3-ARYLTHIANAPHTHENES

PART I - SYNTHESIS

PART II - ULTRAVIOLET SPECTRA

By

Leon Ciporin

A THESIS

Submitted to the School of Graduate Studies of Michigan State University of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

1956

ACKNOWLEDGMENT

The author wishes to express his sincere thanks to Dr. Robert D. Schuetz for his wise counsel and valued friendship throughout the course of this investigation.

He is also indebted to his fiance, Laura, for her aid in completing the final draft of this thesis.

****

VITA

Leon Ciporin

candidate for the degree of

Doctor of Philosophy

Final examination, April 27, 1956, 1:30 P. M., Room 128, Chemistry Conference Room

Dissertation: 3-Arylthianaphthenes: Part I - Synthesis; Part II - Ultraviolet Spectra

Outline of Studies

Major Subject: Organic Chemistry
Minor Subjects: Physical and Biological Chemistry

Biographical Items

Born, March 15, 1928, New York City

Undergraduate Studies, B. A., New York University, 1949

Graduate Studies, M. S., Michigan State University, 1951

Additional Graduate Study, Michigan State University, 1953-1956

Experience: Graduate Assistant, Michigan State University, 1949-1951, 1953-1955
Member, United States Air Force, 1951-1952
Research Associate, Northwestern University, 1955-1956

Professional Affiliations: American Chemical Society
The Society of Sigma Xi

3-ARYLTHIANAPHTHENES

PART I - SYNTHESIS

PART II - ULTRAVIOLET SPECTRA

By

Leon Giporin

AN ABSTRACT

Submitted to the School of Graduate Studies of Michigan State University of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Department of Chemistry

Year 1956

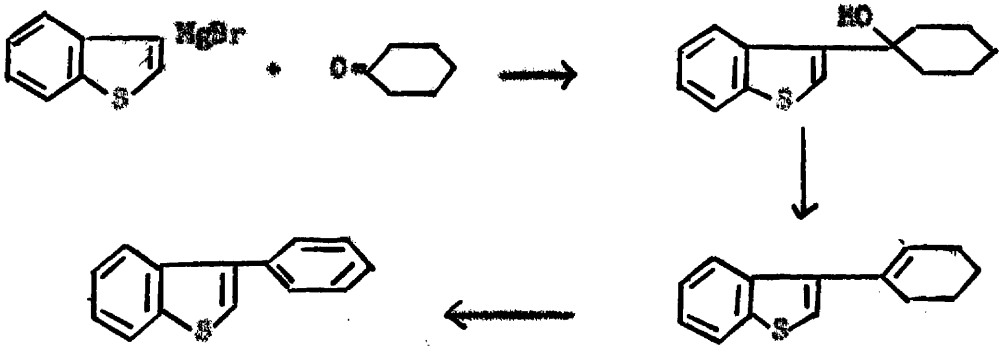
Approved _____

ABSTRACT

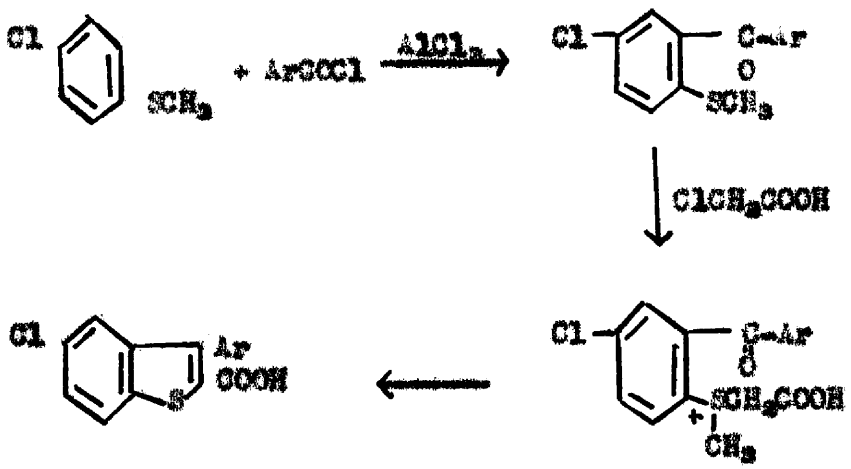
Part I

Three different synthetic methods were utilized to prepare various 3-arylthianaphthenes. 3,3'-Bithianaphthene was prepared by the Ullmann procedure from 3-iodothianaphthene in the presence of copper bronze.

3-Phenylthianaphthene and 3-(1'-naphthyl)-thianaphthene were synthesized by reaction of the appropriate cyclic ketone with 3-thianaphthylmagnesium bromide followed by dehydration and dehydrogenation.



Three 5-chloro-3-aryl-2-thianaphthenecarboxylic acids were prepared by a ring closure reaction involving treatment of the appropriate o-aroyl-p-chlorophenyl methyl sulfide with chloroacetic acid. The o-aroyl-p-chlorophenyl methyl sulfides were prepared by acylation of p-chlorophenyl methyl sulfide in the presence of anhydrous aluminum chloride.



Part II

The ultra-violet absorption curves of six 3-arylthianaphthenes were determined and compared with the curve for thianaphthene. These spectra were interpreted according to a theory of steric hindrance to free rotation about the pivot bond of the two aromatic rings. The principle absorption peak in the spectra of these compounds was decreased in intensity and shifted to shorter wavelengths as hindrance to free rotation was increased. This is explained by the increasing non-coplanarity and consequent decrease in resonance interaction between the two aromatic rings.

TABLE OF CONTENTS

LIST OF TABLES

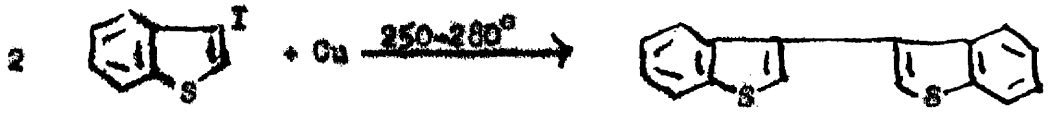
PART I - SYNTHESIS

INTRODUCTION

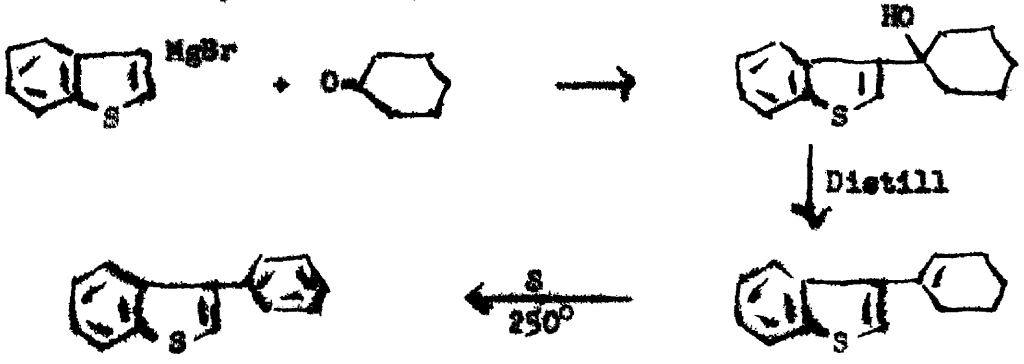
Although thianaphthene has been known since 1893 (7), little of its chemistry has been systematically studied. The early work in thianaphthene chemistry was devoted to the development of methods for the preparation of hydroxythianaphthenes because of their importance as intermediates in the synthesis of thioindigo dyes (4).

The main object of the work described here was to investigate restricted rotation in the 3,3'-bithianaphthene and 3-arylthianaphthenes and thus initially the study involved an investigation of methods for the preparation of such compounds.

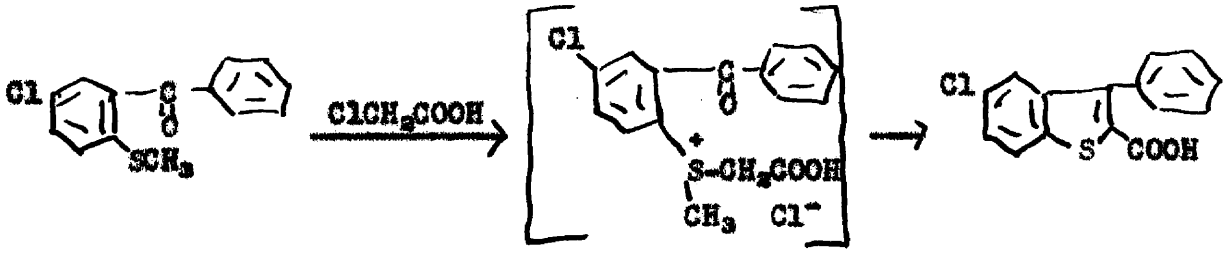
The Ullmann reaction, employing a 3-halothianaphthene,



was used for the preparation of symmetrical 3,3'-bithianaphthene. The condensation of a cyclic ketone with 3-thianaphthylmagnesium bromide followed by dehydration and dehydrogenation was used where the cyclic ketone was readily available.



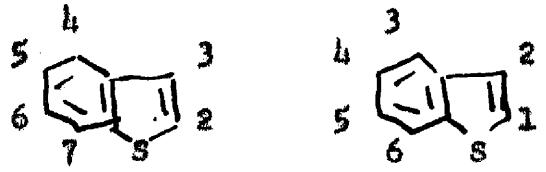
Ring closure of o-aroylaryl alkyl sulfides with chloroacetic acid was studied to determine the utility of the reaction for preparation of a variety of 3-aryl-2-thianaphthene carboxylic acids.



HISTORICAL

Thianaphthene

Thianaphthene has been used as the preferred name for the ring system (I) following current usage of Chemical Abstracts. The name thionaphthene



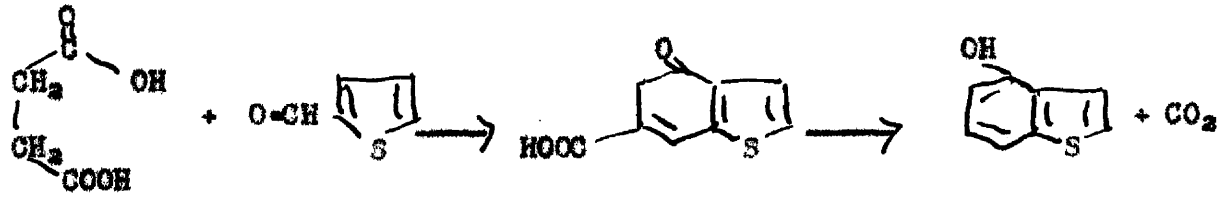
I II

was preferred by Chemical Abstracts prior to 1937, was first used by the original German investigators, and is still in use by British Abstracts. The alternate numbering system (II) is occasionally found in the early literature. The name benzothiophene has been suggested by the committee on nomenclature of the Petroleum Division of the American Chemical Society (1).

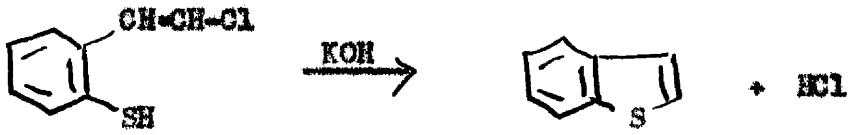
The chemistry of thianaphthene has been well summarized by Steinkopf (2) in a section of his book, "Thiophene," by Fukushima (3), and more recently by Hartough and Meisel (4) in their excellent monograph which contains the majority of the leading references on the subject through May, 1952.

Meyer, in 1886, predicted there should exist a compound having the relation to naphthalene which thiophene has to benzene. In the same year, Biedermann (6) prepared the first thianaphthene derivative,

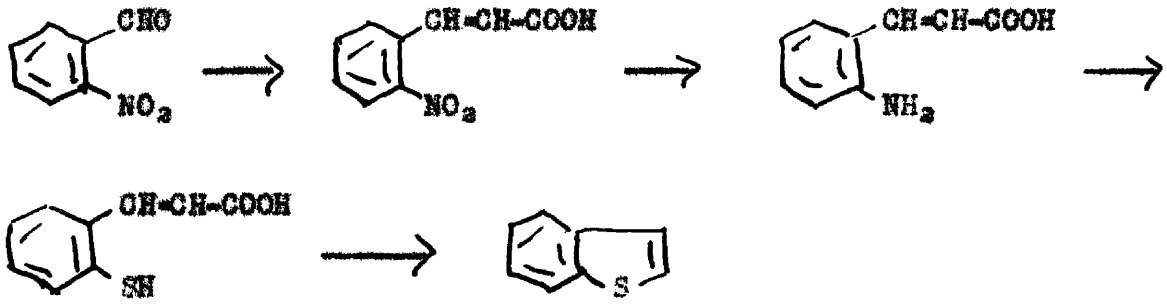
4-Hydroxythianaphthene, from thiophene-2-aldehyde and sodium succinate by treatment with acetic anhydride. This reaction is identical to that used to prepare α-naphthol from benzaldehyde



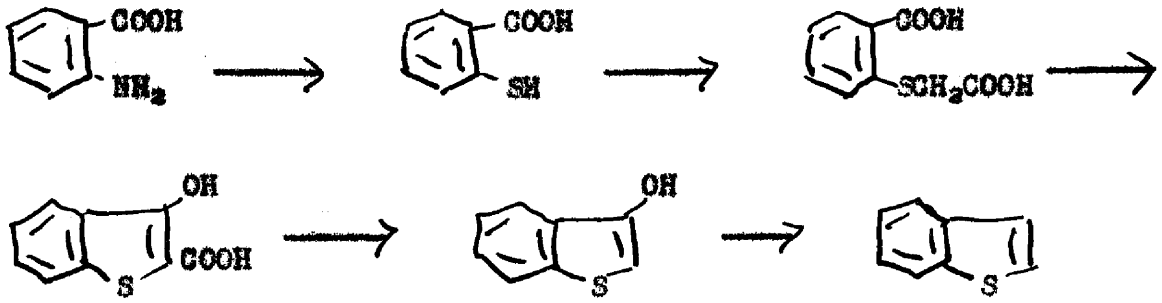
The parent compound, thianaphthene, was first obtained by synthetic methods rather than by isolation from natural sources. The original synthesis of thianaphthene is credited to Gattermann and Lockhart (7) who prepared it by the cyclisation of o-mercaptochlorostyrene with potassium hydroxide.



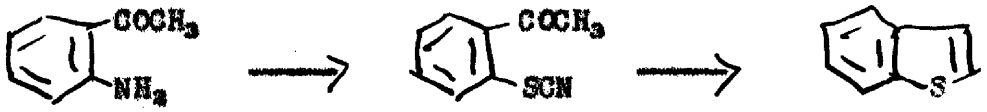
The method of Friedlander (8) involves an oxidation of o-mercapto-cinnamic acid with ferric salts. This is a tedious process due to the inaccessibility of the appropriate cinnamic acid.



The reduction of 3-hydroxythianaphthene (9) with zinc dust and acetic acid forms thianaphthene. The hydroxythianaphthene is prepared from anthranilic acid.



The acid reduction of o-thiocyanoacetophenone produces thianaphthene (10). The method involves diazotization of o-aminoacetophenone followed by treatment with potassium thiocyanate.



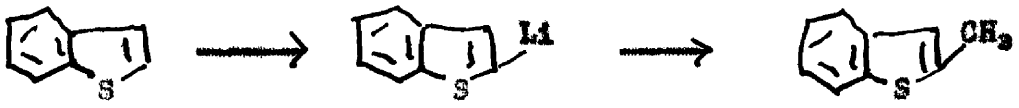
More recently, thianaphthene has become available by the vapor phase catalytic dehydrogenation of a mixture of styrene (11) or ethylbenzene (13) and hydrogen sulfide, or of o-ethylthiophenol alone (12).

The isolation of thianaphthene from natural sources was first reported by Boes (14) in 1902. He successfully separated thianaphthene from the naphthalene fraction of coal distillates by formation of its picrate. Weissgerber (15) developed a more efficient method which involved treating crude naphthalene with sulfuric acid followed by cleavage of the resulting sulfonic acids. Final purification was accomplished by preparing the sodio-derivative from solutions of the crude material with sodamide.

