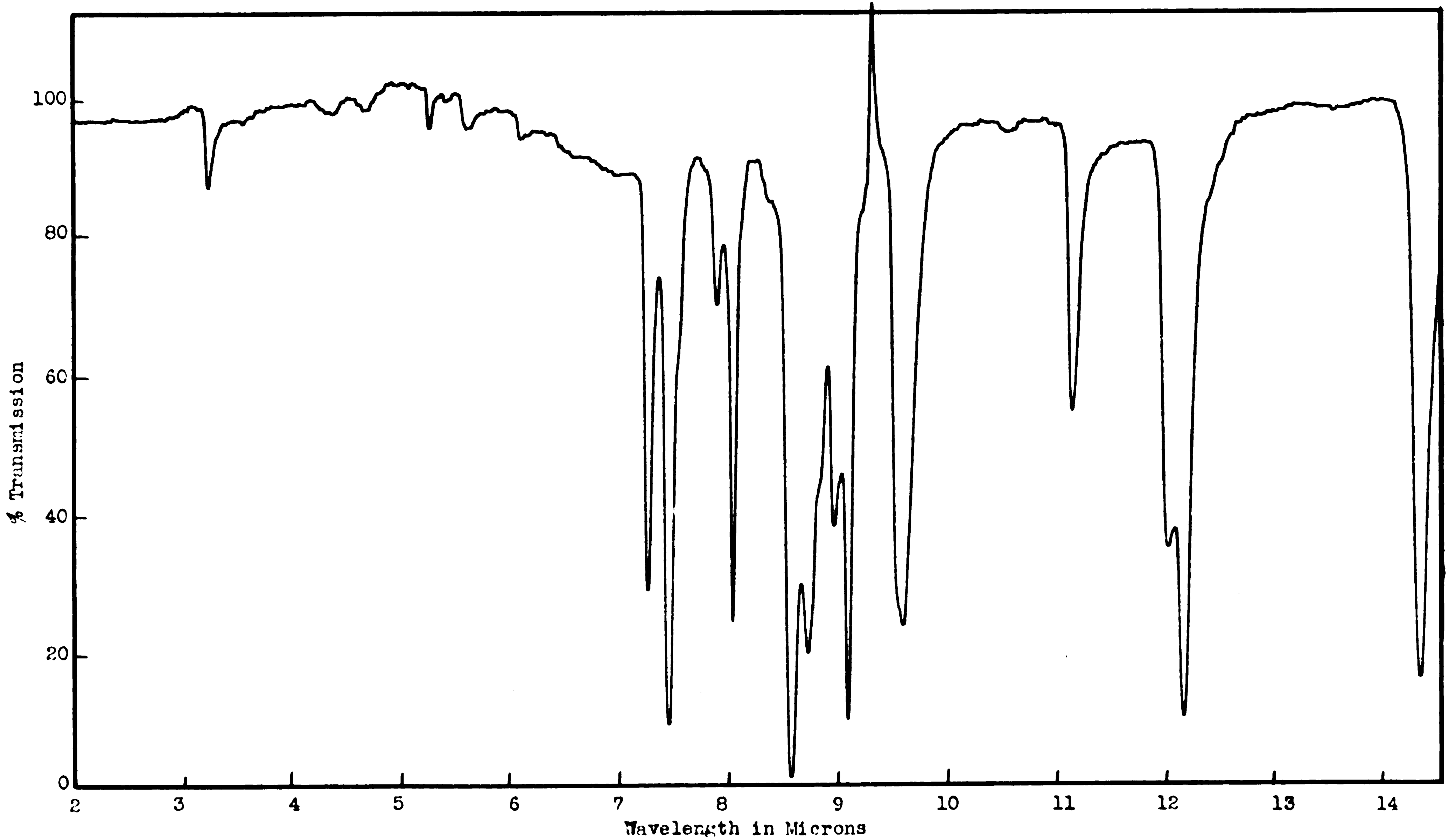

Figure 39. Infra-red Spectrum of Bis (2,5-Dichlorophenyl) Sulfone (0.065 Molar in CS_2)

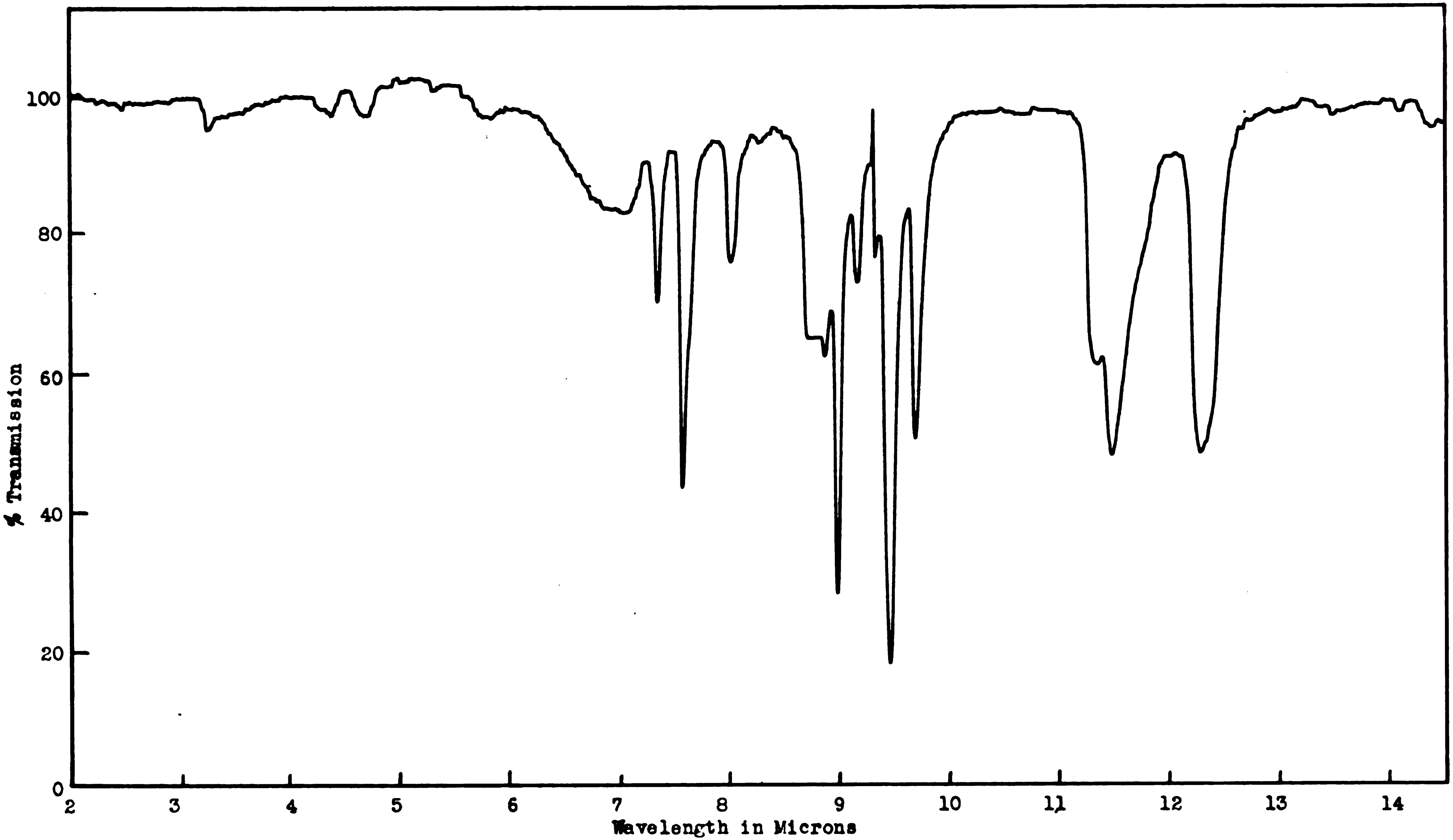

Figure 40. Infra-red Spectrum of 2,4,5-Trichlorophenyl 3',4'-Dichlorophenyl Sulfide (0.065 Molar in CS_2)

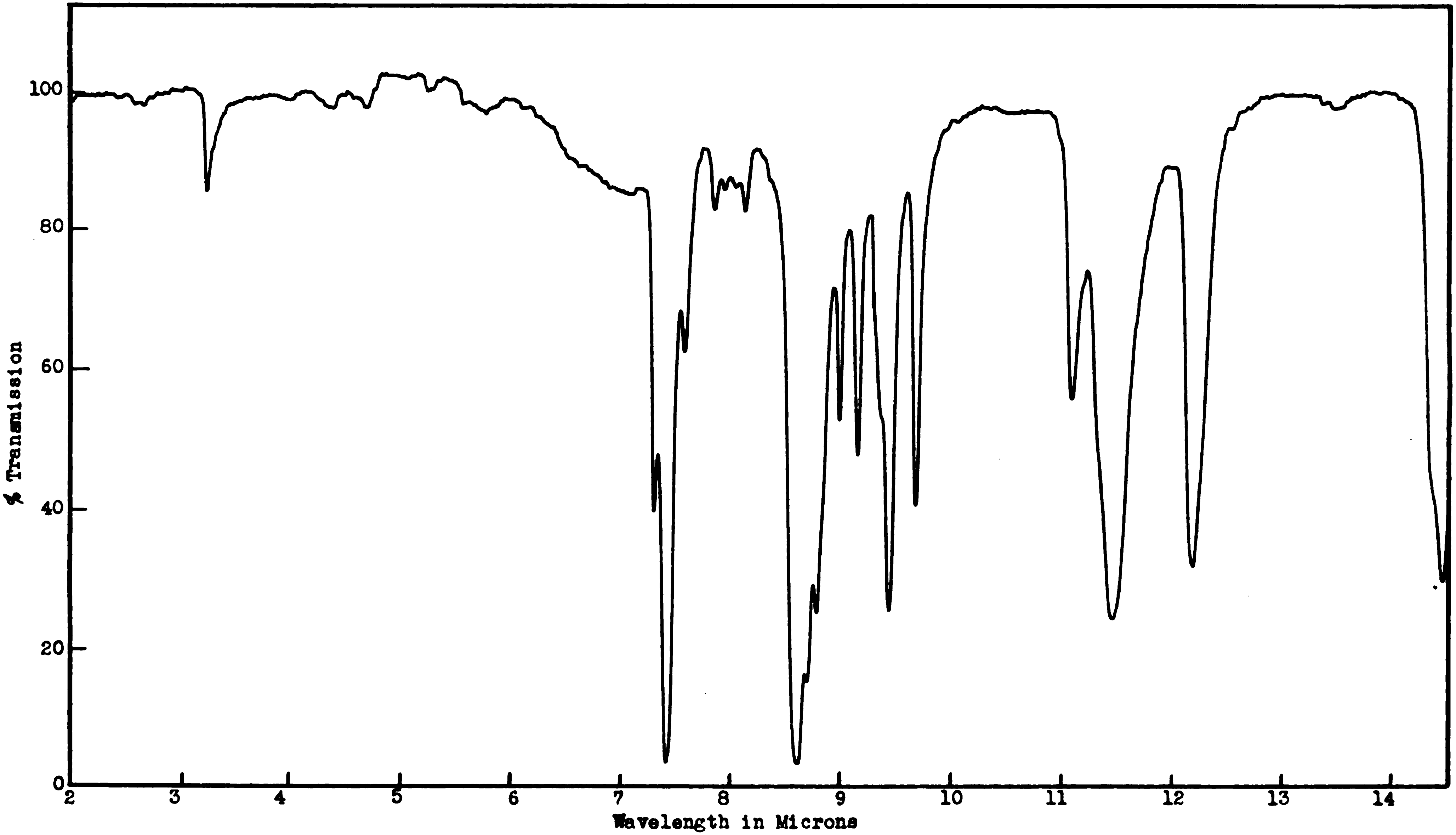

Figure 41. Infra-red Spectrum of 2,4,5-Trichlorophenyl 3',4'-Dichlorophenyl Sulfone (0.065 Molar in CS_2)

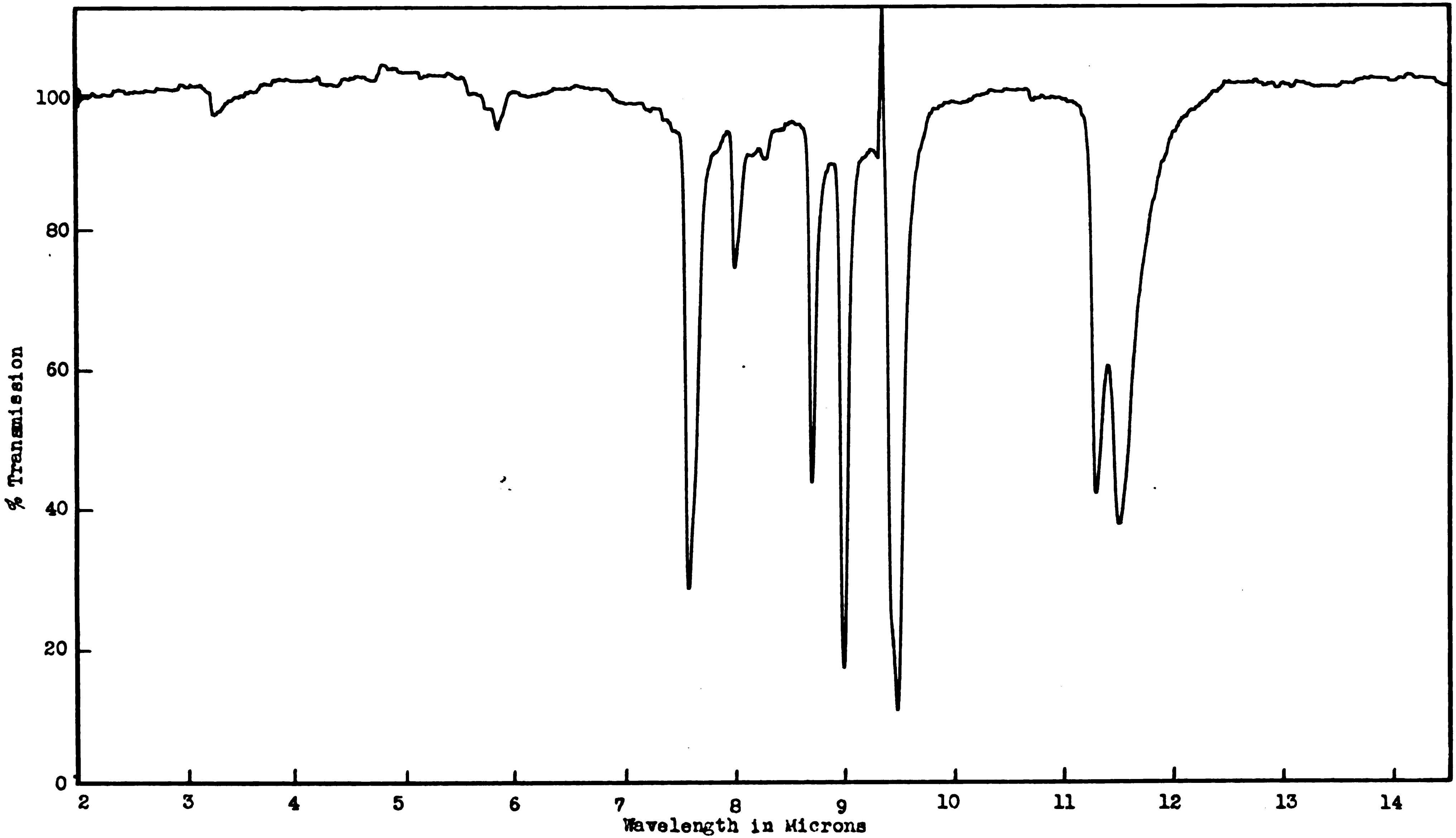

Figure 42. Infra-red Spectrum of Bis(2,4,5-Trichlorophenyl) Sulfide (0.065 Molar in CS_2)

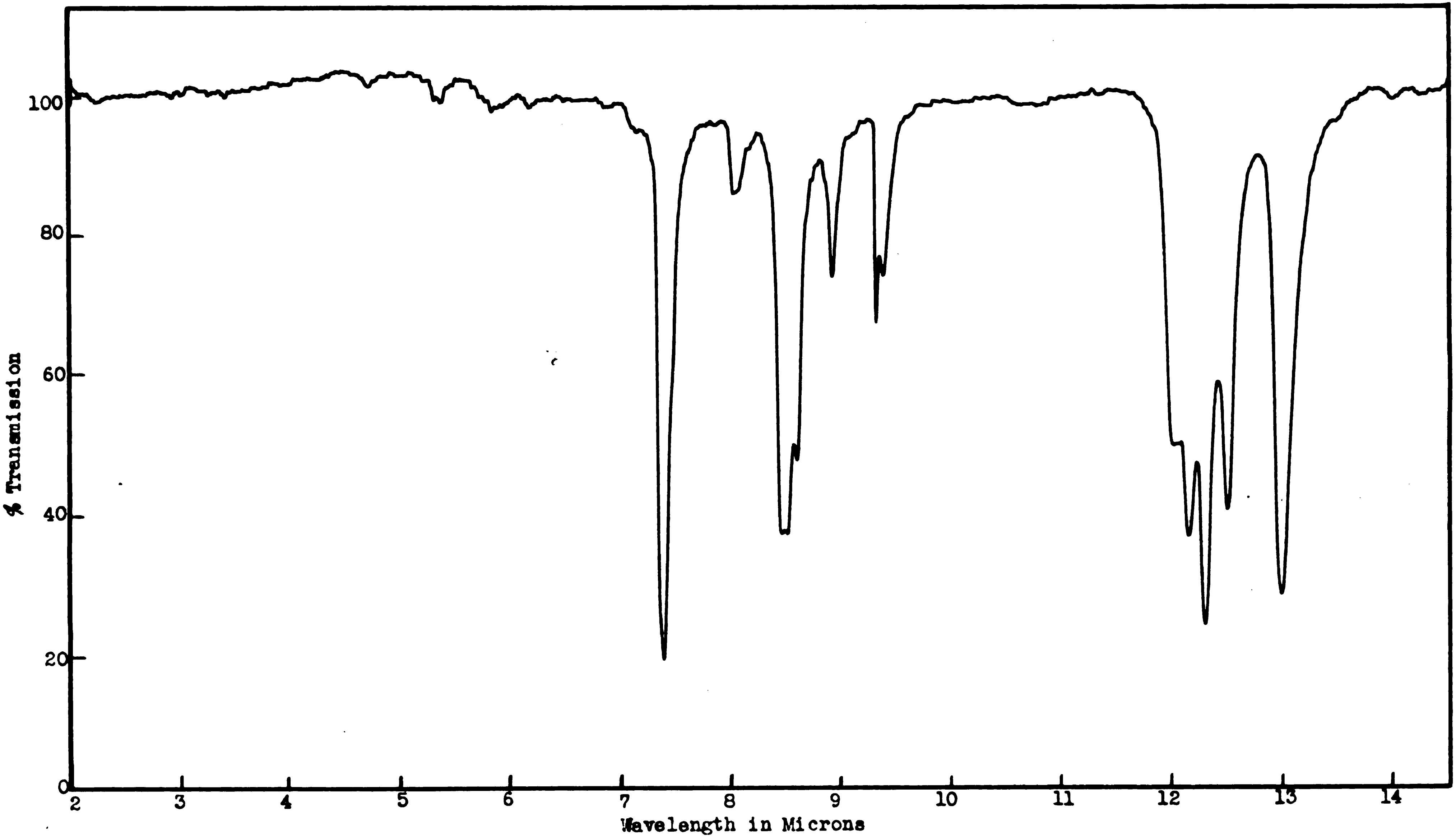

Figure 43. Infra-red Spectrum of Bis(2,3,4-Trichlorophenyl) Sulfide (0.065 Molar in CS_2)

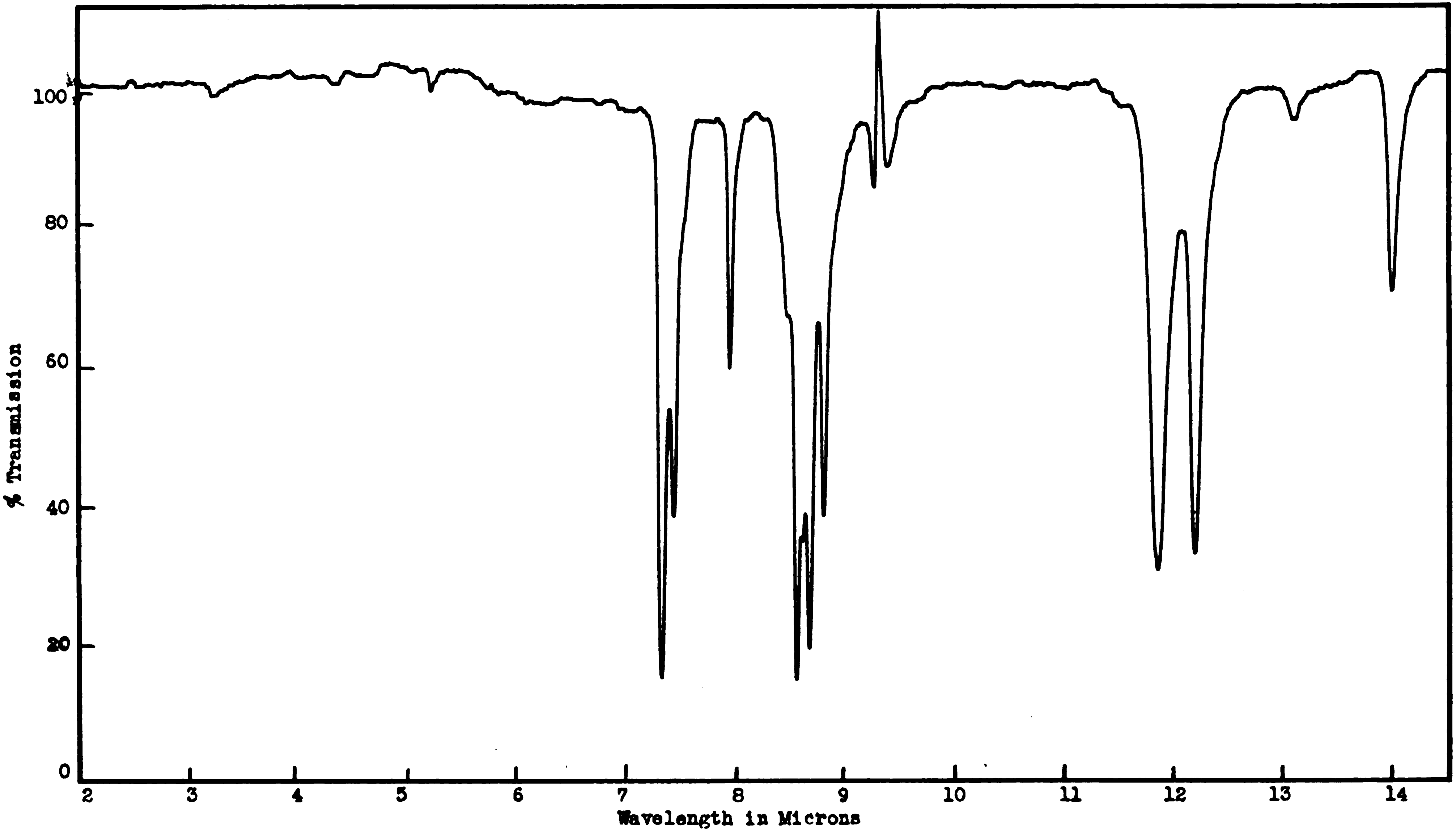

Figure 44. Infra-red Spectrum of Bis(2,3,4-Trichlorophenyl) Sulfone (0.032 Molar in CS_2)