Alkylthianaphthenes

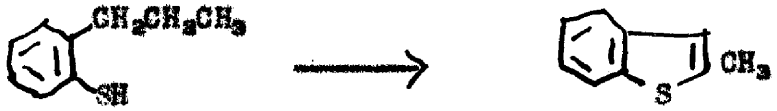
There are approximately twenty known thianaphthene homologs (4). These have been prepared by a variety of methods, all of which involve

either a ring closure procedure or direct substitution in the thianaphthene nucleus. The latter method is illustrated by the preparation of 2-methylthianaphthene from 2-thianaphthenyllithium by interaction with methyl tosylate (16).

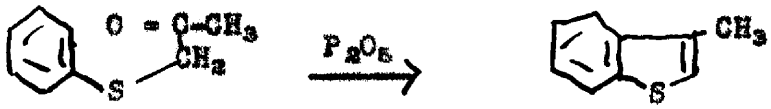


Such a process would not be applicable to the preparation of thianaphthenes substituted in the 3-position as metalation of thianaphthene occurs almost exclusively in the position adjacent to the heteroatom (16).

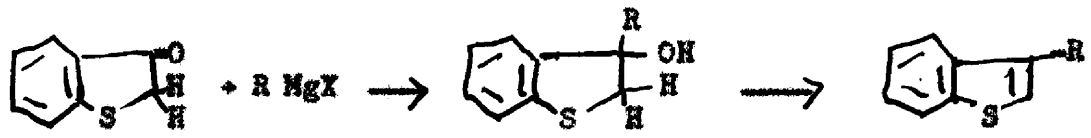
2-Methylthianaphthene has also been prepared by the vapor phase catalytic dehydrogenation of 2-n-propylthiophenol (12). This is an illustration of a ring closure method.



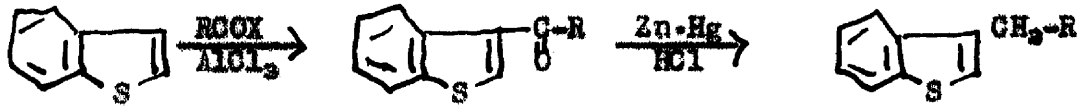
3-Methylthianaphthene has been prepared by dehydration of phenyl acetonyl sulfide (17).



3-Methylthianaphthene, as well as the 3-ethyl homolog, has been prepared in low yield by the action of a Grignard reagent on the keto form of 3-hydroxythianaphthene (18,19).

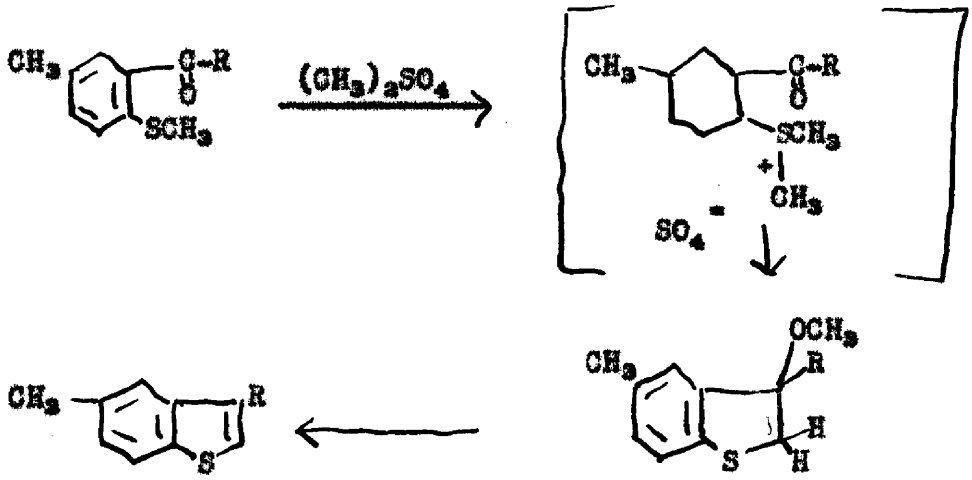


The preparation of monoalkylthianaphthenes by direct alkylation of thianaphthene with alkyl halides has not been reported. The 3-ethyl n-propyl, and n-butylthianaphthenes have been obtained by acylation of thianaphthene followed by a Clemmenson reduction of the respective ketones (20,21).

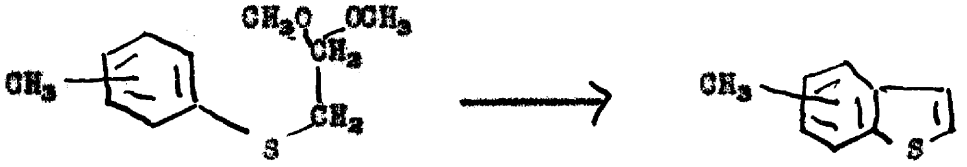


This latter method would not be applicable to the preparation of 2-alkylthianaphthenes since electrophilic substitution occurs primarily at the 3-position (24).

A number of thianaphthene homologs have been synthesized through a series of sulfonium salts (18,19). This will be treated in greater detail later.



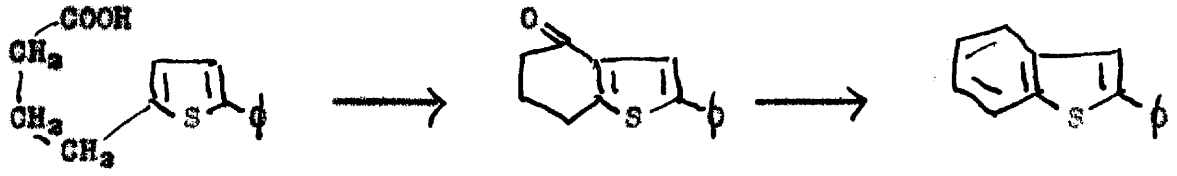
A recent synthesis of thianaphthene homologs involves the addition of a 2,2-dimethoxyethyl phenyl sulfide to phosphoric acid at high temperature and low pressure whereupon the resultant thianaphthene immediately distills from the reaction mixture (22,23). Methylthianaphthenes with the alkyl group in the 5,6, and 7 position have been obtained by this method.



Arylthianaphthenes

For convenience, previously prepared arylthianaphthenes with references to the original literature have been listed in Table I. These compounds have been synthesized by more varied methods than those previously described for the alkylthianaphthenes.

2-Phenylthianaphthene has been prepared by cyclizing 2-phenyl-5-thienyl-butyric acid with a dehydrating agent, followed by reduction and hydrogenation of the intermediate cyclic ketone (25).



Gaertner (26) has prepared 2-phenylthianaphthene in low yield by the free radical arylation of thianaphthene using N-nitrosoacetanilide as a source of phenyl free radicals.

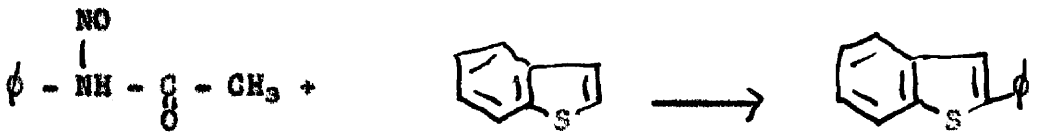


TABLE I

KNOWN ARYLTHIANAPHTHENES[a,b]

Substituent	Reference
2-Phenyl	25,26
3-Phenyl-5-methyl	18
3-Phenyl-6-hydroxy	27
3-Phenyl-2-phenoxy	28
3-Phenyl-2-thiophenyl	28
3-(o-Carboxyphenyl)-5-methyl-2-carboxy	19
3-(p-Tolyl)-2-phenoxy-6-methyl	28
4-Phenyl	29
2,3-Diphenyl	30
2-(2'-Thianaphthyl)	31,16
2-(3'-Thianaphthyl)	31
3-(3'-Coumarinyl)	32
3-(6'-Bromo-3'-coumarinyl)	32
3-(5',6'-Benzo-3'-coumarinyl)	32
3-(3'-n-Alkyl-2'-indolyl)[c]	33
2-(2'-Pyridyl)-3-hydroxy	34
2-(2'-Quinolinyl)	35
2-(2'-Quinolinyl)-3-hydroxy	34
3-(2'-Quinolinyl)	36
3-(3'-Methyl-2'-quinolinyl)	37
3-(3'-Ethyl-2'-quinolinyl)	37

[a] Up to December, 1954.

[b] Hartough and Meisel's reference to 3-(α-naphthyl) erroneous.

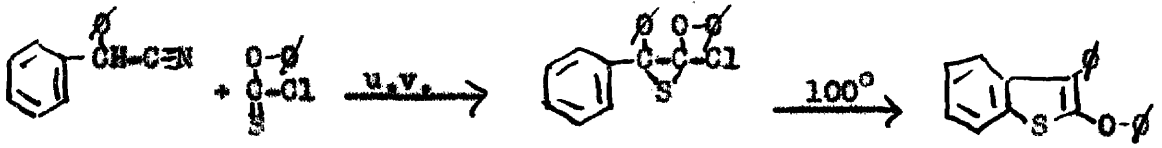
[c] Alkyl = amyl, hexyl, heptyl, octyl, nonyl, decyl, dodecyl, tetradecyl

No conclusions regarding selective orientation were made since other isomers were probably present.

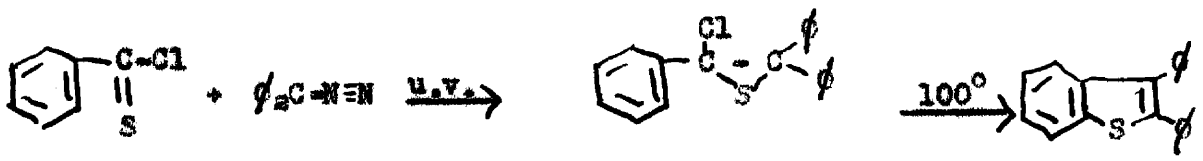
Both 3-phenyl-5-methylthianaphthene and 3-(o-carboxyphenyl)-5-methyl-2-carboxythianaphthene have been prepared via the sulfonium salt intermediates previously mentioned for 3,5-dialkyl derivatives of thianaphthene (18,19).

3-Phenyl-6-hydroxythianaphthene has been prepared by the cyclisation of m-hydroxyphenyl phenacyl sulfide with alcoholic potassium hydroxide (27).

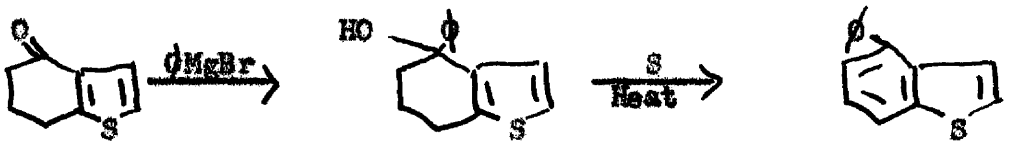
The rearrangement of 1,1-diphenyl-2-phenoxy-2-chloroethylene sulfide to 2-phenoxy-3-phenylthianaphthene has been reported (28). 2-Thiaphenyl-3-phenylthianaphthene and 2-phenoxy-3-(p-tolyl)-6-methylthianaphthene were also obtained by this method. The intermediate sulfide was prepared from diphenylacetonitrile and phenoxythiacarbonyl chloride.



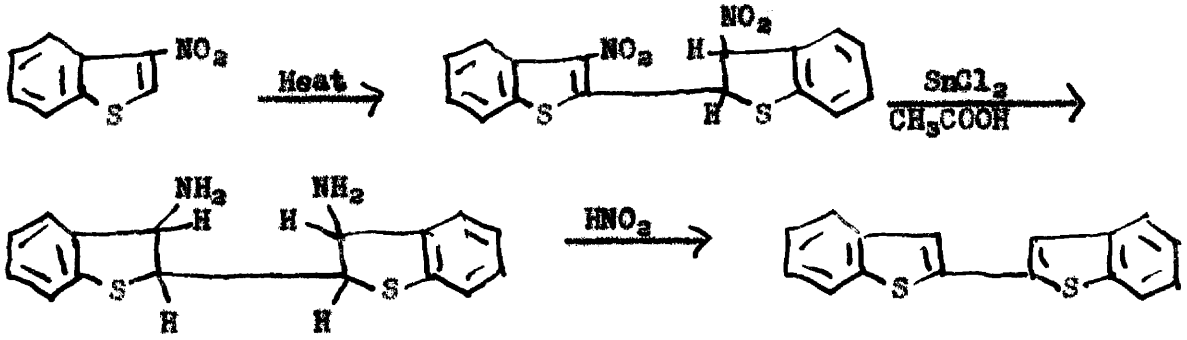
In a similar rearrangement reaction, 2,3 diphenylthianaphthene is reported to be formed when 1,1,2-triphenyl-2-chloroethylene sulfide is heated to 100° (30). This sulfide was prepared from thiobenzoyl chloride and diphenyldiazomethane.



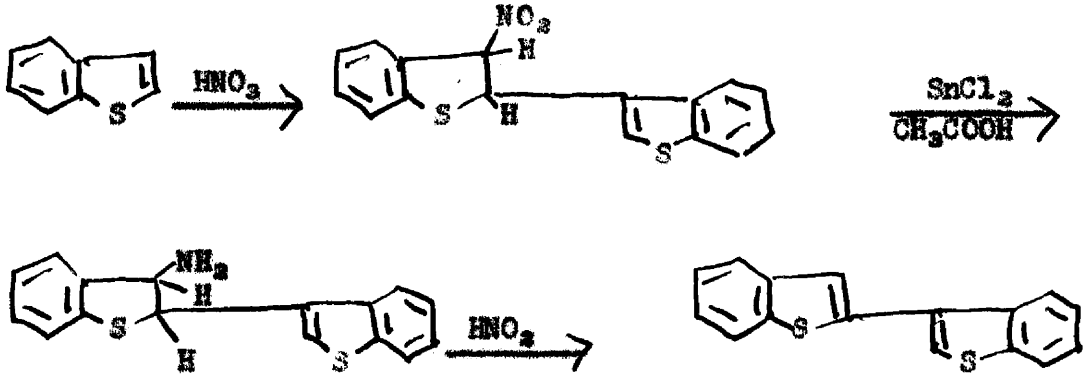
4-Phenylthianaphthene was synthesized by the addition of phenylmagnesium bromide to 4-keto-4,5,6,7-tetrahydrothianaphthene followed by dehydration and dehydrogenation (29) of the intermediate 4-hydroxy-4-phenyl-4,5,6,7-tetrahydrothianaphthene.



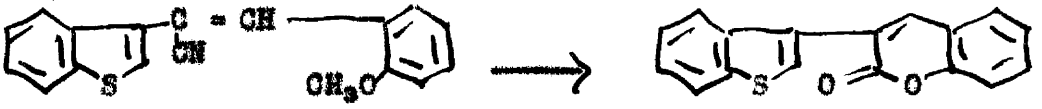
The thermal dimerization of 3-nitrothianaphthene followed by reduction of the nitro groups and subsequent diazotization yields 2,2'-bithianaphthene and 2,3'-bithianaphthene (31). The following sequence of steps have been proposed for the formation of 2-2'-bithianaphthene, which are similar to that given for the polymerization of thiophene (38).



The reaction sequence for the formation of 2,3-bithianaphthene is slightly different.

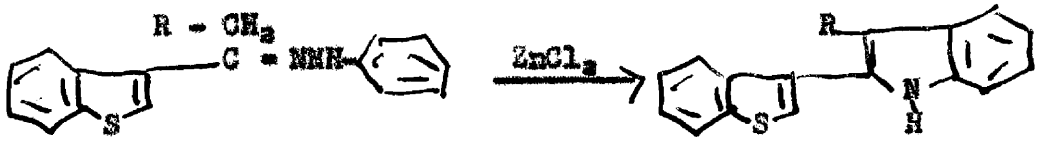


The ring closure of 1-(o-anisyl)-2-(3'-thianaphthenyl)-2-cyano-ethylene in boiling pyridine results in the formation of 3-(3'-coumarinyl)-thianaphthene (32). The substituted ethylene is prepared from 3-thianaphthenylacetonitrile and the methyl ether of salicylaldehyde.