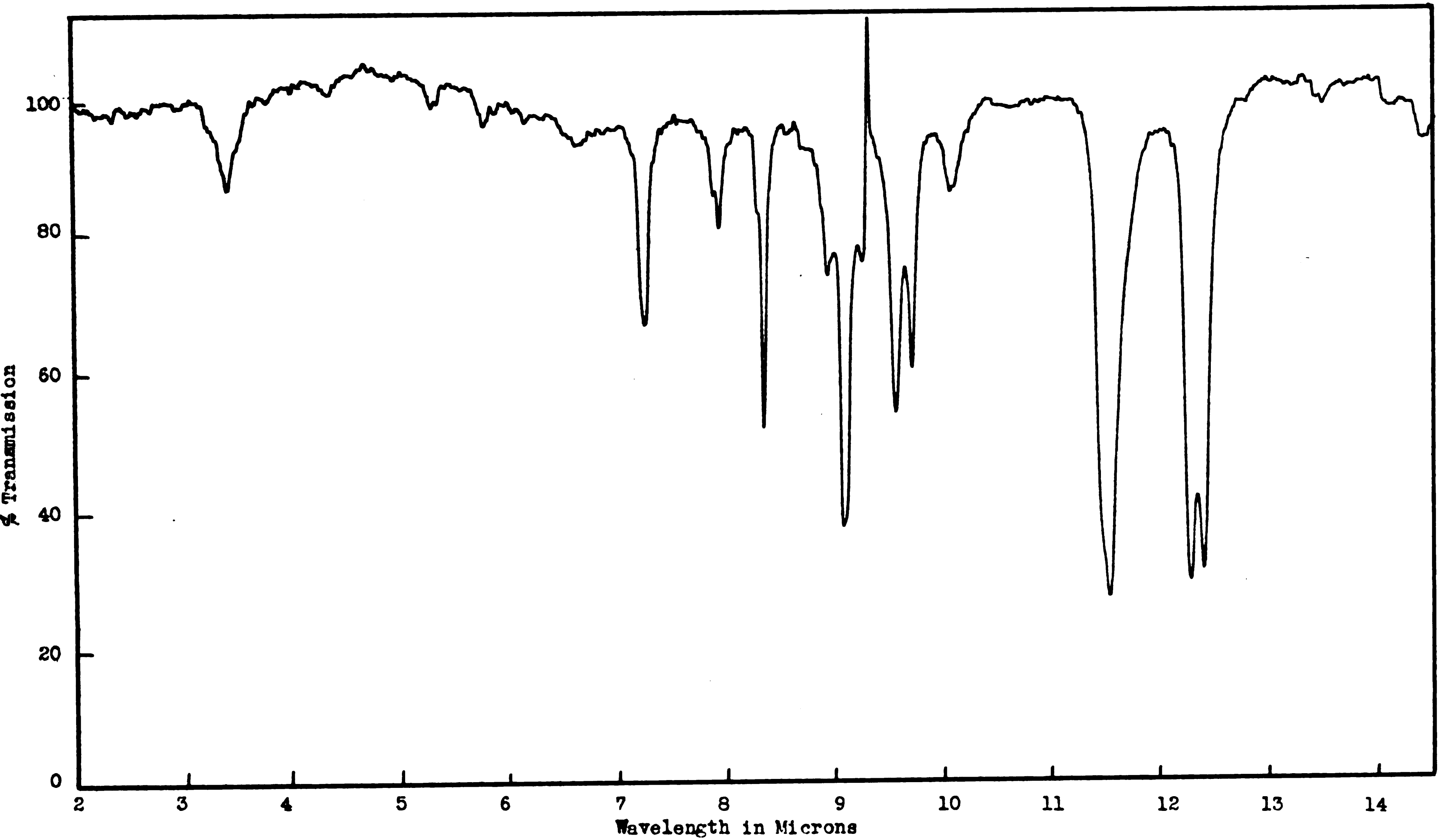

Figure 45. Infra-red Spectrum of Bis(4-Chloro-2-Methylphenyl) Sulfide (0.065 Molar in CS_2)

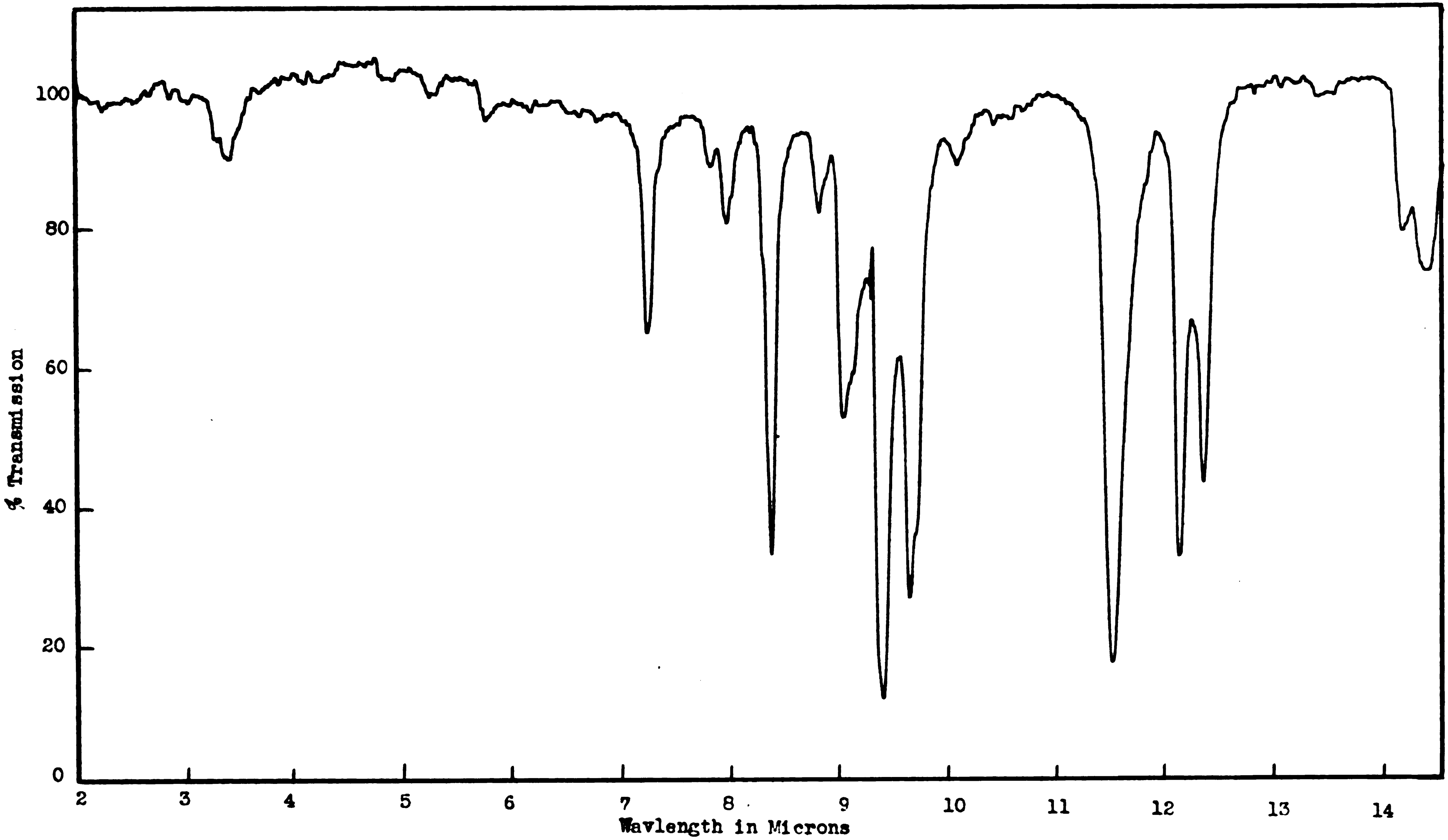

Figure 46. Infra-red Spectrum of Bis(4-Chloro-2-Methylphenyl) Sulfoxide (0.065 Molar in CS_2)

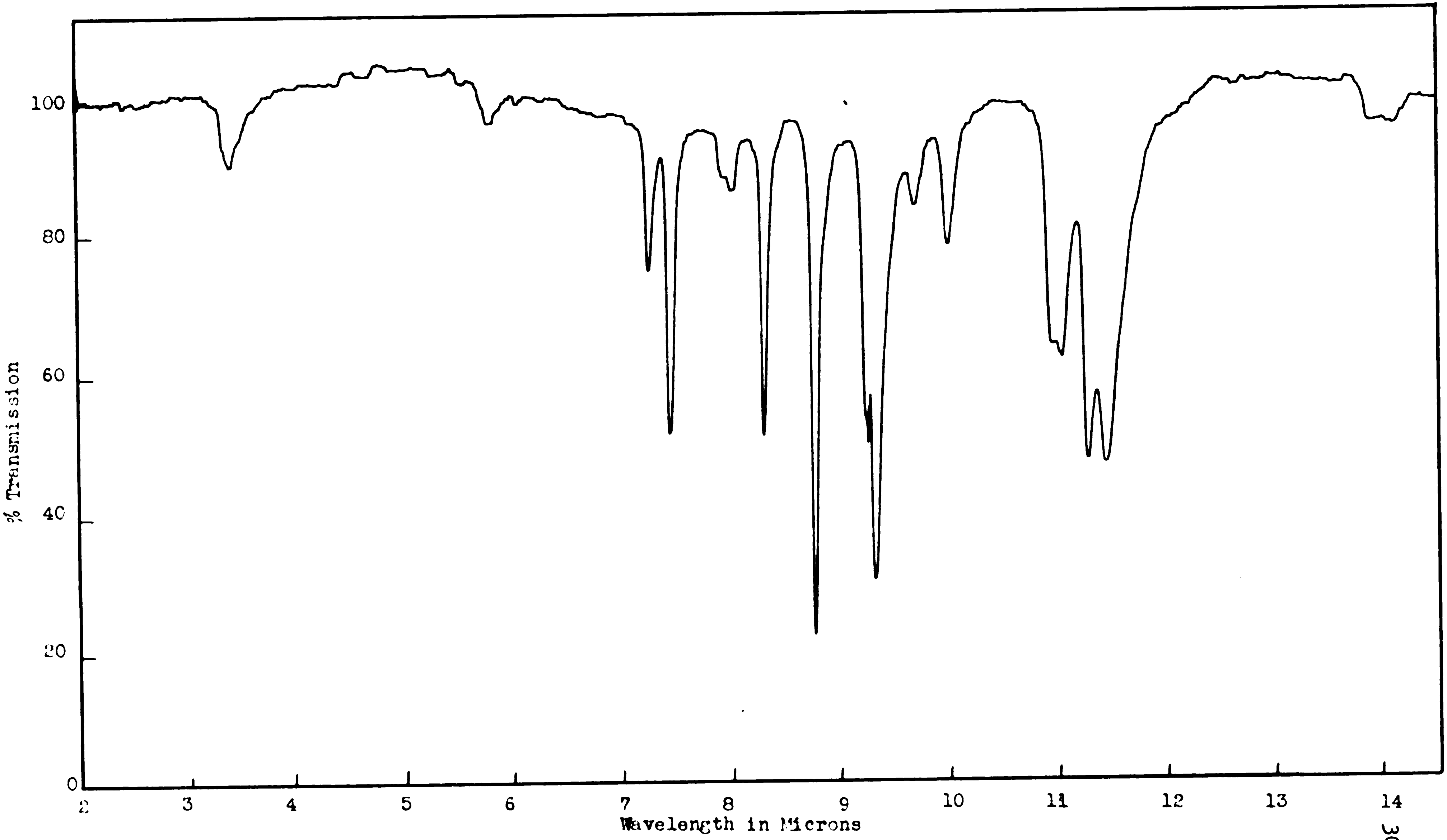

Figure 47. Infra-red Spectrum of Bis(2-Methyl-4,5-Dichlorophenyl) Sulfide (0.065 Molar in CS_2)

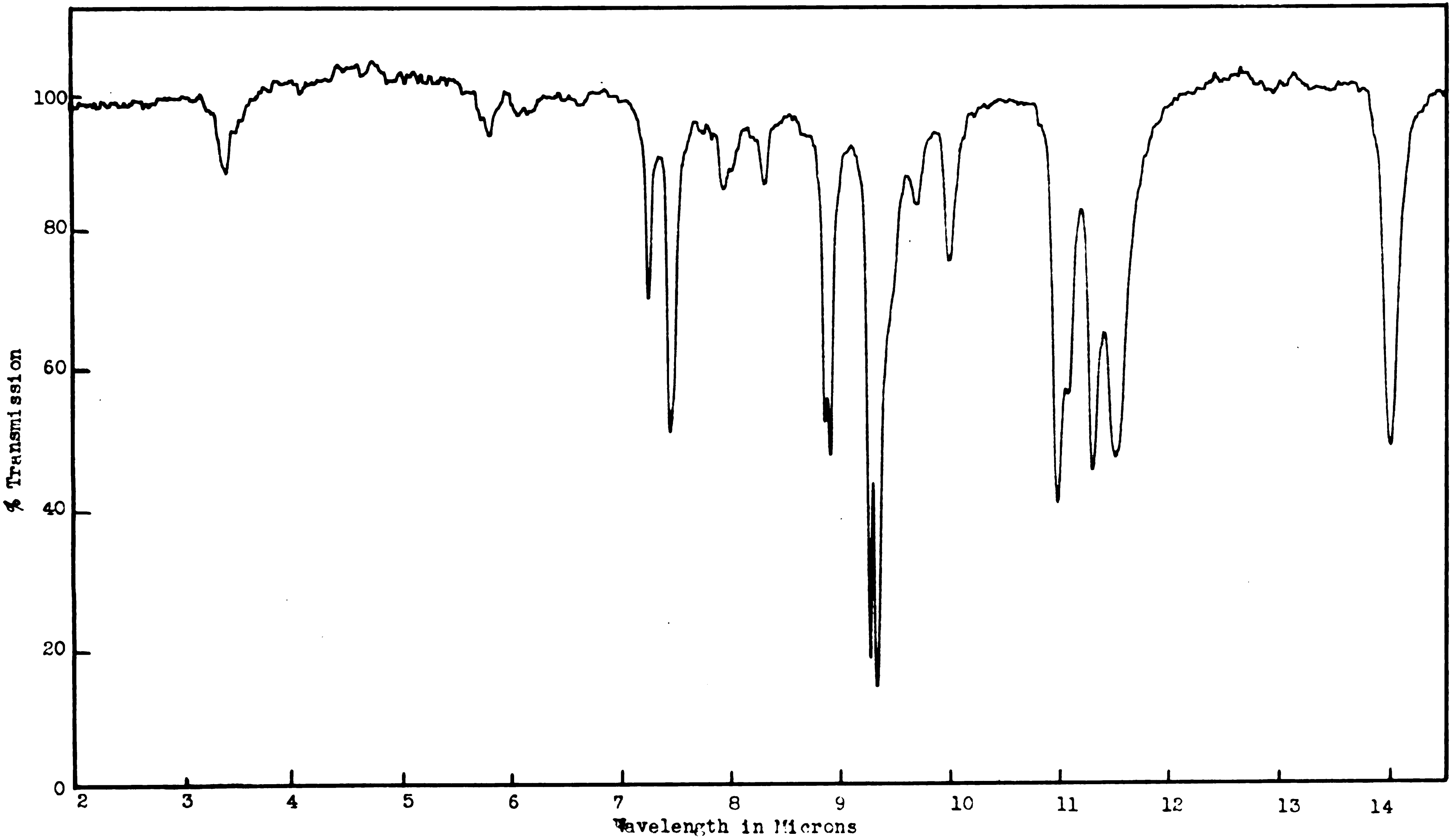

Figure 48. Infra-red Spectrum of Bis(2,4-Dichloro-5-Methylphenyl) Sulfide (0.065 Molar in CS_2)