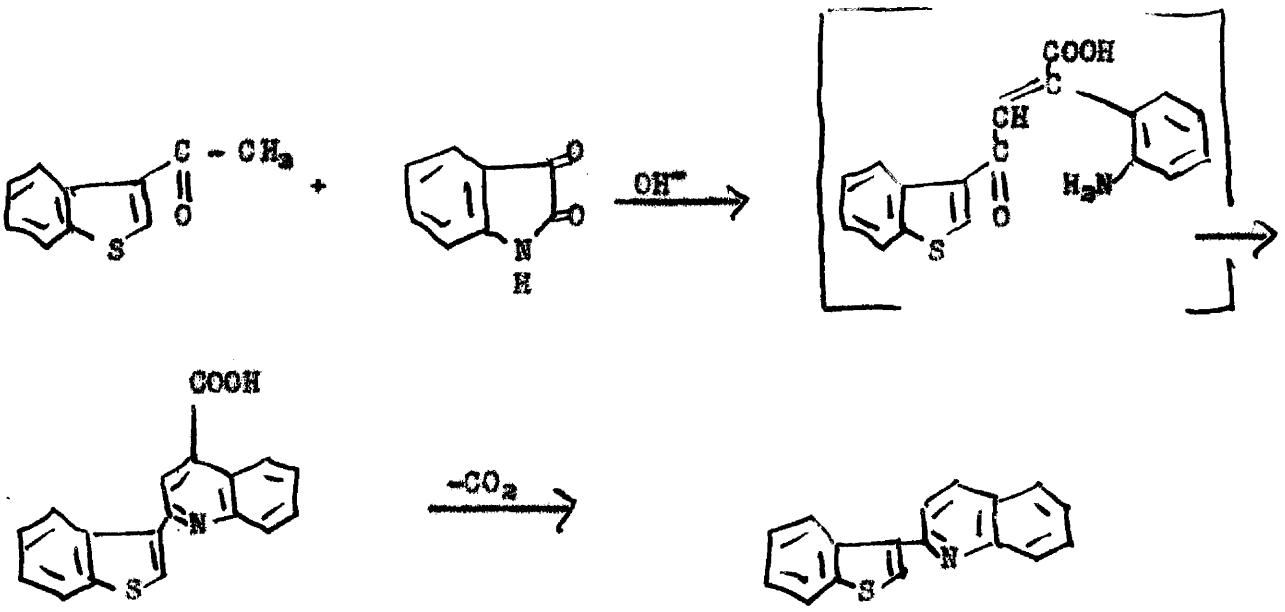


Replacement of the o-anisyl group with the 2-p-bromoanisyl group yields 3-(6'-bromo-3'-coumarinyl)-thianaphthene and the 2-methoxy-1-naphthyl group results in 3-(5',6'-benzo-3'-coumarinyl)-thianaphthene.

The Fischer indole synthesis has been carried out with the phenylhydrazones of eight thianaphthene ketones yielding various 3-(3'-n-alkyl-2'-indolyl)-thianaphthenes (33).

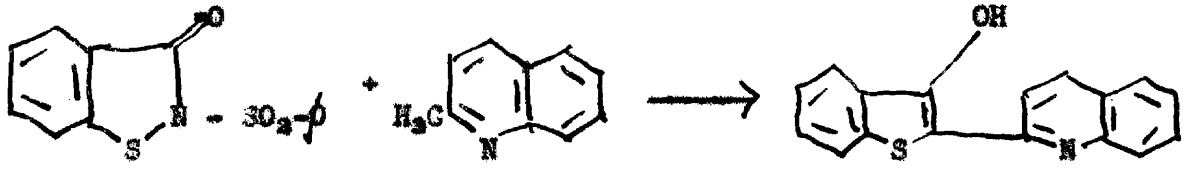


The Pfitzinger reaction of aromatic ketones with isatin has been employed to prepare 3-(2'-quinolinyl)-thianaphthene (36).



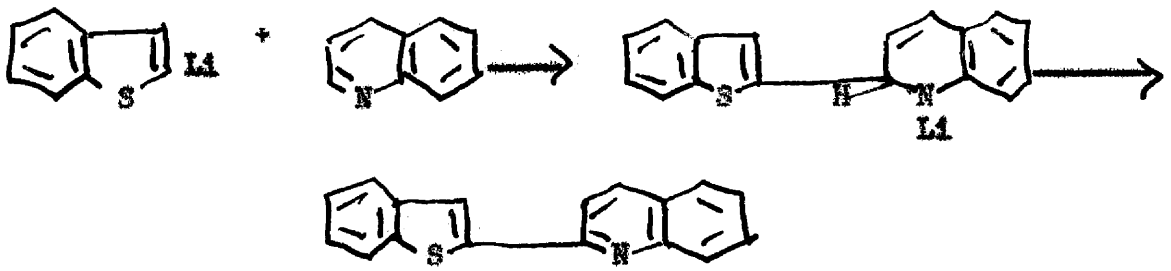
If 3-propionylthianaphthene or 3-butyrylthianaphthene is used, the corresponding 3'-methyl- and 3'-ethyl- derivatives are formed (37).

A reaction utilizing a benzoisothiazole as an intermediate has been used to prepare 2-(2'-quinolinyl)-3-hydroxythianaphthene (34). N-Benzenesulfonylbenzoisothiazole is refluxed with quinaldine in pyridine solution to yield the 3-hydroxythianaphthene.



This latter reaction requires an active methylene group. Thus, α-picoline reacts with the benzoisothiazole in a similar manner to yield 2-(2'-pyridyl)-3-hydroxythianaphthene (34).

Finally, 2-(2'-quinolinyl)-thianaphthene is formed by the addition of 2-thianaphthenyllithium to quinoline, followed by oxidation with nitrobenzene (35).


Li
S
N
S
H
N
Li
S
N

DISCUSSION

Preparation of 3,3'-Bithianaphthene

A general method, of considerable utility, for the preparation of symmetrical biaryls involves the condensation of two molecules of an aryl halide, in the presence of a metallic agent, with the elimination of the halogen as a metal halide:

$$2\ ArX + M \longrightarrow Ar - Ar + MX_2$$

The extensive investigations of Fritz Ullmann (58) showed that copper is a particularly effective metal in this type of condensation, and as a result biaryl formation with the elimination of copper halide has become widely known as the Ullmann reaction. An excellent review of the Ullmann reaction has been made by Fanta (59).

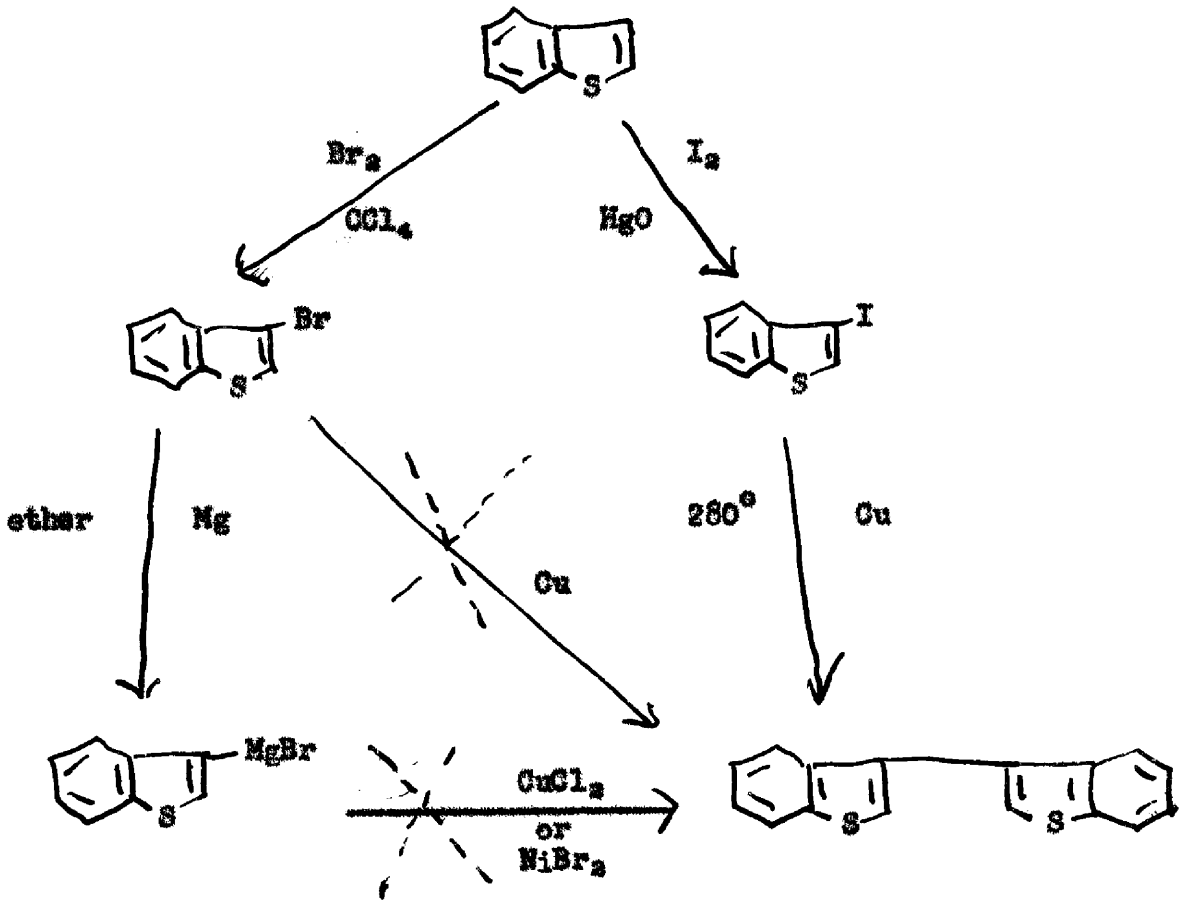
An alternative method of preparing symmetrical biaryls from aryl halides was introduced by Krizewskey and Turner (60). Their synthesis of such compounds involves the intramolecular coupling of an arylmagnesium halide in the presence of metallic salts such as cupric chloride, nickel bromide, or silver bromide.

$$2\ ArMgX + 2MX \longrightarrow Ar - Ar + MgX_2 + 2M$$

The sequences of reactions followed in this work in attempts to synthesize 3,3'-bithianaphthene are shown in Figure I.

The 3-halothianaphthenes used in this investigation were prepared by procedures previously described in the literature. The synthesis

FIGURE I


S
Br_2
CCl_4
I_2
HgO
Br
S
I
S
ether
Mg
Cu
280°
Cu
MgBr
S
$CuCl_2$
or
$NiBr_2$
S
S

of 3-bromothianaphthene was accomplished by the direct bromination of thianaphthene in chloroform as a solvent, following the method of Szmuszkovicz and Modest (46). Monobromination occurred preferentially at the 3-position to give a seventy percent yield of 3-bromothianaphthene.

The method of Gaertner (48) was used in the preparation of 3-iodothianaphthene. Thianaphthene dissolved in benzene was iodinated in the presence of mercuric oxide. After passing the reaction mixture through a column of alumina and activated charcoal, the decolorized solution yielded 3-iodothianaphthene in a thirty-four percent yield based on the original thianaphthene.

The Ullmann reaction was attempted with both 3-bromothianaphthene and 3-iodothianaphthene employing the following general procedure. The aryl halide was placed in an eight centimeter Pyrex test tube and heated to about 150° by means of an oil bath. At this point, while stirring the aryl halide with a thermometer, three to five times the required quantity of copper bronze was added portionwise while the temperature was gradually raised to 250° to 280°. The reaction temperature was maintained at this level for two hours after the addition of the copper bronze had been completed. The resulting solid mass was extracted with hot chloroform.

Prior to its use in these experiments, commercial copper bronze was treated according to a procedure developed by Kleiderer and Adams (50). These authors claim superior results when the copper bronze is activated in the following manner. A small amount of iodine

is allowed to react with copper bronze whereupon cupric iodide forms on the surface of the metal. Upon dissolving the cupric iodide in dilute acid, copper bronze having a greatly increased surface area is obtained.

All attempts to effect the coupling of 3-bromothianaphthene in this manner failed, and the recovery of aryl halide was essentially quantitative. However, 3,3'-bithianaphthene was obtained in rather poor yields of from four to seventeen percent by coupling 3-iodothianaphthene in the presence of copper bronze at a reaction temperature of 280°.

The low reactivity of the 3-bromothianaphthene as compared with the corresponding 3-iodo compound is in accord with the observation that aryl bromides and chlorides undergo the Ullmann reaction satisfactorily only when activated by electron withdrawing groups in the ortho or para positions.

A high melting crystalline substance was isolated as a byproduct during the formation of 3,3'-bithianaphthene from 3-iodothianaphthene. Although no structural studies were made on this substance, elementary analysis indicates that it is probably a polymer of thianaphthene. Steinkopf has observed similar polymer formation when halothiophenes are subjected to the Ullmann reaction.

Treatment of 3-bromothianaphthene with an equimolar quantity of cupric chloride resulted only in an eighty-five percent recovery of the starting material. The residue was an uncrystallizable dark colored amorphous material. When nickel bromide was employed as the

coupling agent, the 3-bromothianaphthene could not be recovered and the product was a noncrystalline intractable material. This reaction might have succeeded with silver bromide as the metallic salt. It has been reported to be a particularly effective coupling agent (81,82).

Preparation of 3-Arylthianaphthenes by Reaction of 3-Thianaphthylmagnesium Bromide with Cyclic Ketones

The synthetic scheme of reaction steps followed in these preparations is outlined in Figure II, where cyclohexanone is used as an illustration. Ketones utilized other than cyclohexanone, were α-tetralone, 2-methylcyclohexanone and 3-hydroxythianaphthene, the last presumed to exist in its keto form.

The method of preparing the 3-cycloalkenylthianaphthenes is essentially that of Szmuskovicz and Modest (46). The 3-thianaphthylmagnesium bromide was allowed to interact with the appropriate cyclic ketone in ether as a solvent. After decomposing the Grignard complex and working up the reaction mixture in the usual manner, the 3-cycloalkenylthionaphthene was isolated by low pressure distillation. The intermediate tertiary alcohol, which undoubtedly was the primary product of the reaction, underwent dehydration during the vacuum distillation. The formation of an olefin from a tertiary alcohol by slow distillation is a general phenomenon (63).

The ketones used in this investigation and the corresponding 3-cycloalkenylthianaphthenes synthesized from them are listed in Table II. Mention should be made of the unsuccessful reaction of 3-thianaphthylmagnesium bromide with 3-hydroxythianaphthene. The tautomerism of 3-hydroxythianaphthene has been known for some years.