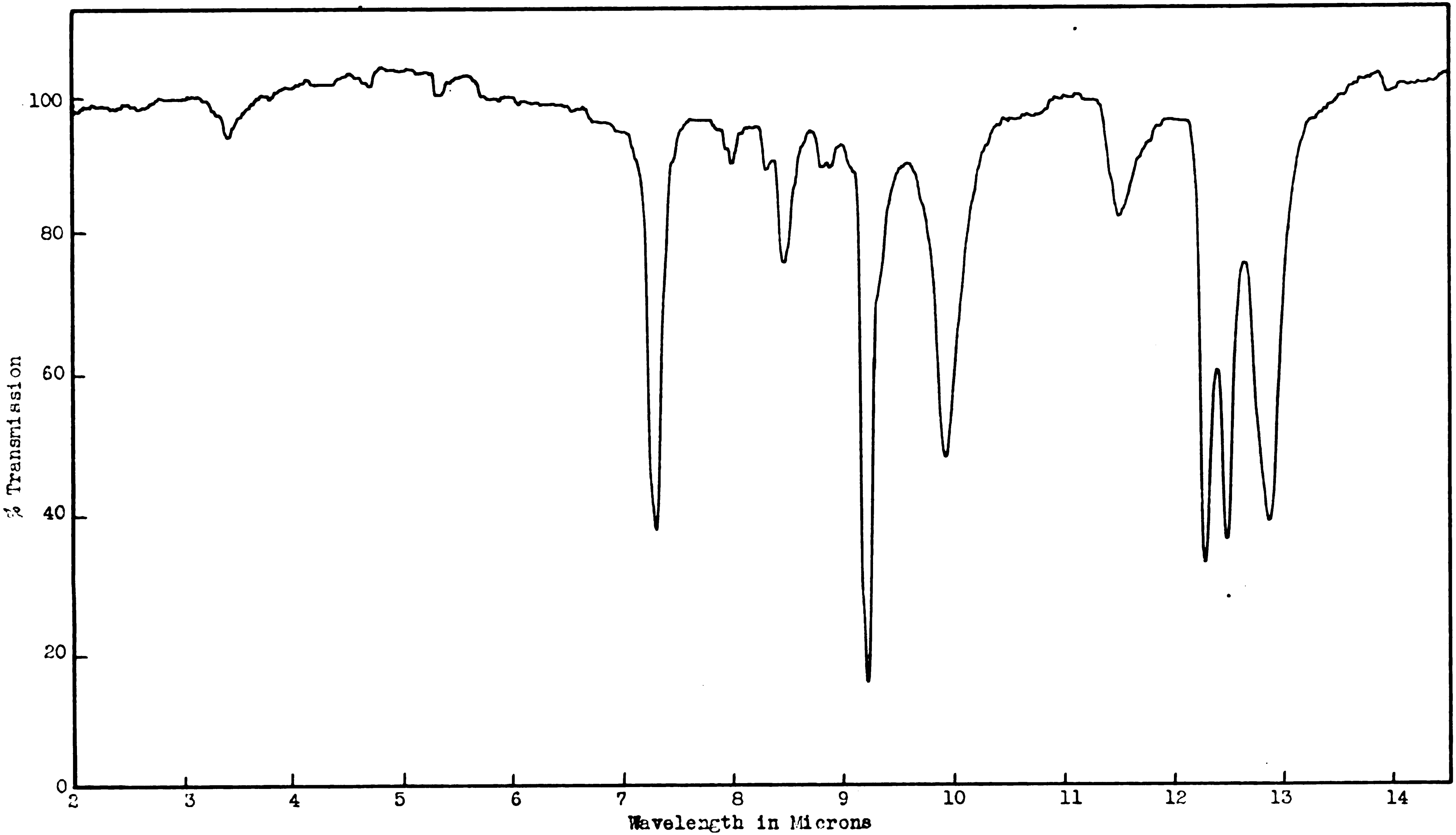

Figure 49. Infra red Spectrum of Bis(2,4-Dichloro-3-Methyl phenyl) Sulfide (0.065 Molar in CS_2)

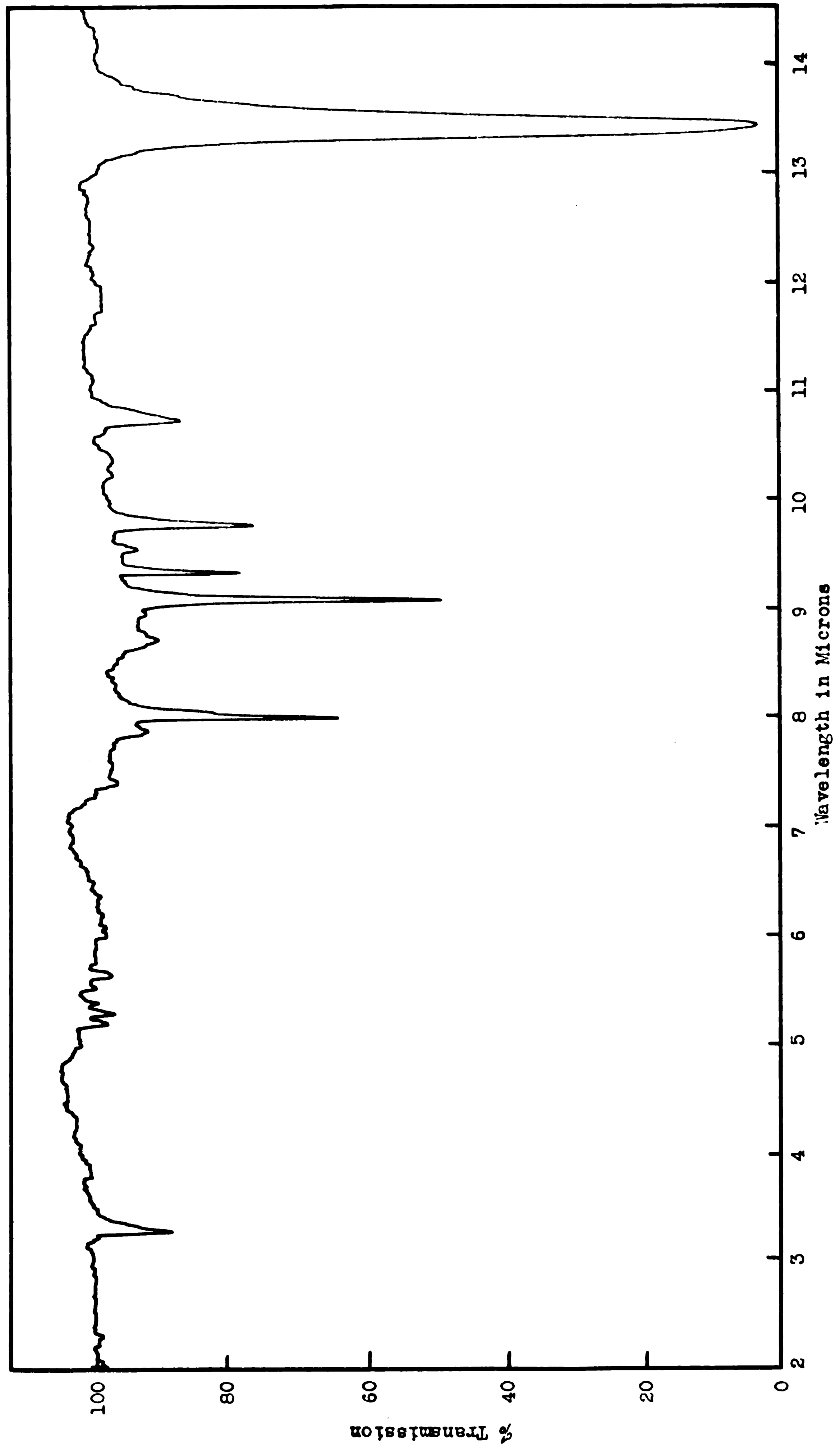

Figure 50. Infra-red Spectrum of Thianthrene (0.065 Molar in CS_2)

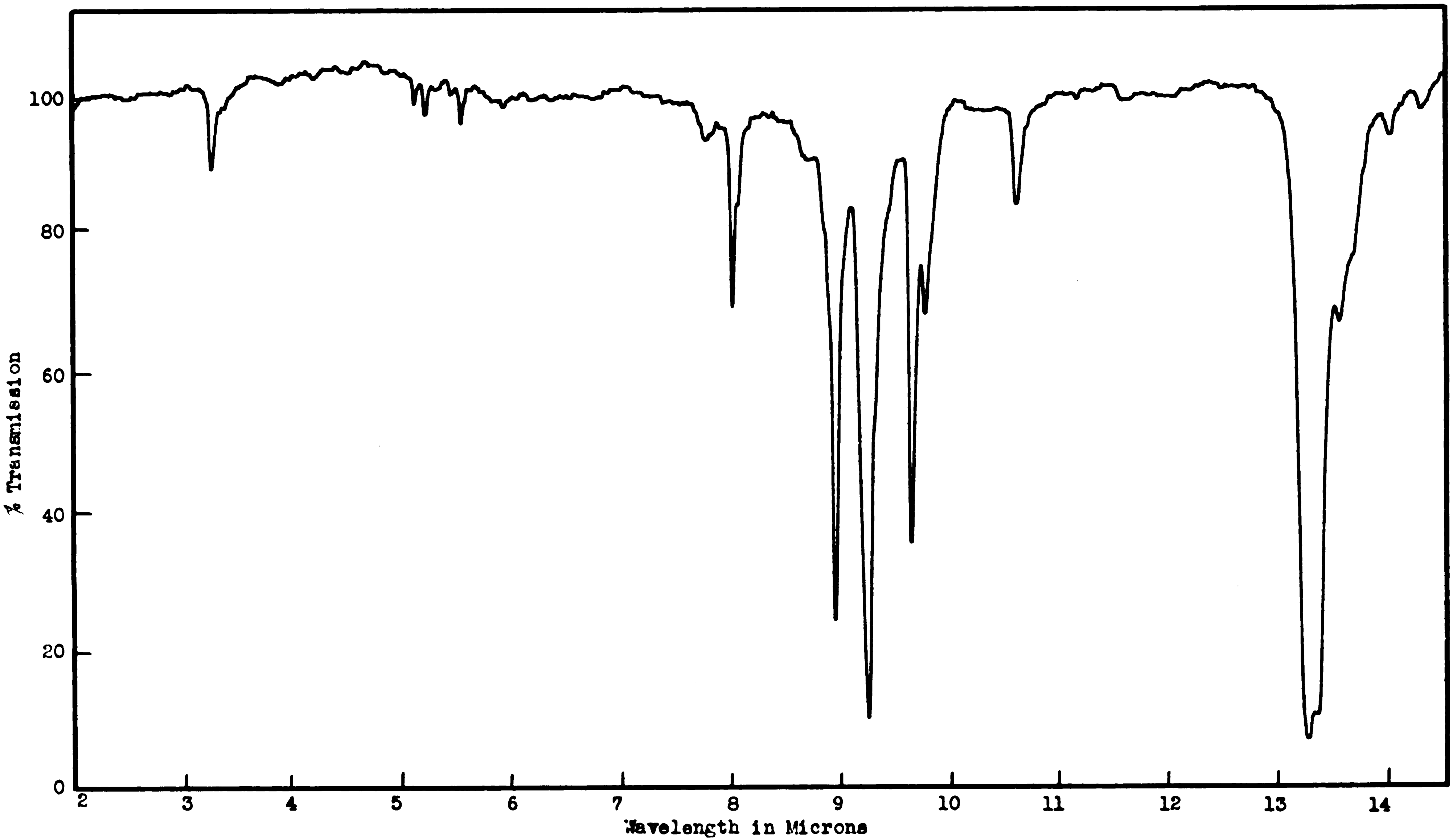

Figure 51. Infra-red Spectrum of Thianthrene-5-Oxide (0.065 Molar in CS_2)

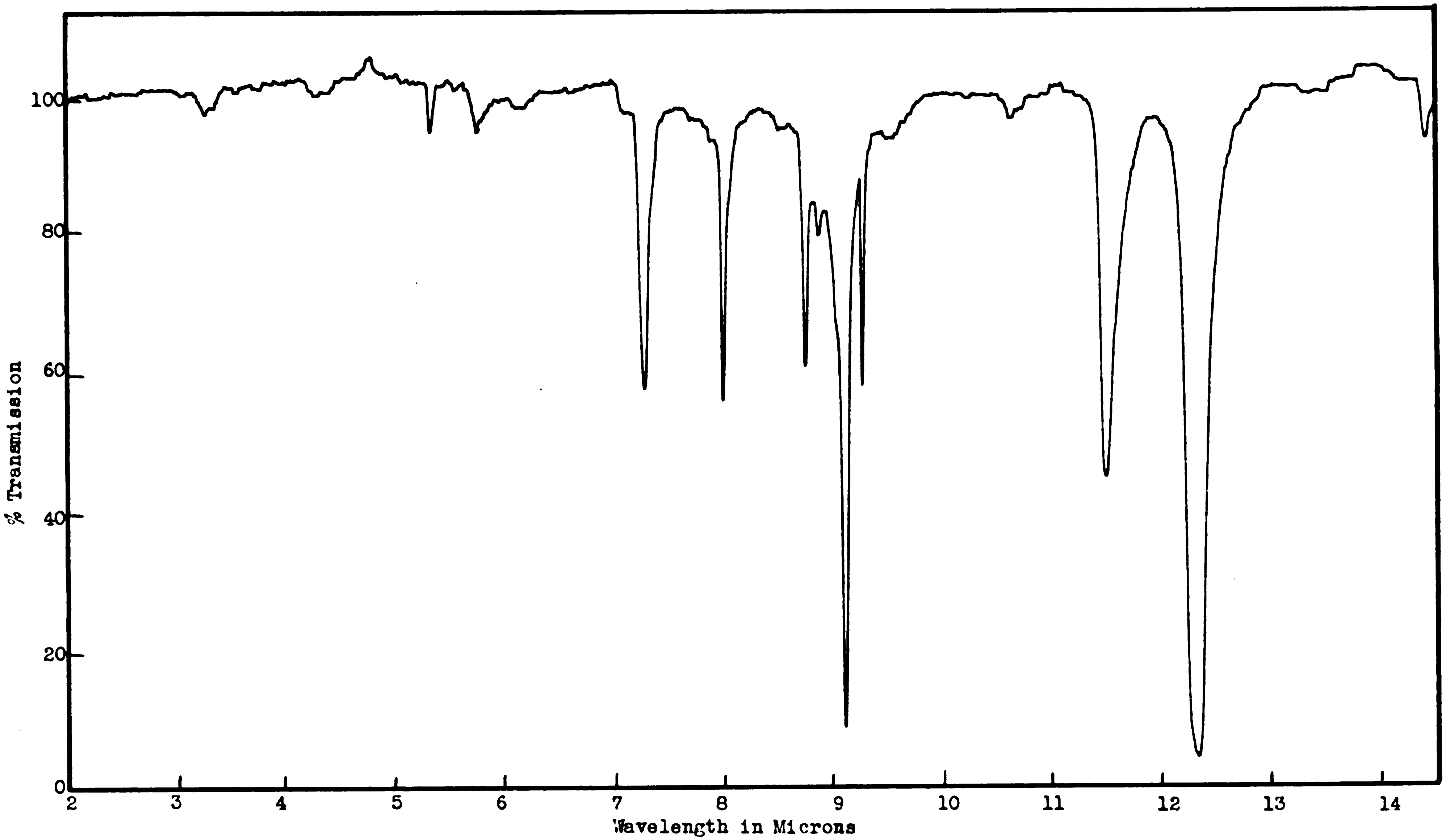

Figure 52. Infra-red Spectrum of 2,7-Dichlorothianthrene (0.065 Molar in CS_2)

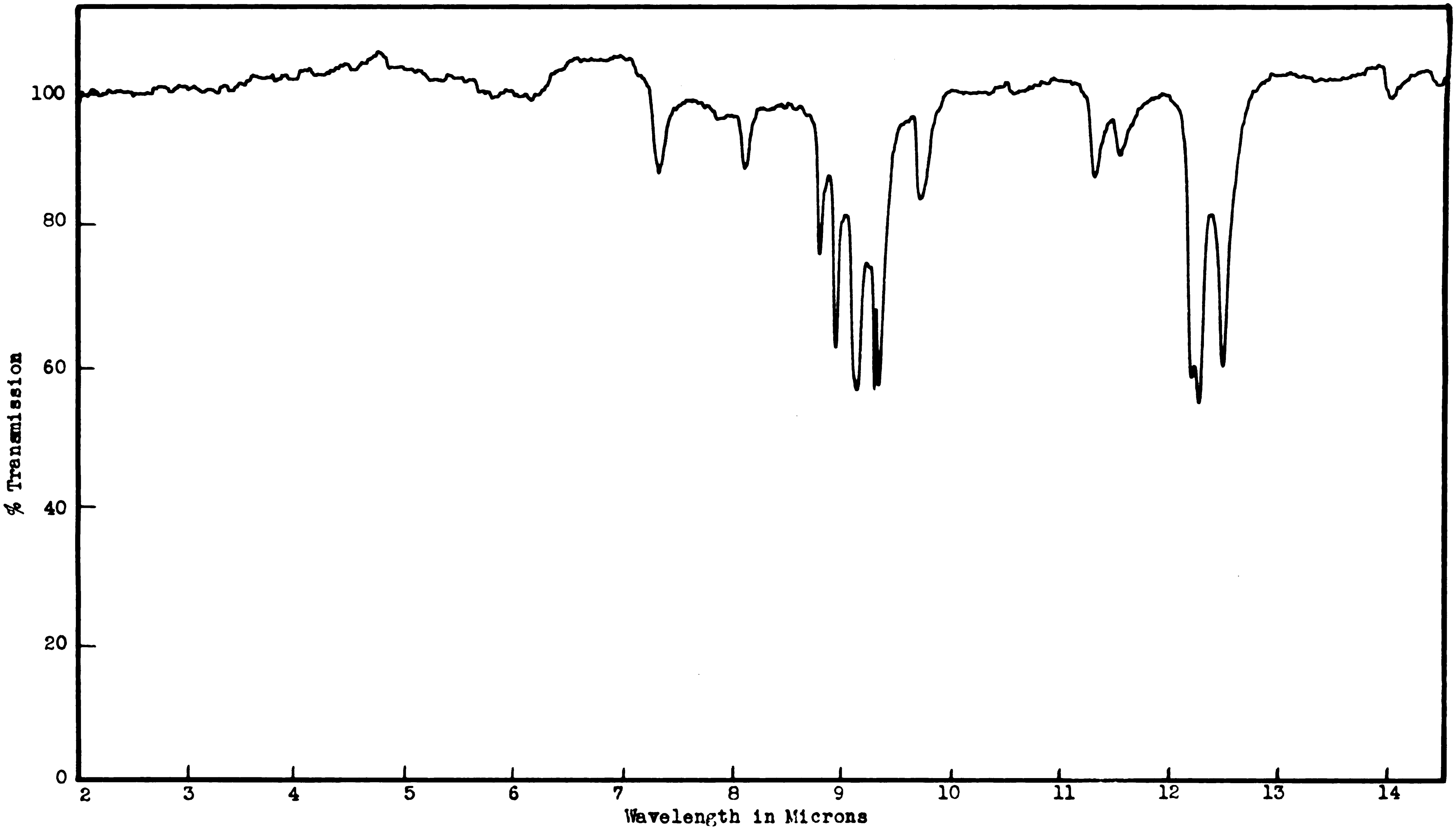

Figure 53. Infra-red Spectrum of 2,7-Dichlorothianthrene-5-Oxide (0.022 Moler in CS_2)

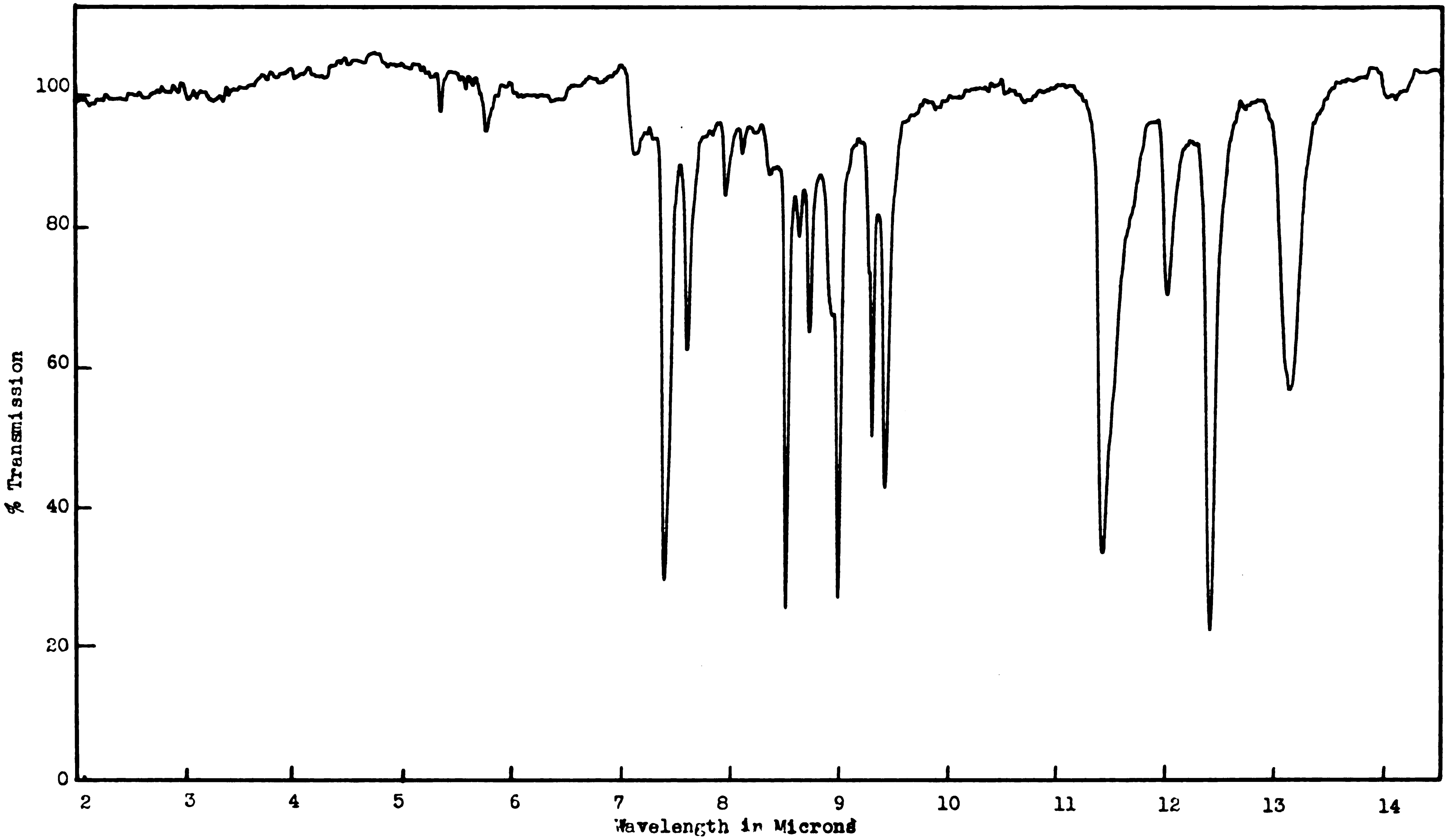

Figure 54. Infra-red Spectrum of 1,2,7,8-Tetrachlorothianthrene (0.065 Molar in CS_2)