FIGURE II

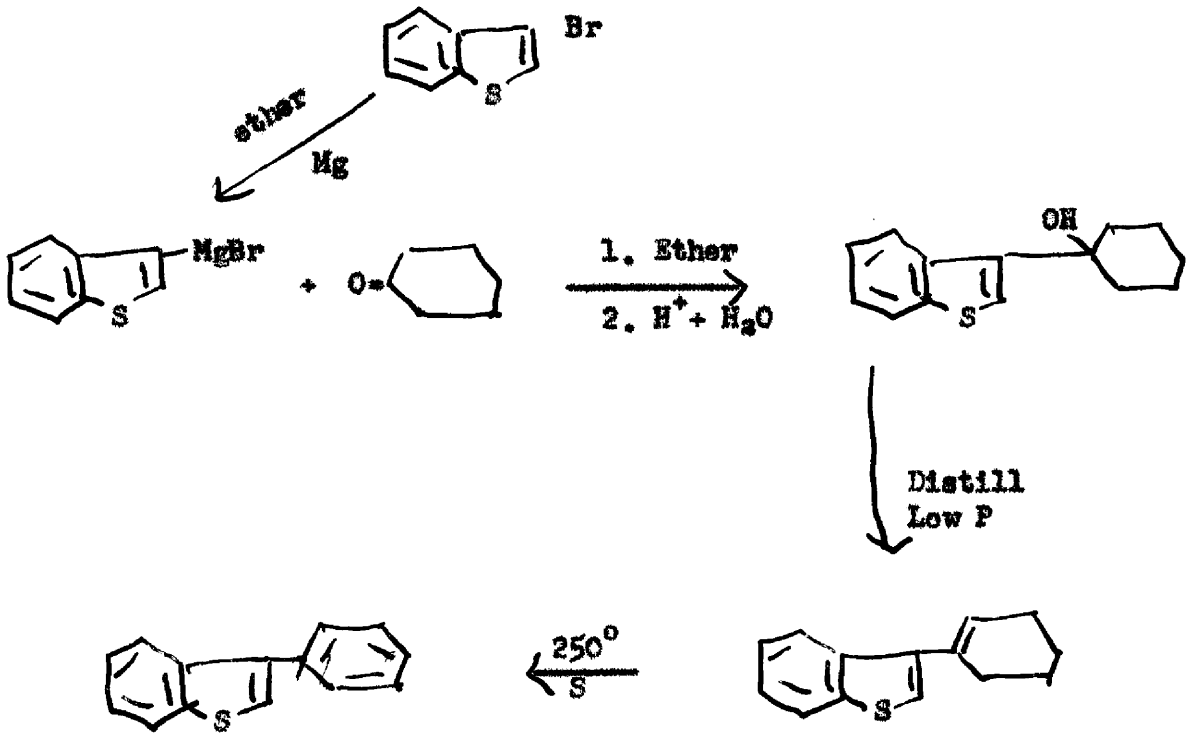
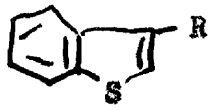
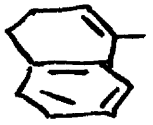


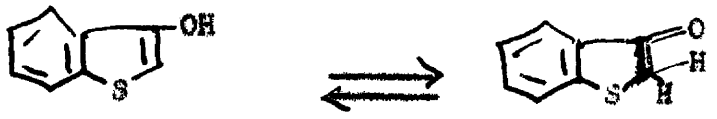
TABLE II

3-CYCLOALKENYLTHIANAPHTHENES

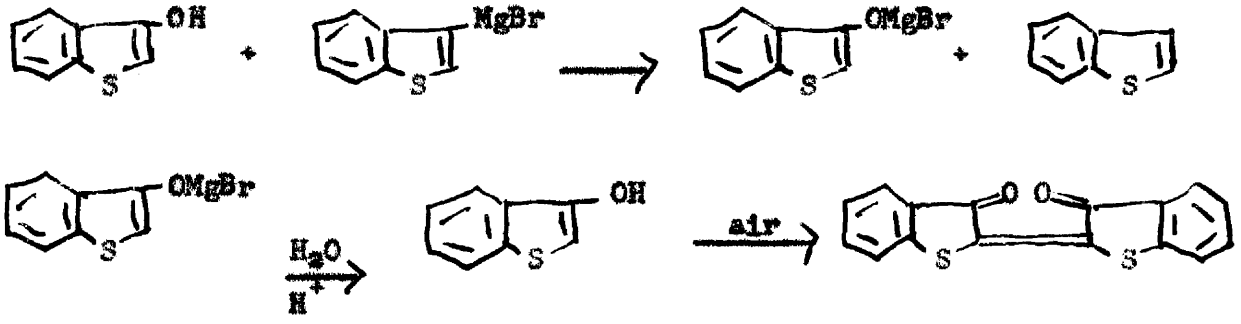


Ketone Reacted	R	Yield	B.p., °C	Mm.
Cyclohexanone		35%	140-150	2
α-Tetralone		26%	205-210	3
2-Methylcyclohexanone		22%	160-170	2
3-Hydroxythianaphthene (Keto form)	No product		--	--

Auwers and Thiess (64) concluded from a semi-quantitative analysis that 3-hydroxythianaphthene exists mainly in the keto form under ordinary conditions.



Krollpfeiffer and his co-workers (18,19) were able to prepare 3-methyl- and 3-ethylthianaphthene in low yields by the interaction of the appropriate Grignard reagent with the keto form of 3-hydroxythianaphthene. The failure of 3-thianaphthylmagnesium bromide to react in a similar manner in the present investigation can probably be ascribed to its reaction with the enol form of 3-hydroxythianaphthene.



In support of this tentative explanation of the failure of the Grignard reagent of 3-bromothianaphthene to react with 3-hydroxythianaphthene is the fact that the only products isolated from such reactions were thianaphthene and a brown polymeric material similar in appearance to thioindigo.

The 3-cycloalkenylthianaphthenes were converted to their corresponding 3-arylthianaphthenes by dehydrogenation, which was accomplished by heating the former compounds with sulfur at a temperature of

approximately 250°. These compounds, which have not been previously described in the literature, are listed in Table III.

The sulfur dehydrogenation of 3-(2'-methyl-1'-cyclohexenyl)-thianaphthene resulted only in producing a very dark amorphous solid from which no crystalline product could be isolated. Elimination of a methyl group in the course of a sulfur dehydrogenation is a fairly common phenomenon (65). This may partially account for the decomposition of the compound during the dehydrogenation procedure.

Preparation of 5-Chloro-3-Aryl-2-Thianaphthenecarboxylic Acids

The sequence of reaction steps employed in the preparation of these substituted thianaphthenecarboxylic acids is outlined in Figure IV. The synthesis of the necessary intermediates, p-chlorobenzenesulfenyl chloride, p-chlorothiophenol, and p-chlorophenyl methyl sulfide were accomplished by utilizing previously reported methods (39,40,41) for the preparation of such compounds. Chlorosulfonation of chlorobenzene gave a ninety percent yield of p-chlorobenzenesulfonyl chloride which on reduction with zinc dust and sulfuric acid resulted in a forty-seven percent yield of the desired p-chlorothiophenol. Methylation of p-chlorothiophenol with dimethyl sulfate produced the required sulfide in an eighty-seven percent yield.

Four different acid chlorides and phthallic anhydride were allowed to react with the p-chlorophenyl methyl sulfide to obtain the five, previously unreported, o-aroyl-p-chlorophenyl methyl sulfides whose properties are summarized in Table IV. Benzoyl chloride and phthallic anhydride were procured from Eastman Kodak Company. The 4- and 3-

TABLE III

3-ARYLTHIANAPHTHENES

Ar	Formula	M.p. °C.	Yield Percent	Carbon, Percent Calc'd.	Carbon, Percent Found	Hydrogen, Percent Calc'd.	Hydrogen, Percent Found
Phenyl	$C_{14}H_{10}S$	172-173	56	79.9	79.3	4.8	4.9
1'-Naphthyl	$C_{18}H_{12}S$	90-92	38	83.0	82.8	4.7	4.9
3'-Thianaphthyl*	$C_{16}H_{10}S_2$	>370	22	72.1	71.9	3.8	3.5

*Prepared by Ullmann reaction.

FIGURE IV

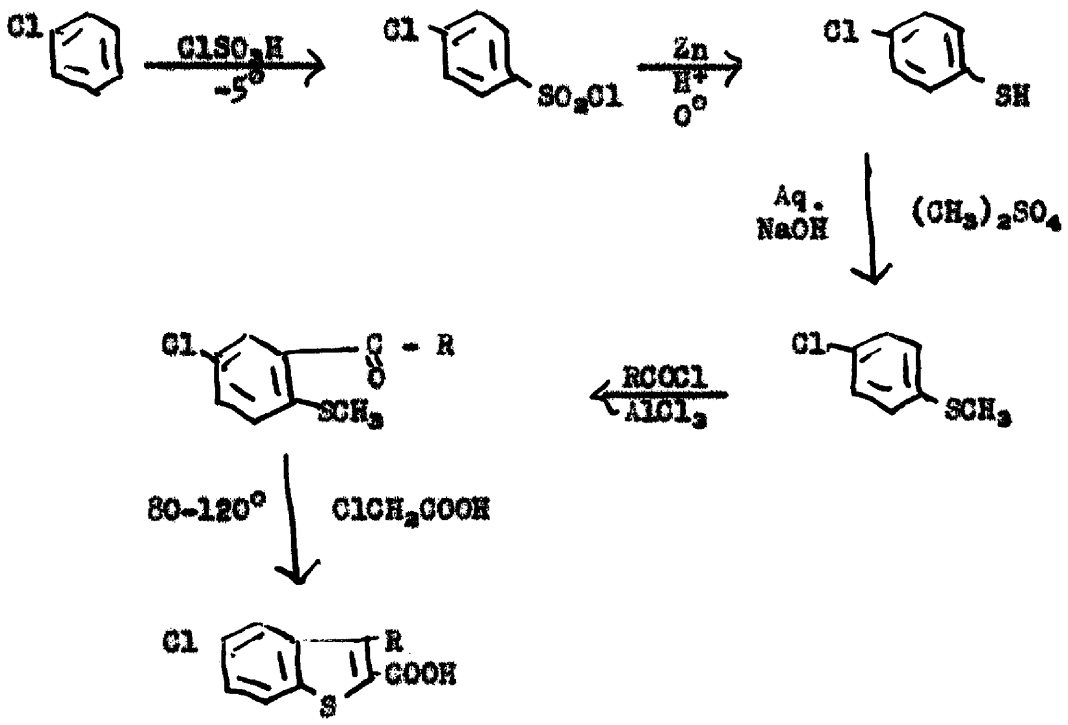
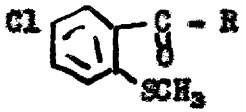

Cl
ClSO3H
-5°
SO2Cl
Zn
H+
0°
SH
Aq.
NaOH
(CH3)2SO4
SCH3
RCOCl
AlCl3
C - R
O
80-120°
ClCH2COOH
R
COOH
S

TABLE IV

o-AROYL-p-CHLOROPHENYL METHYL SULFIDES



R	Formula	M.p., °C.	Yield Percent	Carbon, Percent Calc'd.	Carbon, Percent Found	Hydrogen, Percent Calc'd.	Hydrogen, Percent Found
Phenyl	$C_{14}H_{12}ClOS$	101-103	38	64.0	64.1	4.2	4.1
α-Naphthyl	$C_{18}H_{14}ClOS$	115-117	4	69.1	68.5	4.2	3.9
β-Naphthyl	$C_{18}H_{14}ClOS$	120-121	25	69.1	68.6	4.2	4.0
α-Thienyl*	$C_{11}H_8ClOS_2$	77-78	35	51.9	51.9	2.8	2.7
o-Carboxyphenyl	$C_{15}H_{13}ClO_3S$	183-185	13	58.7	58.4	3.6	3.8

*Isolated as the thiophenol rather than as the methyl sulfide.

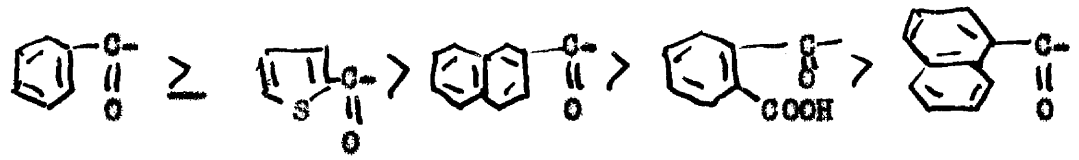
naphthoyl chlorides were prepared by treating the appropriate naphthoic acid with phosphorous pentachloride. The acid chloride of 2-thenoic acid was prepared by treating the acid with thionyl chloride.

The Friedel-Crafts acylation of p-chlorophenyl methyl sulfide took place, with difficulty, at the position ortho to the thioether group. All attempts to synthesize the desired ketones in such typical Friedel-Crafts solvents, as carbon disulfide or S-tetrachloroethane, failed. Nonetheless, an experimental procedure was finally developed which lead to their preparation. Equimolar quantities of the acyl chloride and anhydrous aluminum chloride were brought to a temperature approximately five degrees above the melting point of the acyl chloride by means of an oil bath. Then, one-sixth to one-third of the required quantity of p-chlorophenyl methyl sulfide was added dropwise to the reaction mixture. When all the sulfide had been added, the reaction mixture was held at the original temperature for an additional ten hours. These severer reaction conditions, of elevated temperature and absence of solvent, resulted in the successful preparation of the desired ketones. However, the yields were rather poor, varying from four to thirty-eight percent.

The difficulty of acylation of p-chlorophenyl methyl sulfide can be explained by steric considerations. Friedel-Crafts acylations are notably subject to steric influences, with substitution predominating at the para position rather than at the hindered ortho position. In the present work, the substitution was forced to take place ortho to the large thiomethyl group since the para position was blocked.

Severe conditions are necessary for promoting acylation at such a sterically hindered position. Other experimenters (18,19) have experienced similar difficulty with Friedel-Crafts acylations ortho to a thiomethyl group.

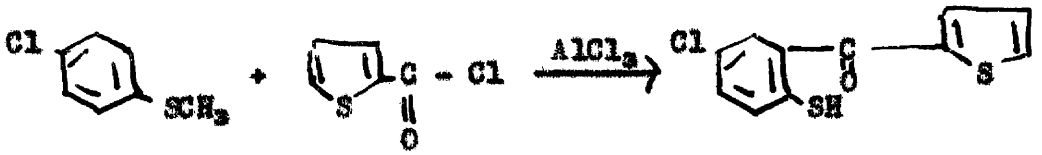
An examination of the yields of the o-aryl-p-chlorophenyl methyl sulfides reported in Table IV offers good evidence for the steric influence of the thiomethyl group to the entering acyl group in these reactions. The acyl groups, listed in order of decreasing yield of the sulfides are as follows



38% 35% 25% 13% 4%

This is precisely the order to be expected on the basis of increasing steric hindrance of the thiomethyl group to the entering acyl group.

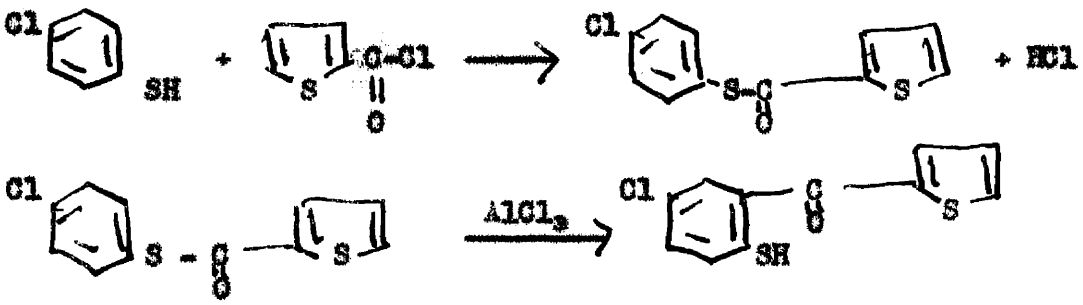
In the acylation of p-chlorophenyl methyl sulfide with 2-thenoyl chloride, cleavage of the thioether occurred and o-(2-thenoyl)-p-chlorothiophenol was obtained as the product of the acylaction reaction.



There is ample precedent for the cleavage of a thioether with anhydrous aluminum chloride. Alkyl aryl ethers can be dealkylated easily by warming with aluminum chloride to yield the free phenol (66). However, it is difficult to explain the absence of thioether cleavage in other

acylations carried out in this work using acyl halides other than 2-thenoyl chloride.

There are at least two different possible sequences of reaction steps in the above synthesis. First, cleavage of the thioether may have occurred after acylation of the aromatic nucleus had taken place. An alternative possibility would be an initial thioether cleavage followed by formation of a thiolester which could then rearrange in a manner analogous to the rearrangement of phenolic esters in the Fries reaction. The latter is effected in the presence of aluminum chloride.

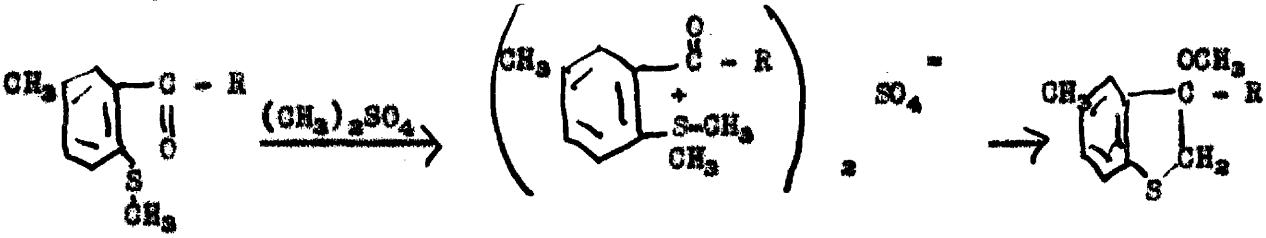


The general procedure used to effect ring closure of the o-aroyl-p-chlorophenyl methyl sulfides was a modification of the cyclization method developed by Krollpfeiffer and co-workers (18,19). The appropriate o-aroyl-p-chlorophenyl methyl sulfide was added to a four to six mole excess of chloroacetic acid. The resulting solution was kept at an elevated temperature, ranging from 80° to 130°, by means of an oil bath for periods of time varying from ten to seventy-two hours. The addition of water to the cooled reaction solution, precipitated the thianaphthene carboxylic acid. The substituted thianaphthenecarboxylic acids prepared by this method and which were not previously described

in the literature are listed in Table V, with some of their properties.