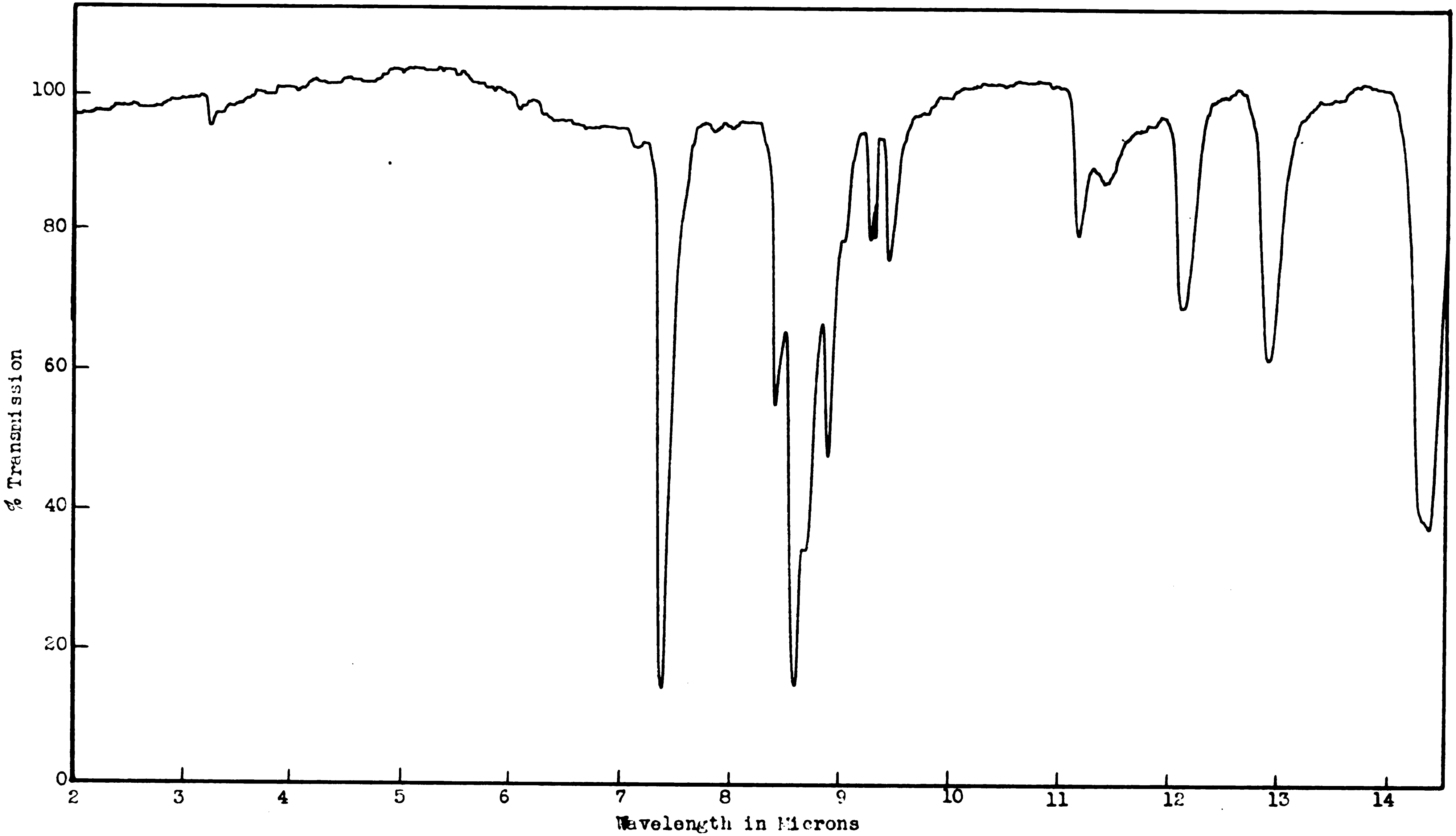

Figure 55. Infra-red Spectrum of 1,2,7,8-Tetrachlorothianthrene-5,5,10,10-Tetroxide (0.022 Molar in CS_2)

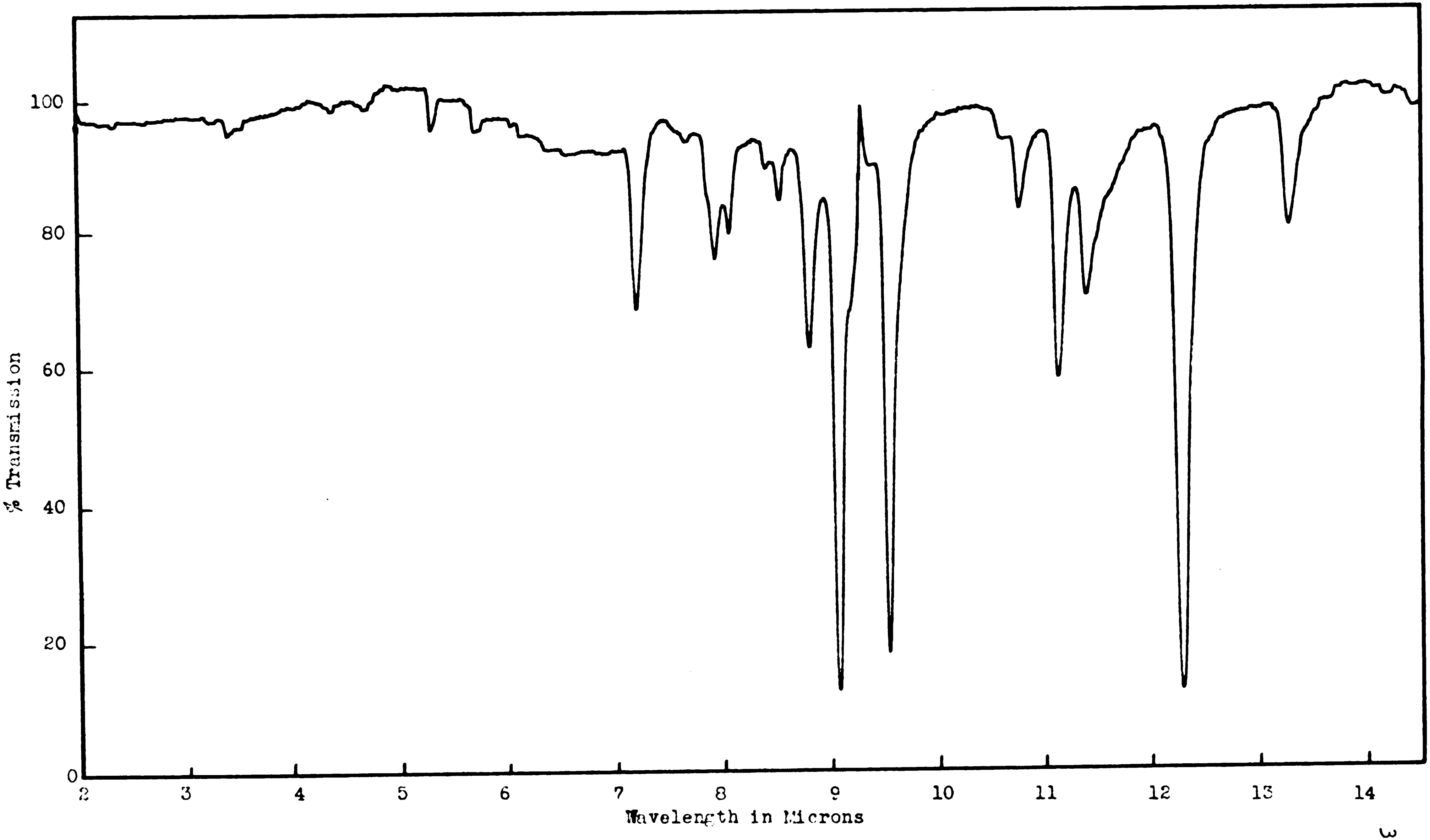

Figure 56. Infra-red Spectrum of 1,4,6,9-Tetrachlorothianthrene (0.065 Molar in CS_2)

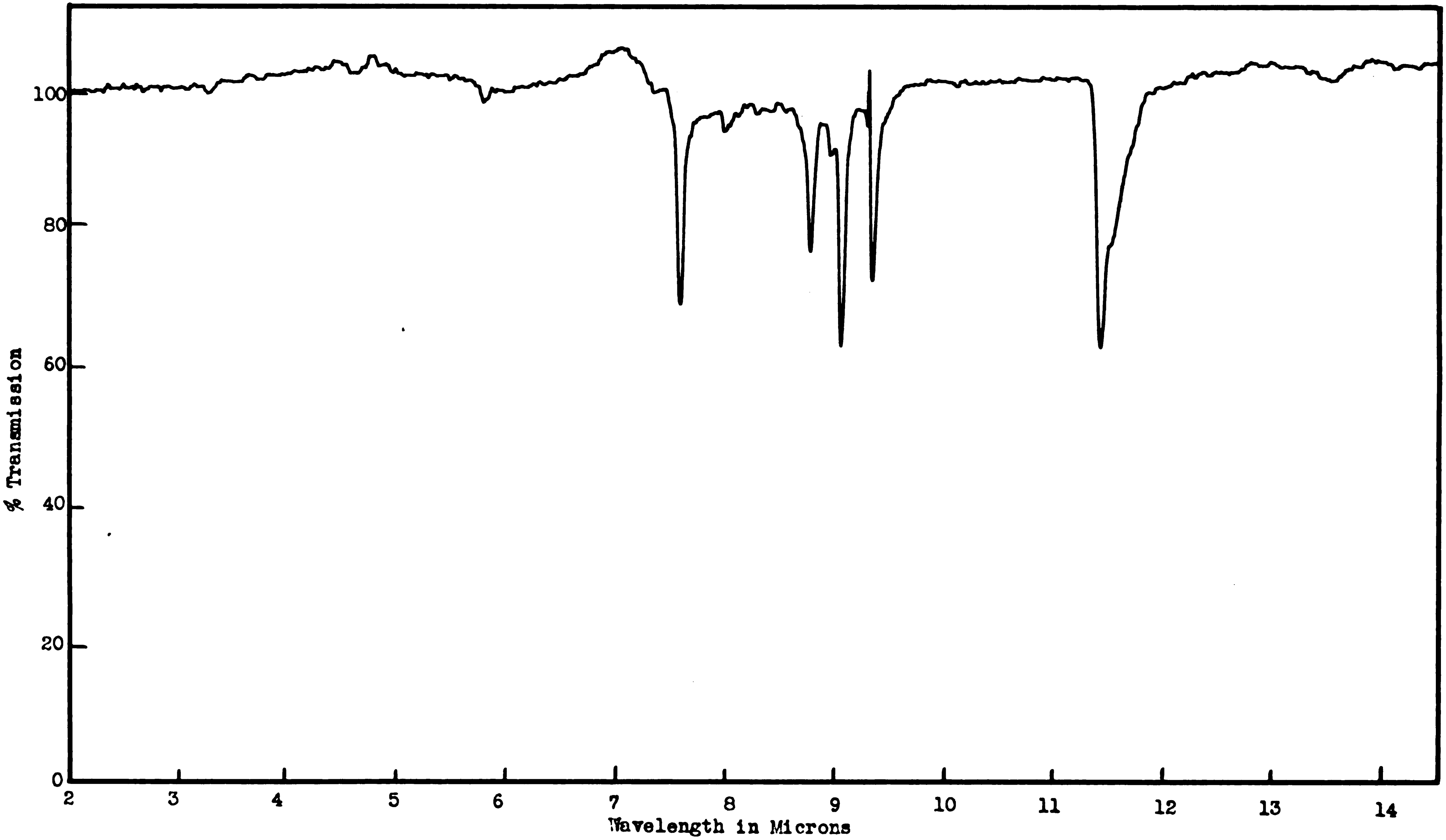

Figure 57. Infra-red Spectrum of 2,3,7,8-Tetrachorothianthrene (0.016 Molar in CS_2)