A mechanism involving a sulfonium salt intermediate has been proposed for a ring closure of this type by Krollpfeiffer (18,19). The steps involved in Krollpfeiffer's mechanism are outlined in Figure V using an o-aroyl-p-chlorophenyl methyl sulfide as an illustrative example.

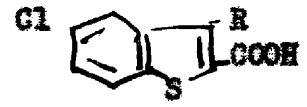
As evidence for this mechanism, Krollpfeiffer cites the isolation of a 3-alkoxy-3-alkyldihydrothianaphthene in a similar ring closure reaction.



In the present work, all attempts to effect a ring closure of either o-(1-naphthoyl)-p-chlorophenyl methyl sulfide or its 2-naphthoyl isomer failed. Instead, ketonic cleavage occurred leading to α-naphthoic acid and β-naphthoic acid from the 1-naphthoyl- and 2-naphthoyl-isomers, respectively, as the only isolable products of these attempted ring closure reactions. o-Benzoyl-p-chlorophenyl methyl sulfide which did yield a ring closure product also underwent some ketonic cleavage, to yield sixteen percent of benzoic acid. These were the only three cases in which this ketonic cleavage phenomenon was observed, and no other products which might have given information as to the fate of the rest of the sulfide molecule were isolated.

TABLE V

5-CHLORO-3-ARYL-2-THIANAPHTHENECARBOXYLIC ACIDS



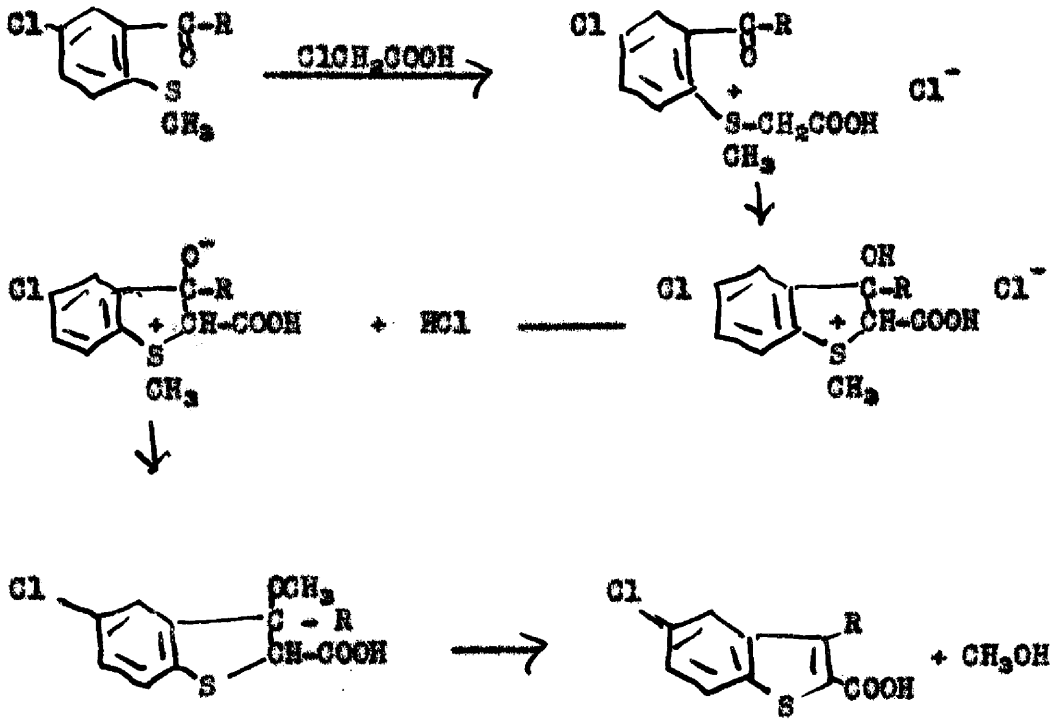
R	Formula	M.p., °C. *	Yield Percent	Neut. Equiv. Calc'd.	Neut. Equiv. Found	Carbon, Percent Calc'd.	Carbon, Percent Found	Hydrogen, Percent Calc'd.	Hydrogen, Percent Found
Phenyl	$C_{15}H_9ClO_2S$	263-265	16	288	287	62.4	62.2	3.1	3.4
-Thienyl	$C_{13}H_8ClO_2S_2$	267-268	53	294	292	52.9	52.7	2.4	2.9
o-Carboxyphenyl**	$C_{16}H_{12}ClO_4S$	282-284	61	179	177	60.3	60.2	3.1	3.3

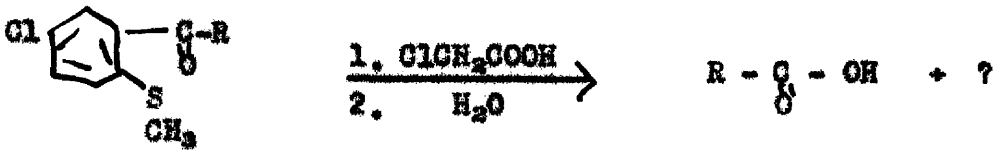
* These compounds decompose at their melting points.

** Analysis is for this compound with one-third mole of benzene of crystallisation.

FIGURE V

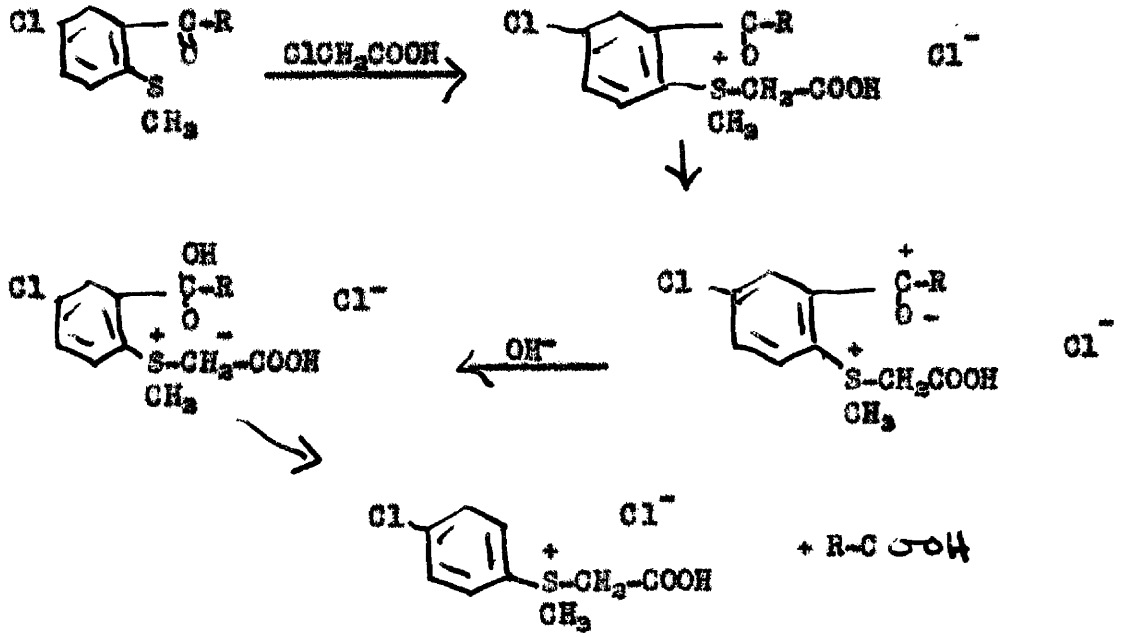
Krollpfeiffer's Proposed Mechanism for the Ring Closure of an o-Aroyl-p-chlorophenyl Methyl Sulfide





It was apparent from the above observations that the ortho thiomethyl group was necessary for the occurrence of ketonic cleavage. To corroborate this, benzophenone was treated with chloroacetic acid using the same experimental procedure as previously described. The benzophenone was recovered from the reaction mixture unchanged.

The following mechanism is offered as a tentative explanation to account for the formation of acid products due to the ketonic cleavage phenomenon observed with o-aroyl-p-chlorophenyl methyl sulfides.



Several factors favor this interpretation. First, the principal cases in which ketonic cleavage occurred were accompanied by failure of the

ring closure reaction. This would strongly suggest that the intermediate sulfonium salt was present at the time water was added to the reaction mixture. Secondly, a strongly positive sulfonium group ortho to the aroyl group would enhance the positive character of the ketonic carbon. The failure to isolate the other fragment resulting from this ketonic cleavage reaction can very probably be ascribed to the high solubility of sulfonium salts in aqueous media.

An attempt was made to dehalogenate 5-chloro-3-phenyl-2-thianaphthenecarboxylic acid through catalytic hydrogenolysis of the carbon-halogen bond by adaptation of a method used by Blanchette and Brown (67) to dehalogenate 2,5-dichloro-3-thienylcarboxylic acid. The failure of this dehalogenation reaction was not entirely unexpected since it is well known that a chlorine atom, in the majority of cases, is considerably less labile when substituted in benzene than when in a position adjacent to the negative heteroatom of a heterocyclic compound.

EXPERIMENTAL

Preparation of 3,3'-Bithianaphthene

Preparation of Activated Copper Bronze

Kleiderer and Adams method for the preparation of active copper bronze (50) was used. Approximately 40 grams of copper bronze was mechanically shaken with 250 ml. of a 2% solution of iodine in acetone for ten minutes, during which time the copper bronze assumed a gray color due to the formation of cupric iodide. The product was filtered and then shaken with 250 ml. of a 50% concentrated hydrochloric acid acetone solution to dissolve the cupric iodide. The activated copper bronze was filtered, washed with 100 ml. of acetone and dried in a vacuum dessicator.

3-Iodothianaphthene

The method used in the preparation of this compound was essentially that of Gaertner (48). The quantities, 27 g. (0.08 mole) of yellow mercuric oxide and 39 g. (0.17 mole) of iodine were added alternately in small portions, over an hours time, to a stirred solution of 22 g. (0.16 mole) of thianaphthene in 40 ml. of benzene, maintained at a temperature of 55 to 65°. The cooled reaction solution was first filtered and then decolorized by passing it through a column of alumina

and Norite to remove unreacted iodine. Removal of the benzene was accomplished by aspiration with a water pump. Fractional distillation of the residue under reduced pressure gave 4.5 g. (0.06 mole; 34%) of 3-iodothianaphthene boiling at 146-152° (7 mm.). The reported boiling point is 120-121° (1.6 mm.) (48).

Preparation of a picrate from the product, melting at 105-106° served as further identification. The reported melting point is 107-108° (49).

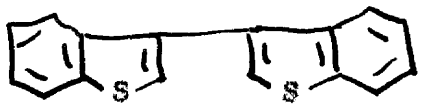
3-Bromothianaphthene

This compound was prepared by the method of Szmuskovicz and Modest (46). In a three liter flask provided with stirrer, dropping funnel and condenser with attached calcium chloride drying tube were placed the quantities, 67 g. (0.5 mole) of thianaphthene, 67 g. of sodium acetate and 300 ml. of chloroform. A bromine solution containing 80.0 g. (26 ml; 0.5 mole) of bromine in 60 ml. of chloroform was added dropwise over a half hour period. The vigorous reaction was controlled by intermittently immersing the reaction flask in an ice water bath. After an additional thirty minutes of stirring, 100 ml. of water were added to the reaction flask and the chloroform layer was separated, washed first with 100 ml. of a 5% aqueous sodium hydroxide solution and then with 100 ml. of water. After drying the chloroform solution over anhydrous sodium sulfate, the chloroform was removed on a steam bath and the crude product was fractionally distilled

under reduced pressure to yield 68 g. (0.32 mole; 65%) of pure product boiling at 117-124° (6 mm.). The reported boiling point of 3-bromothianaphthene is 95° (1.5 mm.) (46).

The product was further identified by preparation of its picrate which melted at 112-113°. The reported melting point of this material is 114-115° (47).

3,3'-Bithianaphthene



Five grams (0.019 mole) of 3-iodothianaphthene were placed in an eight centimeter Pyrex test tube and heated to 150° in an oil bath. As the temperature was gradually raised to 270° over a period of 20 minutes, 2.5 g. (0.039 mole) of activated copper bronze were added in small portions while stirring the reaction mixture with a thermometer. After the addition was complete, the temperature was maintained at 270-280° for two hours. The cooled reaction mass was extracted with two 25 ml. portions of cold chloroform and on evaporation of the solvent yielded 0.2 g. of a light tan polymeric substance which melted at 258-259° after two recrystallizations from benzene. Analysis of the product for carbon and hydrogen gave the following results:

Calc'd for $(C_8H_6S)_x$: C, 71.6; H, 4.5

Found: C, 71.0; H, 4.4

The residue from the chloroform extraction was placed in a Bailey-Walker type extractor and extracted with 30 ml. of hot chloroform

for two hours. Filtration of the cooled solution produced 0.4 g. (0.0015 mole; 16.6%) of crude solid material which after one recrystallization from benzene yielded a white crystalline solid melting above 370°. Analysis of the compound for carbon and hydrogen gave the following results:

Calc'd for $C_{16}H_{10}S_2$: C, 72.1; H, 3.8

Found: C, 71.9; H, 3.5

In several other preparations, run at temperatures below 250°, the yield of 3,3'-bithianaphthene was only four percent or less.

In a subsequent experiment, 6 g. (0.095 mole) of copper bronze and 9 g. (0.035 mole) of 3-iodothianaphthene were placed in a sealed tube and maintained at a temperature of 270-280° for five hours. After treating the reaction mixture as previously described, 1.0 g. (0.0038 mole; 22%) of 3,3'-bithianaphthene was isolated.

Attempted Preparation of 3,3'-Bithianaphthene Utilizing the Ullmann Reaction with 3-Bromothianaphthene

To 11.0 g. (0.052 mole) of 3-bromothianaphthene in an eight centimeter Pyrex test tube, immersed in an oil bath at 230°, were added in small portions 6 g. (0.095 mole) of activated copper bronze, while stirring with a thermometer. The temperature of the reaction mixture was maintained at 230-250° for a half hour following the addition of the copper bronze. The cooled reaction mixture was extracted with two 25 ml. portions of hot chloroform and filtered. After evaporating the chloroform, the residue was vacuum distilled to yield 10.5 g., a 95% recovery of the starting material, 3-bromothianaphthene boiling at 115-117° (6 mm.).

In several additional experiments, reaction temperatures up to 300° were employed and in all cases there was practically total recovery of the starting material, 3-bromothianaphthene.

Attempted Preparation of 3,3'-Bithianaphthene by Coupling of 3-Thianaphthylmagnesium Bromide

A mixture of 1.6 g. (0.065 gram atom) of magnesium turnings, 15 ml. of dry ether, 14 g. (0.065 mole) of 3-bromothianaphthene and a small crystal of iodine was warmed until a reaction had started. The precipitate initially formed was dissolved by the addition of 20 ml. of sodium dried benzene. After the exothermic reaction had subsided, the reaction mixture was refluxed for an hour. The solution of 3-thianaphthylmagnesium bromide thus obtained was slowly added, while excluding atmospheric moisture from the apparatus, to 9 g. (0.065 mole) of cupric chloride suspended in 50 ml. of dry ether. The reaction mixture was heated at its reflux temperature for an hour and then treated with dilute hydrochloric acid until the cupric chloride had dissolved. The organic layer, after separation, was washed first with 25 ml. of dilute hydrochloric acid, then with 25 ml. of ammonia water, and finally with 25 ml. of water. After drying over anhydrous calcium chloride, evaporation of the solvent gave a residue which on fractional distillation yielded only thianaphthene and unreacted 3-bromothianaphthene. The residual tar remaining after the distillation could not be crystallized.

In a subsequent experiment, nickel bromide was used in place of cupric chloride as the coupling agent following the method of

Gilman and Lichtenwalter (51) but no crystalline product could be isolated from the reaction mixture.

Preparation of 3-Arylthianaphthenes

3-(1'-Cyclohexenyl)-thianaphthene

A mixture of 1.88 g. (0.077 mole) of magnesium turnings, 40 ml. of dry ether and 16 g. (0.076 mole) of 3-bromothianaphthene was warmed until a reaction had initiated. An initially formed precipitate was dissolved by the addition of 20 ml. of dry benzene, after which the reaction mixture was refluxed for an hour. After cooling the reaction solution in an ice bath, 8.2 g. (0.084 mole) of cyclohexanone dissolved in 50 ml. of dry benzene was added dropwise. Following the addition of the cyclohexanone, the reaction mixture was heated at its reflux temperature for 18 hours and then allowed to cool to room temperature. The Grignard complex was decomposed with 100 ml. of a 20% solution of sulfuric acid containing an equal volume of cracked ice. The organic layer was separated, washed with a saturated sodium carbonate solution, then with water, after which it was dried over anhydrous sodium sulfate. The benzene and ether were removed by evaporation and the residue was vacuum distilled to obtain 5.5 g. (0.025 mole; 33%) of a viscous yellow oil which boiled at 140-150° (2 mm.). The reported boiling point for this compound is 135° (0.1 mm.) (46).

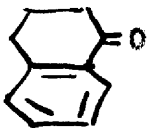
3-Phenylthianaphthene

An intimate mixture of 5.5 g. (0.025 mole) of 3-(1'-cyclohexenyl)-thianaphthene and 1.8 g. (0.056 mole) of powdered sulfur was heated in an oil bath maintained at 240-250° until hydrogen sulfide evolution ceased as indicated by the failure of escaping gas to turn a saturated lead acetate solution black. The cooled reaction mass was dissolved in 50 ml. of hot benzene and the unreacted sulfur was removed by filtration. The cooled benzene solution was washed with two 25 ml. portions of 10% aqueous sodium sulfite and dried over anhydrous sodium sulfate. The benzene was removed by evaporation on a steam bath and the solid residue was sublimed at a temperature of 230° (10 mm.). Three grams (0.014 mole; 56%) of sublimate were collected, which on recrystallization from 95% ethanol, yielded a white crystalline product melting at 172-173°. Carbon and hydrogen analysis of the compound gave the following results:

Calc'd for $C_{14}H_{10}S$: C, 79.9; H, 4.8

Found: C, 79.3; H, 4.9

α-Tetralone



α-Tetralone was prepared by the air oxidation of tetralin following a method given in "Organic Syntheses" (52). In a three

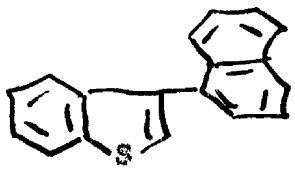
necked flask fitted with a thermometer, condenser and gas diffusion tube, was placed 230 g. (1.74 mole) of tetralin. A slow stream of air was drawn through the tetralin for a twenty-four hour period while it was maintained at a temperature of 72-78° by heating on a steam bath. The partially oxidized tetralin was poured into 300 ml. of well stirred 2N sodium hydroxide solution, which was then warmed to 50° and kept at that temperature for one hour. After being cooled, the basic solution was brought almost to neutrality with 6N sulfuric acid and the organic layer was separated. It was washed first with 80 ml. of 0.5N sulfuric acid and then with 100 ml. of a 1% aqueous ferrous sulfate solution. After drying over anhydrous sodium sulfate, the partially oxidized tetralin was distilled. Following a forerun of 160 g. (1.21 mole) of tetralin, 13 g. (0.089 mole; 17% based on unrecovered tetralin) of α-tetralone boiling at 90-100° (1 mm.) was isolated. The reported boiling point of this compound is 105-107° (2 mm.) (52).

3-(3',4'-Dihydro-1'-naphthyl)-thianaphthene

In the same manner as previously described, the Grignard reagent was formed from 16 g. (0.076 mole) of 3-bromothianaphthene and 1.88 g. (0.077 mole) of magnesium turnings in 40 ml. of dry ether. The quantity, 10.7 g. (0.074 mole) of α-tetralone dissolved in 50 ml. of dry benzene was added dropwise to the cooled solution, after which the

mixture was heated at its reflux temperature for 19 hours to complete the reaction. When the reaction mixture had cooled, the Grignard complex was decomposed with 100 ml. of a 10% solution of sulfuric acid containing an equal volume of crushed ice. The organic layer was separated, washed with saturated sodium carbonate solution and then with water. After drying the solution over anhydrous sodium sulfate, the ether was removed by evaporation on a steam bath. Vacuum distillation of the crude product gave 5 g. (0.019 mole; 26%) of a viscous orange oil boiling at 205-210° (3 mm.). The boiling point reported for this compound is 165° (1 mm.) (46).

3-(1'-Naphthyl)-thianaphthene

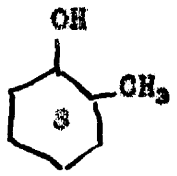


A uniform mixture containing 4 g. (0.015 mole) of 3-(3',4'-dihydro-1'-naphthyl)-thianaphthene and 0.6 g. (0.032 mole) of powdered sulfur was kept at a temperature of 240-260° by means of an oil bath until the evolved gas failed to darken a lead acetate solution. The crude dehydrogenation product was purified by sublimation at 240° (10 mm.) to yield 1.5 g. (0.0058 mole; 38%) of a sublimate, which after recrystallising twice from 95% ethanol melted at 90-92°. Analysis of this material for carbon and hydrogen gave the following results:

Calc'd for $C_{18}H_{12}S$: C, 83.0; H, 4.7

Found: C, 82.8; H, 4.9

2-Methylcyclohexanol



This compound was prepared according to a procedure developed by Ugnade and Nightingale (53). A 100 mg. quantity of metallic sodium was added to 59 g. (0.5 mole) of o-cresol which was then warmed until the metal had dissolved. The solution was then transferred to a glass hydrogenation bomb liner and 2.5 g. of Raney nickel were added. The hydrogenation was carried out immediately in a Parr High Pressure Hydrogenation apparatus at an initial hydrogen pressure of 2700 p.s.i. and a maximum temperature of 120°. When the initial pressure had dropped 1000 p.s.i., the reaction was considered complete and the bomb was opened. After transferring the hydrogenation mixture to a suitable container, the bomb and liner were rinsed with 100 ml. of benzene. The combined washings and reaction solution was filtered to remove spent catalyst and then washed twice with 25 ml. quantities of 10% sodium hydroxide solution, once with 25 ml. of saturated sodium bicarbonate solution and finally with 50 ml. of water. After drying the benzene solution over potassium hydroxide, the solvent was removed by evaporation on a steam bath. Distillation of the crude product gave 36 g. (0.32 mole; 64%) of a product boiling at 160-165°. The reported boiling point for this compound is 165-166° (53).

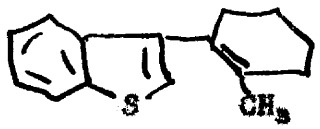
2-Methylcyclohexanone

This compound was prepared by employing the procedure of Carlin (57). In a one liter flask, equipped with stirrer, condenser and dropping funnel, was placed an oxidising solution containing 55 g. (0.21 mole) of sodium dichromate and 52 g. (0.50 mole; 29 ml.) of concentrated sulfuric acid in 300 ml. of water. To this solution, 24 g. (0.21 mole) of 2-methylcyclohexanol dissolved in 40 ml. of glacial acetic acid was added, with stirring, at a rate sufficient to maintain the reaction temperature between 50 and 55°. Stirring was continued for an additional hour and a half after the addition of the alcohol was complete. The reaction mixture was then transferred to a separatory funnel and extracted with three 100 ml. quantities of ether. The combined ether extracts were washed with three 100 ml. portions 5% sodium hydroxide solution.

After evaporating the ether on a steam bath, the crude ketone was added to a solution of 23 g. (0.21 mole) of semicarbazide hydrochloride, 25 g. of sodium acetate, 100 ml. of water and 5 ml. of 10% aqueous sodium hydroxide contained in a one liter bottle. The bottle was mechanically shaken for 21 hours and the precipitated semicarbazone was recovered by filtration. The crude material melted at 186-188°. The reported melting point for this semicarbazone is 193-194° (54). After decomposing the semicarbazone with 800 ml. of 12% sulfuric acid solution, the solution was extracted with ether and the ether extract was

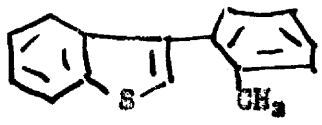
dried over anhydrous sodium sulfate. The ether was removed on a steam bath and the residue distilled yielding 14 g. (0.13 mole; 62%) of a product boiling at 158-163°. The reported boiling point of this cyclic ketone is 166° (57).

3-(2'-Methyl-1'-cyclohexenyl)-thianaphthene



The Grignard reagent was formed as previously described from 16 g. (0.076 mole) of 3-bromothianaphthene and 1.9 g. (0.077 mole) of magnesium turnings in 40 ml. of dry ether. To the cooled solution, were added 9.5 g. (0.085 mole) of 2-methylcyclohexanone dissolved in 50 ml. of dry benzene at a rate sufficient to maintain a constant reflux of ether. The reaction mixture was kept at its reflux temperature for 8 hours after the addition of ketone was complete. The Grignard complex was then decomposed with 100 ml. of 10% aqueous sulfuric acid and the organic layer separated. It was washed with saturated sodium carbonate solution, then with water, and dried over anhydrous sodium sulfate. Following removal of the ether on a steam bath, the residue was fractionally distilled to yield 3.8 g. (0.016 mole; 21%) of crude product boiling at 160-170° (2 mm.).

Attempted Synthesis of 3-(o-Tolyl)-thianaphthene



Following the experimental procedure previously described for the sulfur dehydrogenation of similar compounds, an intimate mixture of 3.8 g. (0.016 mole) of crude 3-(2'-methyl-1'-cyclohexenyl)-thianaphthene and 1.4 g. (0.044 mole) of powdered sulfur was heated at a temperature of 250-260° until the evolution of hydrogen sulfide had ceased. The reaction mass was extracted with benzene, filtered, washed with 50 ml. of 10% aqueous sodium sulfite and dried over anhydrous sodium sulfate. After removing the benzene on a steam bath, the residue was subjected to sublimation at 190° (3 mm.) but only decomposition was observed to occur and no sublimate could be obtained.

3-Hydroxythianaphthene

This compound was prepared by the method of Hutchison and Smiles (55). The quantity, 51 g. (0.390 mole) of ethylacetoacetate was added to 30 g. (0.195 mole) of o-mercaptobenzoic acid in 250 ml. of concentrated sulfuric acid at a rate sufficient to maintain the reaction temperature between 50 and 55°. When the evolution of carbon dioxide ceased, the reaction mixture was poured onto crushed ice, and the resulting precipitate collected by filtration and then steam distilled to yield 4 g. (0.027 mole; 14%) of a crude product melting at 67-69°. The reported melting point of 3-hydroxythianaphthene is 71° (56). The low yield of product resulted from the air oxidation of the 3-hydroxythianaphthene to thioindigo during the steam

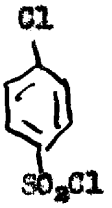
distillation. The yield could very probably be improved by using a nitrogen atmosphere throughout the operation.

Attempted Preparation of 3,3'-Bithianaphthene from 3-Hydroxy- and 3-Bromothianaphthene

The Grignard reagent was prepared as previously described from the interaction of 2.5 g. (0.012 mole) of 3-bromothianaphthene and 0.4 g. (0.016 mole) of magnesium turnings in 30 ml. of ether as a solvent. To the Grignard reagent, at room temperature, was added 2 g. (0.013 mole) of 3-hydroxythianaphthene dissolved in 15 ml. of dry benzene which resulted in no observable reaction. The reaction mixture was then refluxed at its boiling point for an eighteen hour period and then treated with 25 ml. of ten percent aqueous sulfuric acid, and the organic layer was separated. After washing with saturated sodium carbonate solution and then with water, the organic layer was dried over anhydrous sodium sulfate. The ether was removed on a steam bath and vacuum distillation of the residue yielded only thianaphthene and unreacted 3-bromothianaphthene. The red-brown colored residue remaining after the distillation appeared to be polymeric and could not be further purified.

Preparation of 5-Chloro-3-aryl-2-thianaphthene-carboxylic Acids

p-Chlorobenzenesulfenyl chloride



To 350 g. (3 mole; 195 ml.) of chlorosulfonic acid kept at a temperature of -5 to -10° and stirred, were added dropwise 113 g. (1 mole; 103 ml.) of chlorobenzene over a period of three hours. Stirring was continued at the same temperature for an additional three hours to complete the reaction. After being set aside overnight, at room temperature, the reaction mixture was poured onto ice and resulted in the precipitation of the p-chlorobenzenesulfonyl chloride. This was recovered by filtration and after drying weighed 190 g. (0.90 mole; 90%). It had a melting point of 42-44°. The reported m.p. is 53° (39).

p-Chlorothiophenol

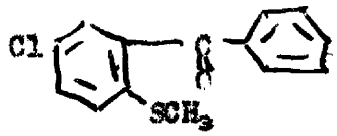
A mixture of 312 g. (1.47 mole) of crude p-chlorobenzenesulfonyl chloride, 1500 g. of ice and 807 g. (8.22 mole; 440 ml.) of concentrated sulfuric acid was cooled to 0° and stirred while 392 g. (6.00 mole) of zinc dust were added over a period of one hour. To insure completeness of reaction, stirring was continued at 0° for an additional two hours and then the reaction mixture was set aside overnight at room temperature. Steam distillation of the reaction mixture gave 100 g. (0.69 mole; 47%) of a solid, after separation from the distillate, which melted at 52-53°. The reported m.p. is 53° (40).

p-Chlorophenyl Methyl Sulfide

A 100 g. (0.69 mole) quantity of p-chlorothiophenol was dissolved in 350 ml. of ten percent aqueous sodium hydroxide. To this solution, while being stirred, were added dropwise over a one half hour period, 177 g. (1.40 mole) of dimethyl sulfate. During the course of the reaction an additional 150 ml. of 10% aqueous sodium hydroxide was added to the reaction mixture to maintain its alkalinity. The resultant oily product was extracted with ether and dried over anhydrous sodium sulfate. The ether was removed on a steam bath and the residue fractionally distilled to yield 94.7 g. (0.60 mole; 87%) of a product boiling at 107° (14 mm.); n_D^{20} 1.5997. The reported b.p. is 170° (760 mm.) (41).

For further characterization, the sulfone was prepared by oxidizing 0.5 g. of the p-chlorophenyl methyl sulfide dissolved in 1 ml. of glacial acetic acid with 0.7 g. of potassium permanganate contained in 25 ml. of water. The excess oxidizing agent was destroyed by adding dropwise saturated aqueous sodium bisulfite solution until the permanganate color was discharged. Ice was then added and the resulting precipitate was filtered and recrystallized once from methanol. It melted at 97.5-98°. The reported m.p. for this derivative is 96° (42).

o-Benzoyl-p-chlorophenyl Methyl Sulfide



In a 300 ml. three necked flask supported in an ice bath and fitted with a stirrer, reflux condenser and dropping funnel, were placed 39.8 g. (0.30 mole) of anhydrous aluminum chloride and 41.9 g. (0.30 mole) of benzoyl chloride. After starting the stirrer, 10 g. (.063 mole) of p-chlorophenyl methyl sulfide were added dropwise over a period of a half hour. Following the addition of the sulfide, stirring was continued, at room temperature, for ten hours at which time the reaction mixture had taken on a deep red color. After being set aside overnight at room temperature, the reaction mixture was cautiously poured into a slurry of 250 ml. of dilute hydrochloric acid, containing an equal volume of crushed ice, and extracted with ether. The ether extract, after washing with three 70 ml. portions of 10% sodium hydroxide solution, was dried over anhydrous sodium sulfate. After removing the ether on a steam bath the residue was fractionally distilled and gave 5.6 g. (.024 mole; 38%) of a fluorescent green oil boiling at 156-160° (3 mm.) which solidified on being set aside at room temperature. It was recrystallized from ligroin as a white solid and melted at 101-103°. Analysis of the compound for carbon and hydrogen gave the following results:

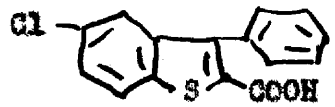
Calc'd for $C_{14}H_{11}OSCl$: C, 64.0; H, 4.2

Found: C, 64.1; H, 4.1

The semicarbazone of this ketone melted at 83-85° after recrystallization from methanol.