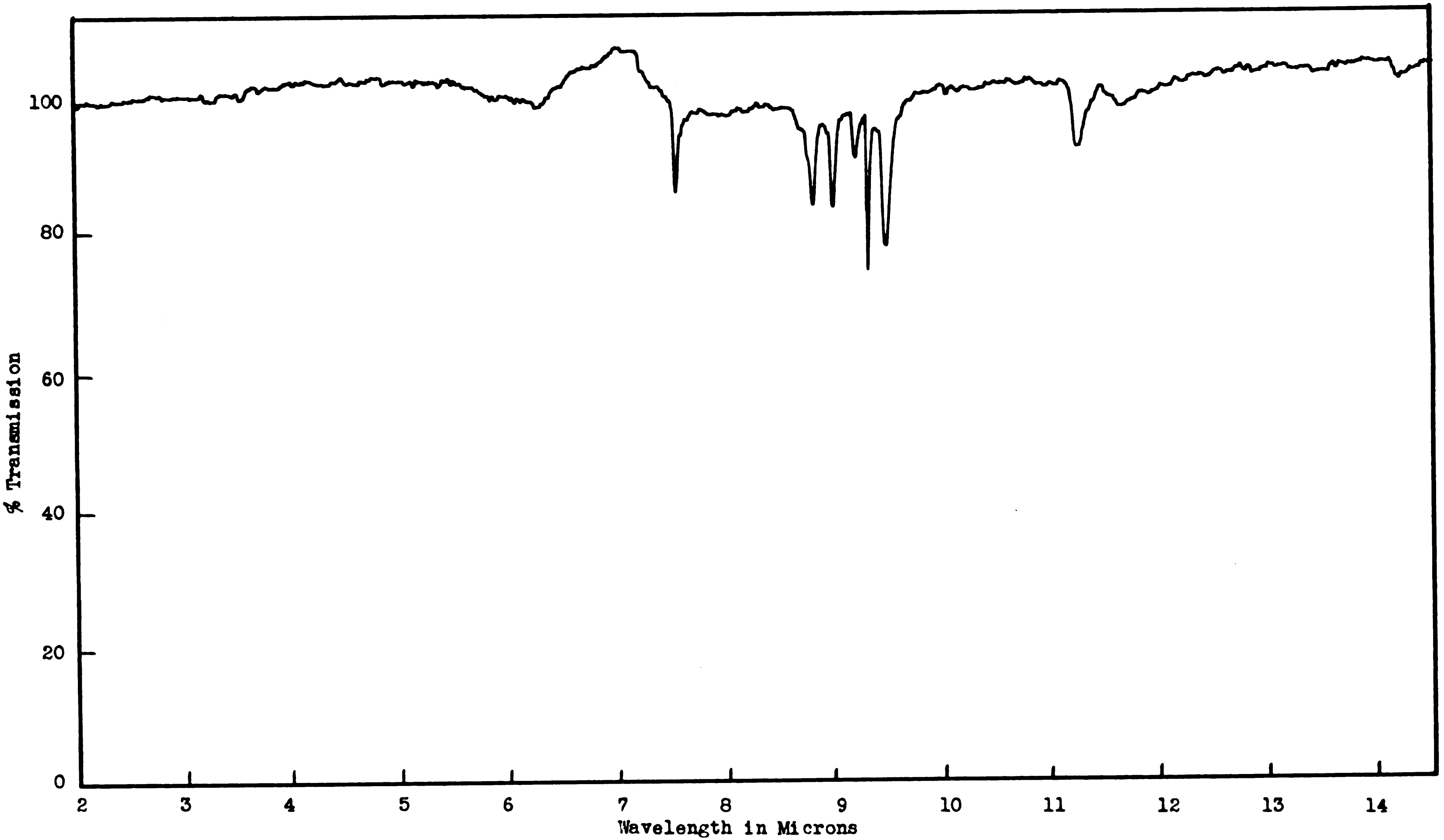

Figure 58. Infra-red Spectrum of 2,3,7,8-Tetrachlorothianthrene-5-Oxide (0.013 Molar in CS_2)

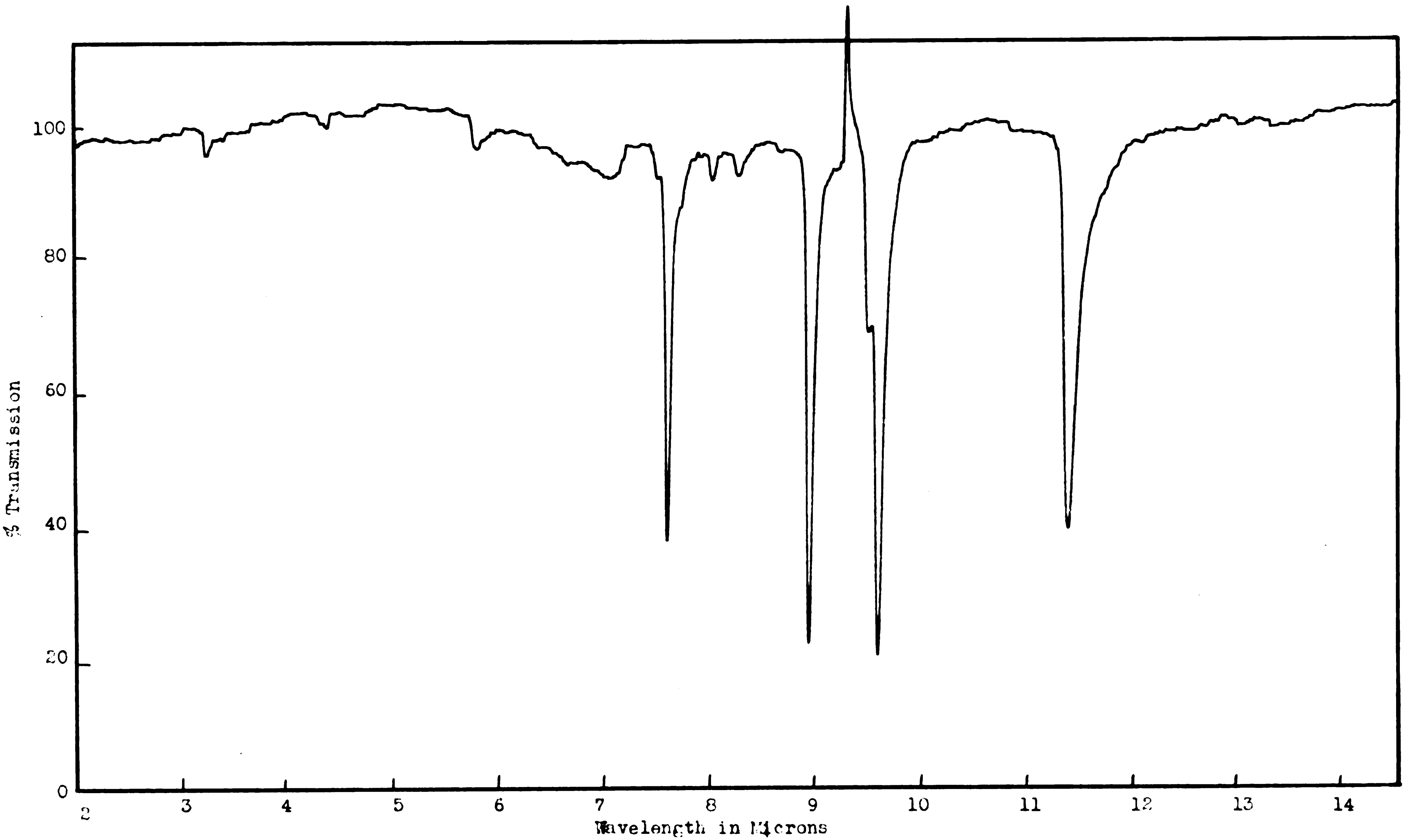

Figure 59. Infra-red Spectrum of 1,4-Dibromo-2,5-Dichlorobenzene (0.065 Molar in CS_2)

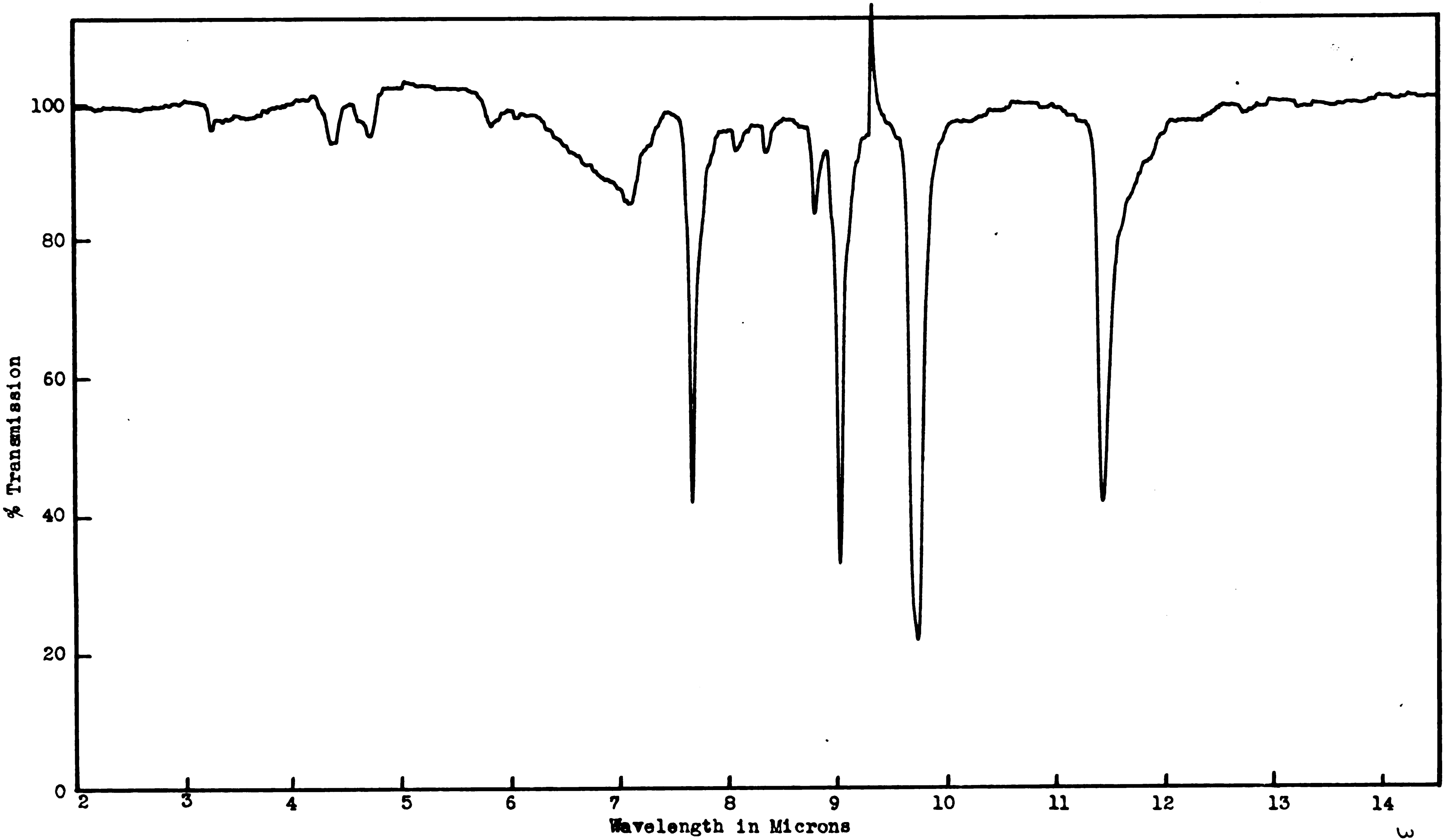

Figure 60. Infra-red Spectrum of 1,2,4-Tribromo-5-Chlorobenzene (0.065 Molar in CS_2)

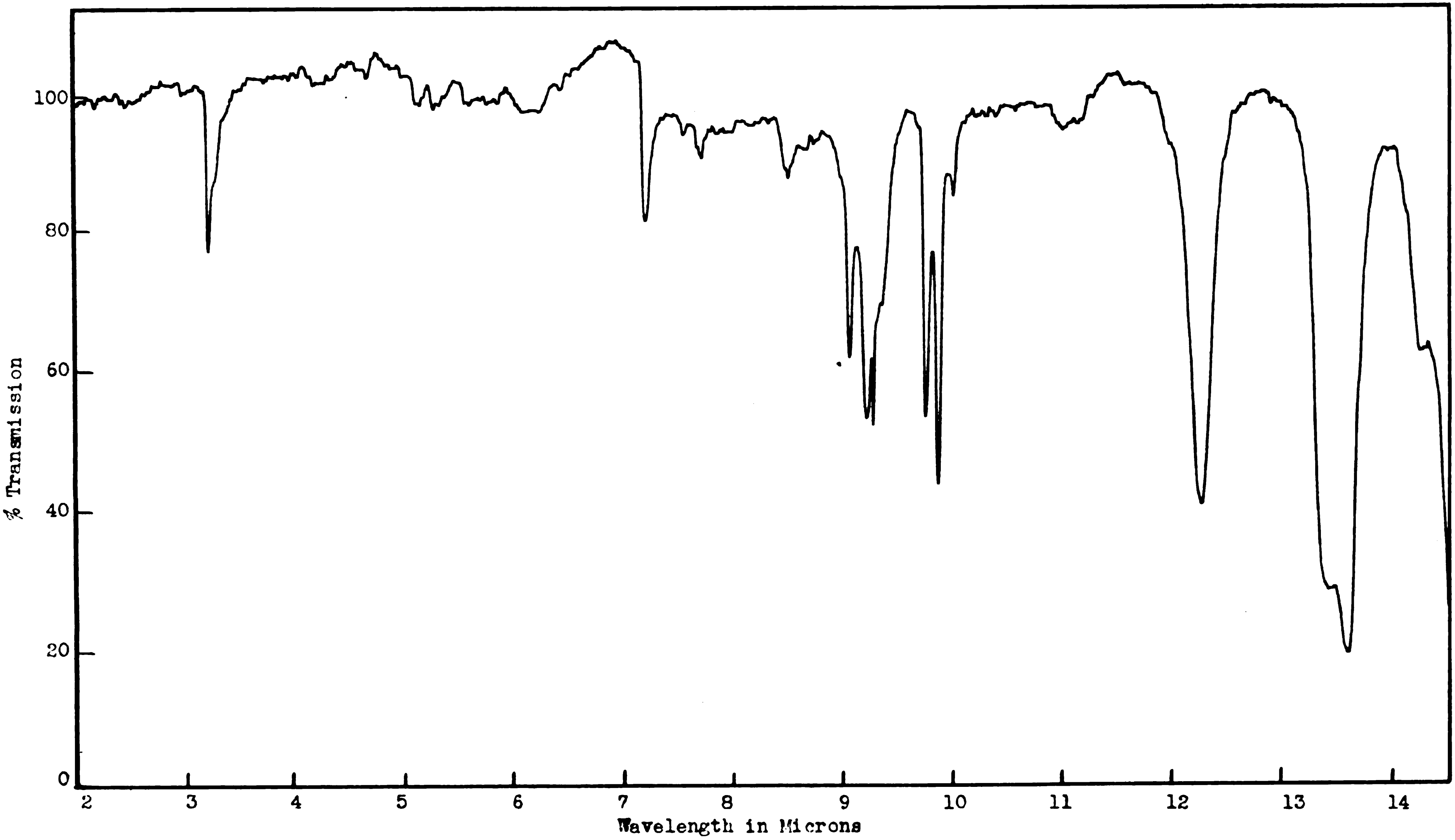

Figure 61. Infra-red Spectrum of 1,4-Bis(Phenylmercapto) Benzene (0.065 Molar in CS_2)