In two additional preparations of this compound using the same molar ratios of reactants, the yields were 9.2% and 21.9% using reaction periods of seven and seventeen hours respectively.

5-Chloro-3-phenyl-2-thianaphthenecarboxylic Acid



A mixture of 8.6 g. (0.033 mole) of o-benzoyl-p-chlorophenyl methyl sulfide and 17 g. (0.18 mole) of chloracetic acid was heated on a steam bath for eight hours and then at 130° for an additional thirteen hours. After allowing the reaction mixture to cool to room temperature, water was added until precipitation of the product was complete. It weighed 1.5 g. (0.0052 mole) after filtration and drying which corresponded to a 16% yield of the crude thianaphthenecarboxylic acid. The product melted at 263-265° with decomposition, after a single recrystallization from benzene. Analysis of this compound for carbon and hydrogen gave the following results:

Calc'd for $C_{15}H_9O_2SCl$: C, 62.4; H, 3.1

Found: C, 62.2; H, 3.4

The neutralization equivalent was found to be 287 g. as compared with a calculated value of 288 g.

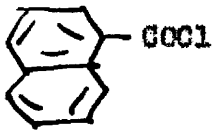
The filtrate obtained after removal of the crude thianaphthenecarboxylic acid was evaporated and a 0.95 g. (0.0078 mole) quantity of benzoic acid was isolated. It melted at 121-122° and showed no depression in its melting point when mixed with an authentic sample of benzoic acid.

In a subsequent experiment, 4.3 g. (0.016 mole) of o-benzoyl-p-chlorophenyl methyl sulfide and 7.4 g. (0.078 mole) of chloroacetic acid yielded 1.8 g. (0.015 mole) of benzoic acid as a byproduct after a reaction period of four and a third days at 130°.

Attempted Preparation of 3-Phenyl-2-thianaphthenecarboxylic acid From the 5-Chloro Derivative By Catalylic Hydrogenolysis

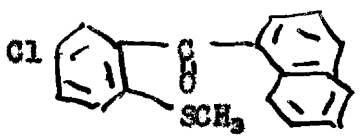
A mixture of 1.2 g. (0.0042 mole) of 5-chloro-3-phenyl-2-thianaphthenecarboxylic acid, 2.4 g. of a charcoal supported palladium catalyst, 150 ml. of methanol, 10 ml. of water, and 2 ml. of concentrated sulfuric acid were placed in a Parr Low Pressure Hydrogenation Apparatus. Hydrogenation was carried out for four hours at room temperature and an initial pressure of 25 p.s.i. The catalyst was removed by filtration and the filtrate concentrated on a steam bath until precipitation of the product occurred. After filtering and drying, the precipitate melted at 263-265° and was indistinguishable from the original starting material.

α-Naphthoyl Chloride



A mixture of 25 g. (0.15 mole) of α-naphthoic acid and 30 g. (0.15 mole) of phosphorous pentachloride was heated on a steam bath until the evolution of hydrogen chloride ceased. The resulting clear solution was submitted to fractional distillation. After removing phosphorous oxychloride below 50° (18 mm.), 25.0 g. (0.13 mole; 87%) of α-naphthoyl chloride which boiled at 187-191° (18 mm.) was collected. Its reported b.p. is 168° (10 mm.) (43).

o-(1-Naphthoyl)-p-chlorophenyl Methyl Sulfide



The experimental procedure employed was the same as that used in the preparation of o-benzoyl-p-chlorophenyl methyl sulfide. The quantities of material used in the synthesis were 18.3 g. (0.11 mole) of α-naphthoyl chloride, 12.9 g. (0.098 mole) of anhydrous aluminum chloride and 6.7 g. (0.042 mole) of p-chlorophenyl methyl sulfide. Distillation of the crude o-(1-naphthoyl)-p-chlorophenyl methyl sulfide yielded 0.5 g. (0.0016 mole; 4%) of a product boiling at 185-190° (3 mm.). A single recrystallization from ligroin gave a white crystalline solid which melted at 115-117°. Analysis of this compound for carbon and hydrogen gave the following results:

Calc'd for $C_{18}H_{13}OSCl$: C, 69.1; H, 4.2

Found: C, 68.5; H, 3.9

Attempted Preparation of 5-Chloro-3-(1'-naphthyl)-2-thianaphthenecarboxylic Acid

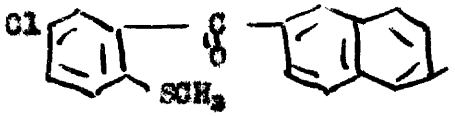
A mixture of 0.30 g. (0.001 mole) of o-(1-naphthoyl)-p-chlorophenyl methyl sulfide and 1.0 g. (0.01 mole) of chloroacetic acid was heated on the steam bath for 18 hours. After allowing the reaction mixture to cool to room temperature, water was added to it until the precipitation of the product was complete. The latter was recovered by filtration and after drying it weighed 0.24 g. (0.0008 mole). It was identified, after repurification, as unreacted starting material by its melting point and mixed melting point with an authentic sample of the original compound. The recovered starting material from the above process on extraction with a 10% solution of sodium hydroxide yielded approximately 50 mg. (0.0003 mole) of α-naphthoic acid which melted at 160-161° and showed no depression in its melting

point when mixed with an authentic sample of ∝-naphthoic acid. No other products were isolated from the reaction mixture

β-Naphthoyl chloride

This material was prepared in the same manner as its ∝-isomer using the same molar quantities of reactants as were used in the preparation of the ∝-isomer. Distillation of the crude product yielded 21.6 g. (0.11 mole; 76%) of pure β-naphthoyl chloride boiling at 176° (13 mm.) which solidified to a white solid which melted at 40-42°. The reported physical constants for this compound are: b.p. 304-306° (760 mm.); m.p. 43° (44).

o-(2-Naphthoyl)-p-chlorophenyl Methyl Sulfide



To a stirred mixture of 11.1 g. (0.058 mole) of β-naphthoyl chloride and 7.8 g. (0.058 mole) of anhydrous aluminum chloride contained in a three necked flask and kept at a temperature of 46° were added dropwise 5 g. (0.031 mole) of p-chlorophenyl methyl sulfide over a one-half hour period. Stirring was continued at 46° for an additional three hours following the addition of the sulfide. After the reaction had been set aside, at the same temperature, for four hours, the addition complex was decomposed with 200 ml. of ice cold dilute hydrochloric acid and extracted with ether. The ether was removed on a

steam bath and the solid residue was extracted with dilute sodium hydroxide solution and filtered. The product was washed on the filter four times with small quantities of cold petroleum ether. Finally, recrystallization of the white solid from ligroin yielded 2.4 g. (0.0077 mole; 25%) of a pure product melting at 120-121°. Analysis of the compound for carbon and hydrogen gave the following results:

Calc'd for $C_{18}H_{13}OSCl$: C, 69.1; H, 4.2

Found: C, 68.6; H, 4.0

In an earlier preparation of this compound, 15.1 g. (0.11 mole) of anhydrous aluminum chloride were added over a period of forty minutes to a stirred cooled solution of 21.6 g. (0.11 mole) of β-naphthoyl chloride and 10.5 g. (0.067 mole) of p-chlorophenyl methyl sulfide in 40 ml. of carbon disulfide. Stirring was continued at room temperature for two hours after the addition and the reaction mixture was set aside overnight. On working up the reaction mixture in the usual manner, an almost total recovery of starting materials resulted and none of the desired sulfide was obtained.

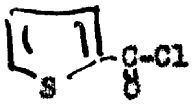
Attempted Preparation of 5-Chloro-3-(2'-naphthyl)-2-thianaphthene-carboxylic Acid

A mixture of 0.40 g. (0.0013 mole) of α-(2-naphthoyl)-p-chlorophenyl methyl sulfide and 1.2 g. (0.012 mole) of chloroacetic acid was heated for half a day at a temperature of 120° in an oil bath. After allowing the reaction mixture to cool to room temperature, water was added to it until the precipitation of the product was complete. After filtering and drying it amounted to 0.38 g. (0.0012 mole) of

impure starting material which was identified as such, after purification of a sample, by its melting point and mixed melting point with the original starting material. Extraction of the recovered starting material from the above process with 50 ml. of 10% aqueous sodium hydroxide followed by acidification with dilute hydrochloric acid yielded approximately 60 mg. (0.0002 mole) of β-naphthoic acid which melted at 184-186° and showed no depression in its melting point when mixed with an authentic sample of β-naphthoic acid.

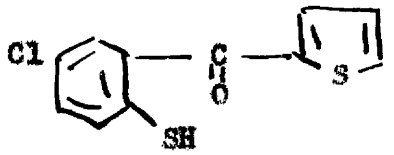
In several additional attempted preparations of 5-chloro-3-(2'-naphthyl)-2-thianaphthenecarboxylic acid, reaction temperatures of 80°, 100°, and 130° were used. In all three cases, the only isolable product was a small quantity of β-naphthoic acid.

2-Thenoyl chloride



A 25 g. (0.20 mole) quantity of 2-thenoic acid was allowed to interact with 131 g. (1.10 mole; 80 ml.) of thionyl chloride at room temperature for a five hour period after which the reaction mixture was heated on the steam bath until the evolution of hydrogen chloride and sulfur dioxide ceased. The excess thionyl chloride which boiled at 78° (760 mm.) was removed by distillation and the residue was fractionally distilled to yield 23 g. (0.16 mole; 80%) of 2-thenoyl chloride boiling at 203° (760 mm.). The reported b.p. of this compound is 201° (760 mm.) (45).

o-(2-Thenoyl)-p-chlorothiophenol



To a mixture of 11.5 g. (0.078 mole) of 2-thenoyl chloride and 10.5 g. (0.078 mole) of anhydrous aluminum chloride contained in a three necked flask, supported in an ice bath, and fitted with a stirrer, condenser, and droppling funnel, were added 6.4 g. (0.040 mole) of p-chlorophenyl methyl sulfide over a quarter hour period. The reaction mixture was stirred for an additinnal three hours, at room temperature, after all the sulfide had been added after which it was set aside overnight. Following decomposition of the addition complex and extraction with ether as previously described, the ether was removed on a steam bath. Distillation of the residue yielded 3.5 g. (0.014 mole; 35%) of a red viscous oil boiling at 170-175° (2 mm.) which solidified on being set aside at room temperature. The solid, after four washings, on a filter, with small quantities of petroleum ether yielded a white crystalline solid melting at 77-78°. Analysis of the compound for carbon and hydrogen gave the collowing results:

Calc'd for $C_{11}H_7OS_2Cl$: C, 51.9; H, 2.8

Found: C, 51.9; H, 2.7

5-Chloro-3-(2'-thienyl)-2-thianaphthenecarboxylic Acid

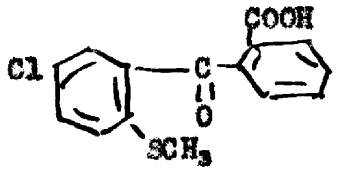
A solution of 0.40 g. (0.0016 mole) of o-(2-thenoyl)-p-chlorothiophenol in 1.0 g. (0.01 mole) of chloroacetic acid was heated at 120° in an oil bath for seven hours. The reaction mixture was allowed to cool to room temperature at which point water was added to it until the precipitation of crude 5-chloro-3-(2'-thienyl)-2-thienaphthenecarboxylic acid was complete. This was filtered and then extracted with 50 ml. of 5% aqueous sodium hydroxide. The basic extract was acidified with hydrochloric acid and the resulting precipitate was collected by filtration and on recrystallization from benzene, yielded 0.25 g. (0.00085 mole; 53%) of a material which melted at 267-268° with decomposition. Analysis of this compound for carbon and hydrogen gave the following results:

Calc'd for $C_{13}H_7O_3S_2Cl$: C, 52.9; H, 2.4

Found: C, 52.7; H, 2.9

The neutralization equivalent of this compound was found to be 292 g. as compared with its calculated value of 294 grams.

o-(2-Carboxybenzoyl)-p-chlorophenyl Methyl Sulfide



A mixture of 10 g. (0.062 mole) of p-chlorophenyl methyl sulfide and 4.6 g. (0.031 mole) of phthallic anhydride was treated with 10.5 g. (0.065 mole) of anhydrous aluminum chloride. The latter was added in small portions. Following the complete addition of the aluminum chloride catalyst, the reaction mixture was maintained at a temperature

of 80° for four hours by immersion of the reaction flask in an oil bath. After allowing the reaction mixture to cool to room temperature the Friedel and Crafts complex was decomposed with water and the excess p-chlorophenyl methyl sulfide was removed by steam distillation. The residual solid was collected by filtration and extracted with hot chloroform in which the unreacted phthallic anhydride was insoluble. After removing the chloroform on a steam bath, the solid residue was washed three times, on a filter, with small quantities of petroleum ether, and dried. It weighed 1.2 g. (0.004 mole) which corresponded to a 13% yield of the desired product which melted at 183-185°. A single recrystallization from aqueous acetic acid raised the melting point to 184-186°. Analysis of this acid product for carbon and hydrogen gave the following results:

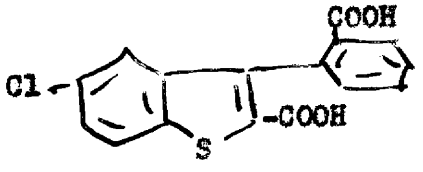
Calc'd for $C_{16}H_{11}O_3SCl$: C, 58.7; H, 3.6

Found: C, 58.4; H, 3.8

The neutralization equivalent of this acid was determined to be 302 g. while the calculated value is 307 grams.

Several previous attempts to prepare o-(2-carboxybenzoyl)-p-chlorophenyl methyl sulfide using carbon disulfide or s-tetrachloroethane as a Friedel-Crafts solvent failed to yield any of the desired product.

5-Chloro-3-(2'-carboxyphenyl)-2-thianaphthenecarboxylic Acid



A mixture of 0.4 g. (0.0013 mole) of o-(2-carboxybenzoyl)-p-chlorophenyl methyl sulfide and 1.0 g. (0.01 mole) of chloroacetic acid was heated on a steam bath for 17 hours. When the reaction mixture had cooled to room temperature, water was added to it until the precipitation of the product was complete. The precipitated dibasic acid was filtered and recrystallized from benzene to yield 0.25 g. (0.0008 mole; 61%) of pure product which melted at 282-284° with decomposition.

This compound crystallized with one-third of a mole of benzene as solvent of crystallization and all attempts to remove the benzene failed. Analysis of the compound for carbon and hydrogen gave the following results:

Calc'd for $C_{16}H_9O_4SCl \cdot 1/3\ (C_6H_6)$: C, 60.3; H, 3.1

Found: C, 60.2; H, 3.3

The neutralization equivalent of the product was determined to be 177 g. as compared with a calculated value of 179 grams.

Attempted Formation of Benzoic Acid from Benzophenone

A mixture of 10.5 g. (0.057 mole) of benzophenone and 42 g. (0.45 mole) of chloroacetic acid was heated on a steam bath for two days. After cooling the reaction mixture to room temperature it was treated with water and the resulting precipitate, after recovery by filtration, was found to be starting material of which there was a total recovery.

SUMMARY

1. The Ullmann synthesis of 3,3'-bithianaphthene was carried out with 3-iodothianaphthene in the presence of copper bronze. The attempted coupling of 3-thianaphthylmagnesium bromide with cupric chloride or nickel bromide failed to yield 3,3'-bithianaphthene.