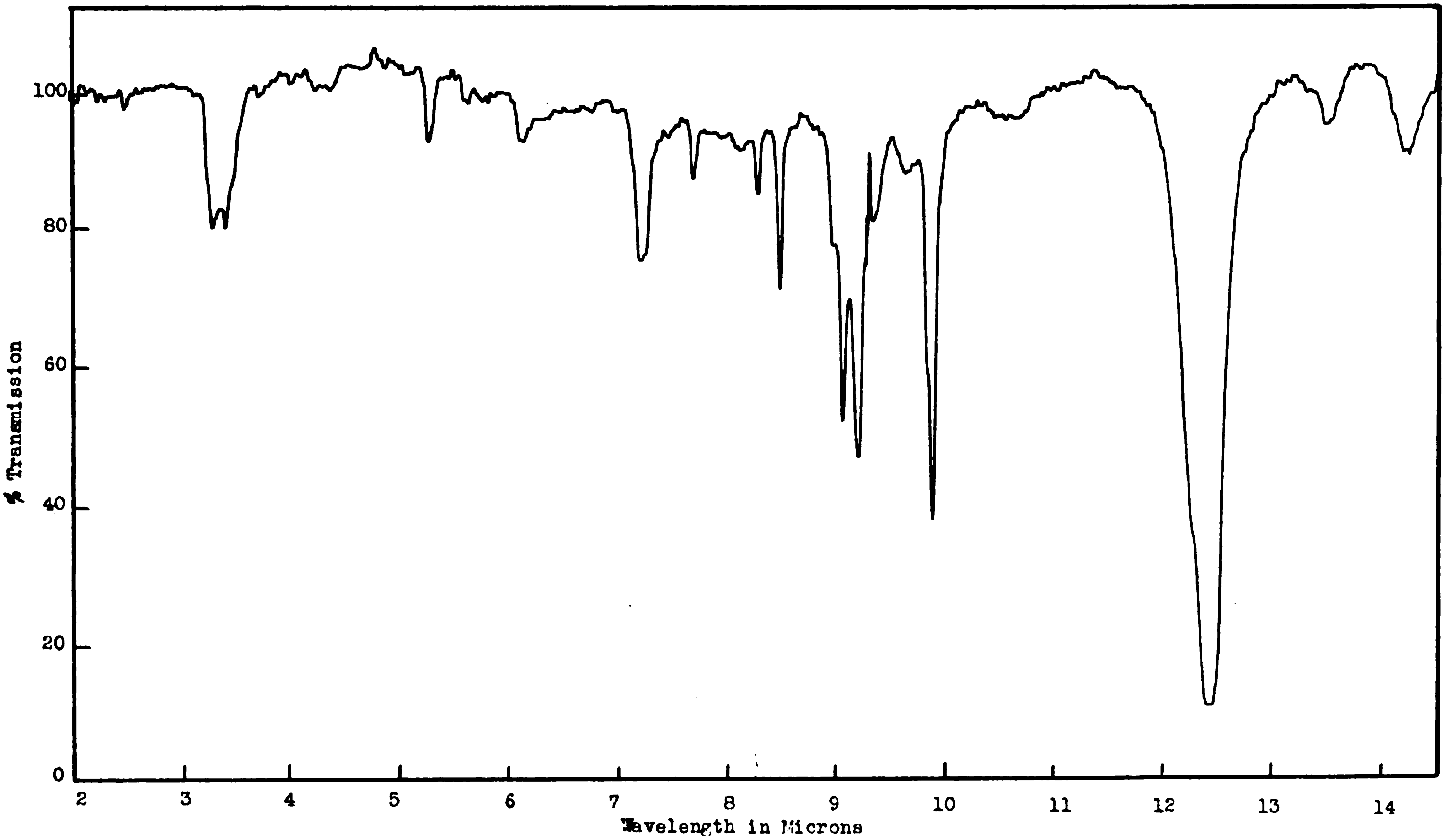

Figure 62. Infra-red Spectrum of 1,4-Bis(p-Tolylmercapto) Benzene (0.065 Molar in CS_2)

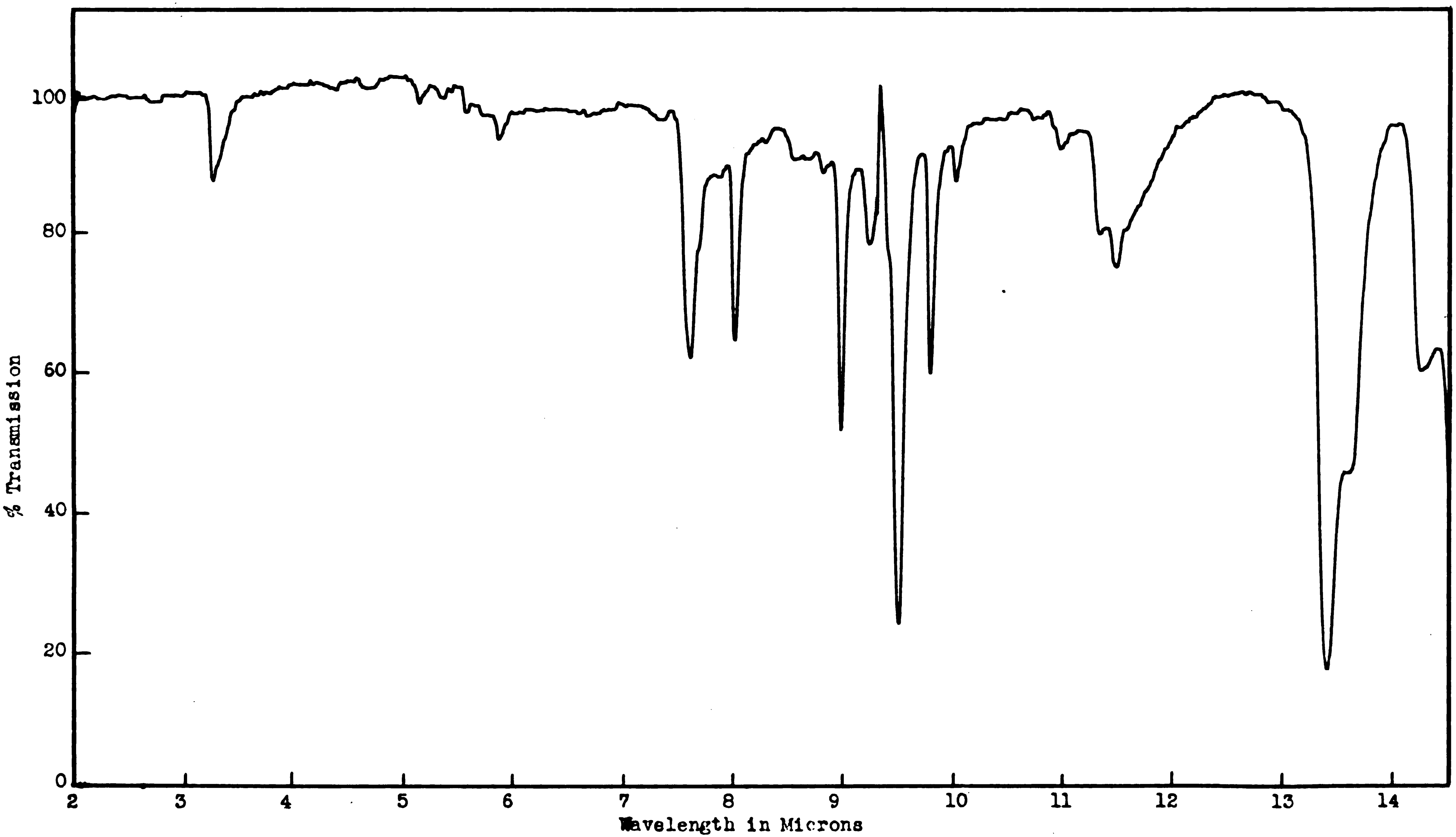

Figure 63. Infra-red Spectrum of 1,4-Dichloro-2,5-Di(phenylmercapto) Benzene (0.065 Molar in CS_2)

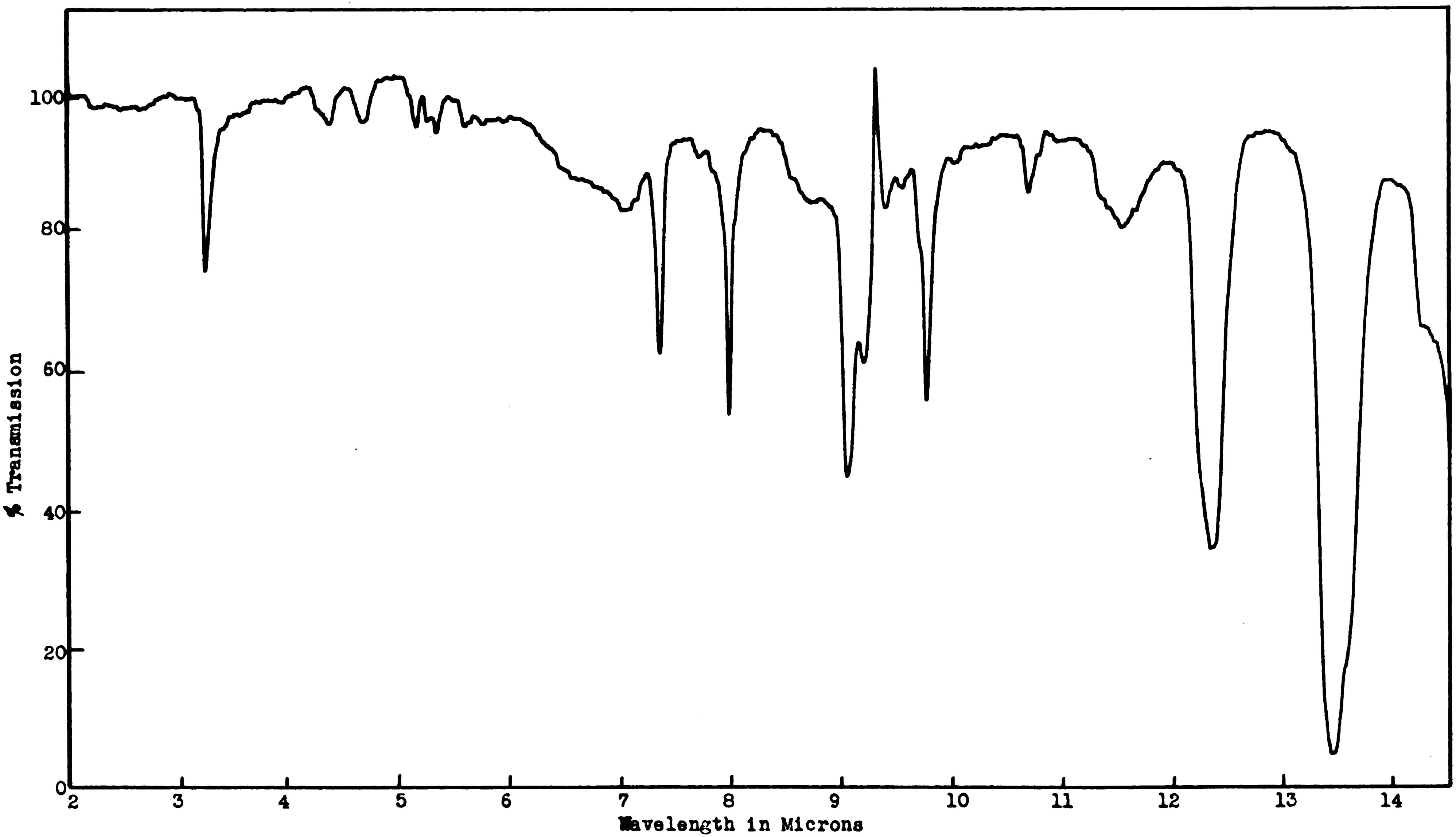

Figure 64. Infra-red Spectrum of Bis(4-(Phenylmercapto) Phenyl) Sulfide (0.065 Molar in CS_2)

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