2. The syntheses of 3-phenylthianaphthene and 3-(1'-naphthyl)-thianaphthene were successful. The properties of the products are reported.

3. Five o-aroyl-p-chlorophenyl methyl sulfides were prepared. The yields were correlated with the amount of steric hindrance involved in formation of the products. The properties of these sulfides are reported.

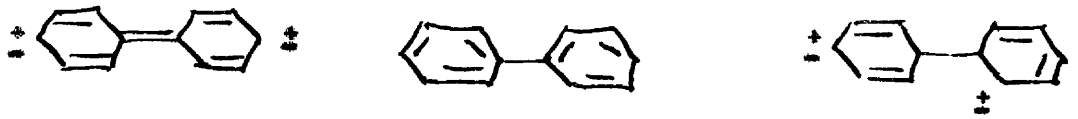
4. Ring closure of three of the five o-aroyl-p-chlorophenyl methyl sulfides was successfully carried out to yield the corresponding 5-chloro-3-aryl-2-thianaphthenecarboxylic acids. The properties of these thianaphthene derivatives are reported. A mechanism has been proposed to account for a ketonic cleavage reaction observed with three of the o-aroyl-p-chlorophenyl methyl sulfides.

PART II - ULTRAVIOLET SPECTRA

INTRODUCTION

The initial investigation of the effect of restricted rotation in biphenyl compounds on the ultraviolet absorption spectra of such substances was made twenty years ago by Pickett and co-workers (68). Since then several other investigators (69-74) have determined the absorption spectra of biaromatic compounds exhibiting restricted rotation and similar studies have now been extended to biaromatic type compounds containing heterocyclic nuclei (75,76).

The theoretical considerations involved in investigations of this kind may be briefly described using biphenyl as an example. In the ground state, indicated by structure b, the rotation around the pivot



a. b. c.

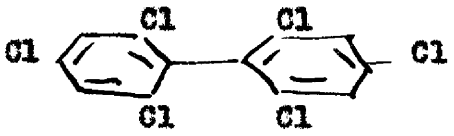
bond is hindered slightly due to the mutual repulsion of the hydrogen atoms in the ortho positions with respect to the pivot bond. However, if the hindering barrier is not high, some molecules of biphenyl are nearly coplanar as a result of thermal motion. For these molecules, ionic structures such as a and c make significant contributions to the excited states of the molecule which are important in absorption. Such excited states give full extension to the conjugated system and should lead to intense absorption at relatively long wavelengths of

light. These ionic structures require that the two phenyl rings be approximately coplanar. Thus, biphenyl derivatives without hindered rotation, particularly those unsubstituted in the positions ortho to the pivot bond, should exhibit an intense absorption characteristic of the entire aromatic ring system. Those biphenyl derivatives with highly hindered rotation, notably those substituted in the ortho positions with respect to the pivot bond, would have more or less difficulty, depending on the substituents, in assuming a coplanar structure, and consequently, should exhibit absorption approximately equivalent to that of the single ring structure.

The purpose of the present investigation herein described was to determine the extent to which rotation was restricted around the pivot bond in 3,3'-bithianaphthene and certain 3-arylthianaphthenes by an examination of their ultraviolet absorption spectra. Results of this study should, it is anticipated, facilitate the selection of compounds of this type amenable to optical resolution which would permit further study in the general problem of restricted rotation and structure in the bithianaphthenes, arylthianaphthenes, and their derivatives.

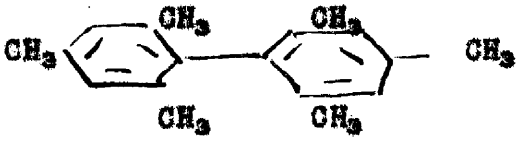
HISTORY

Pickett, Walter, and France (68), in the year 1936, made the original investigation of the effect of restricted rotation on the ultraviolet absorption spectra of biphenyl and its derivatives. Their investigation involved the determination of the spectra of the following compounds.

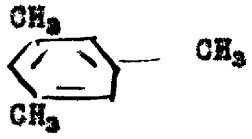


Ia.

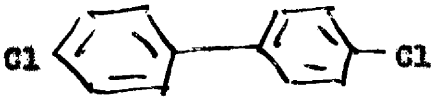
Ib.



IIa.

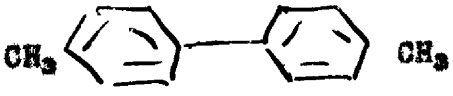


IIb.



IIIa.

IIIb.



IVa.

IVb.

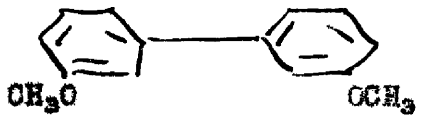
The spectrum of each biphenyl derivative was compared to the analogously substituted benzene compound. The 4,4'-dichlorobiphenyl

(III a) and 4,4'-dimethylbiphenyl (IV a) showed greatly enhanced absorption intensities at longer wavelengths of light than the corresponding chlorobenzene (III b) and toluene (IV b). However, 2,4,6,2',4',6'-hexamethylbiphenyl (II a) and 2,4,6,2',4',6-hexachlorobiphenyl gave absorption spectra almost identical with their respective single ring analogs, 2,4,6-trichlorobenzene (I b) and mesitylene (II b). These observations were interpreted to support the very reasonable contention that Ia and IIa could not achieve coplanarity due to the steric hindrance to free rotation supplied by the four ortho substituents, and as a result the important ionic structures of the latter two compounds could not contribute to their absorption of light.

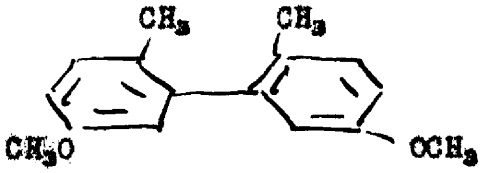
Following publication of these results, other investigators employed the same technique with considerable success. The following year, Pestemer and Mayer-Pitsch (69) studied several singly substituted biphenyls. In general, their results showed that biphenyl with a single ortho substituent had absorption spectra of reduced intensity compared to unsubstituted, meta-substituted, or para-substituted biphenyls.

Calvin (70), in 1939, discussed the theoretical aspects of the effect of conjugated resonance forms on the absorption spectra of biphenyls. He predicted that certain non-resolvable tetra-ortho-substituted biphenyls should show a spectrum characteristic of the entire conjugated molecule, since such molecules could approach a degree of coplanarity. On the other hand, certain resolvable biphenyls should have spectra similar to the uncoupled parts of the biphenyl molecule due to loss of free rotation about the pivot bond.

Calvin's predictions were confirmed by O'Shaughnessy and Rodebush (71) in an extensive study covering some twenty compounds in which the various effects of conjugation, coplanarity, and restricted rotation were thoroughly investigated. For example, they determined the spectra (Figure VI) of 3,3'-dimethoxybiphenyl (V a) and of 5,5'-dimethoxy-2,2'-dimethylbiphenyl (V b).



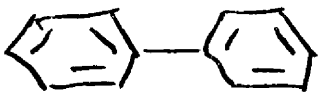
V a.



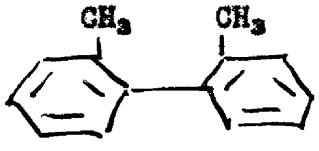
V b.

Examination of these absorption curves shows that there is a maximum or peak for 3,3'-dimethoxybiphenyl (V a) at 260 mu corresponding to biphenyl absorption and a smaller peak at 300 mu corresponding to anisole absorption. In the spectrum of V b, the anisole absorption is practically unaffected whereas the biphenyl absorption has been enormously decreased. This decrease was explained as due to the inability of the molecule to assume a coplanar configuration as a consequence of the steric hindrance presented by the ortho methyl groups.

Another series of compounds studied by O'Shaughnessy and Rodebush were the biphenyl homologs listed below.

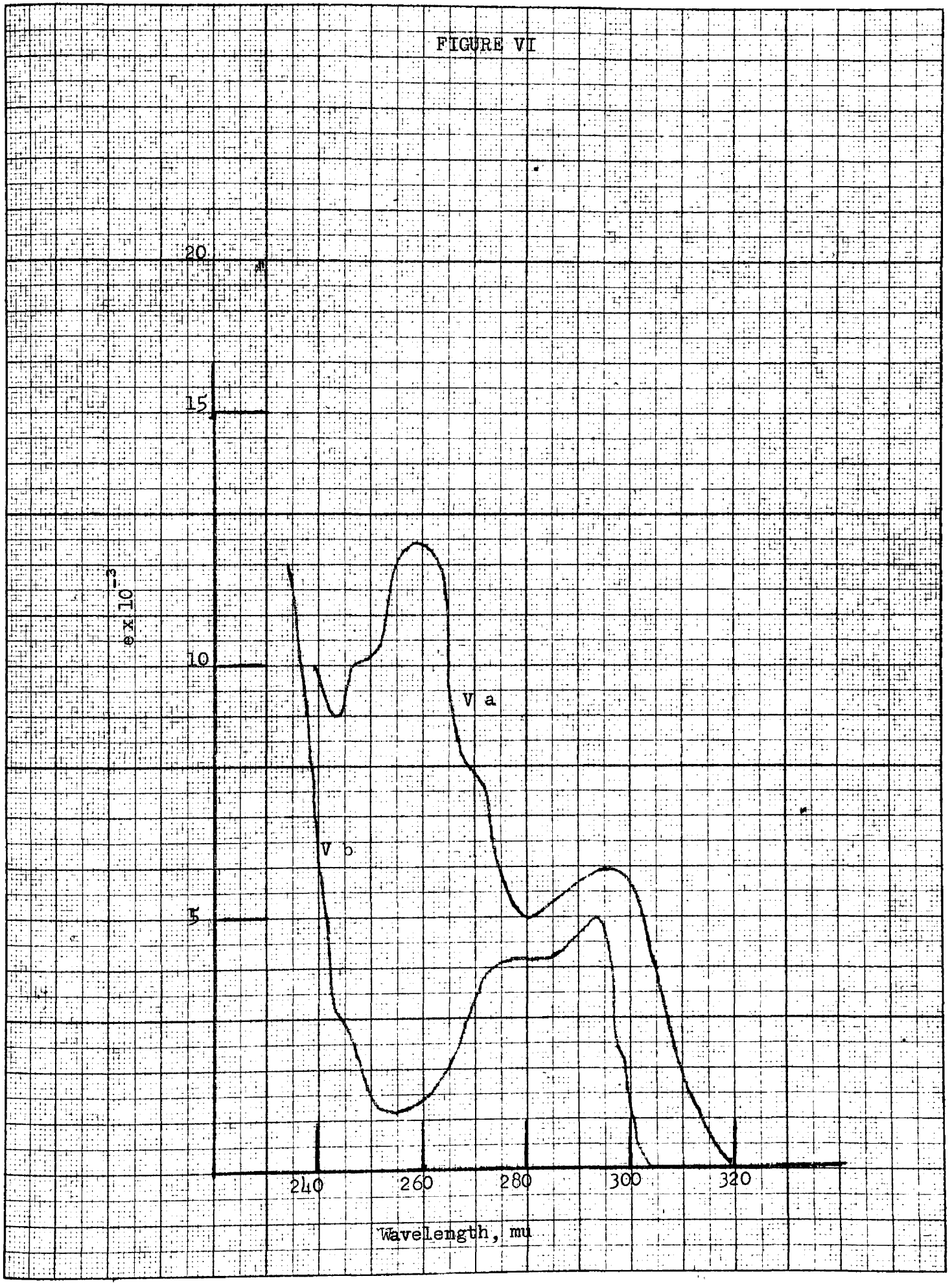


VI



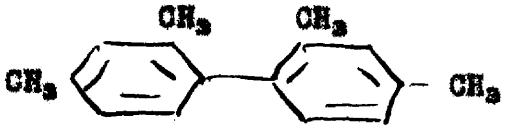
VII

FIGURE VI

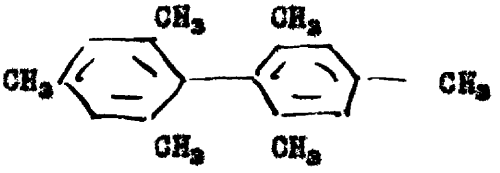

20
15
10
5
$\epsilon \times 10^{-3}$
V a
V b
240
260
280
300
320
Wavelength, mu

VIII

IX



X

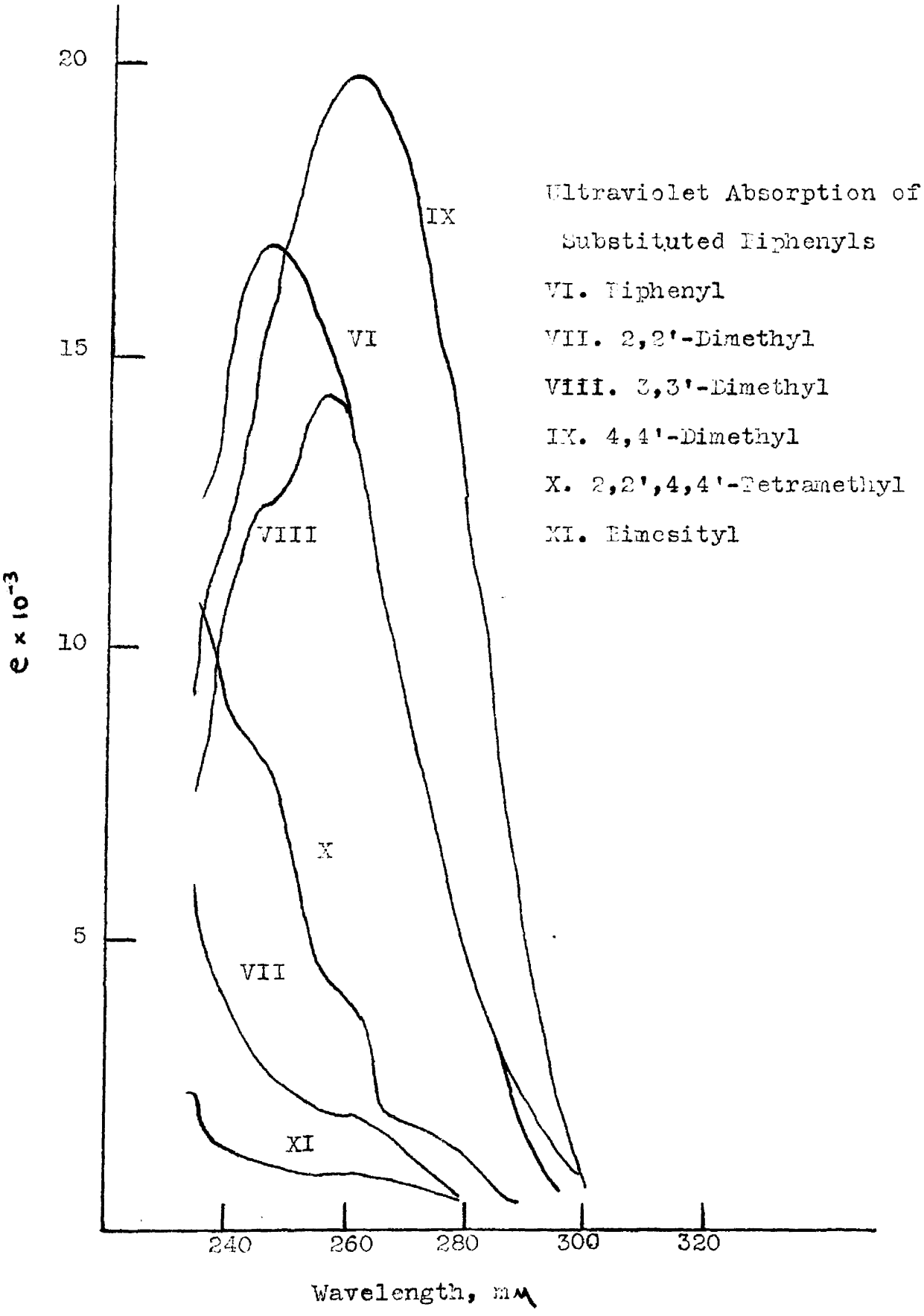


XI

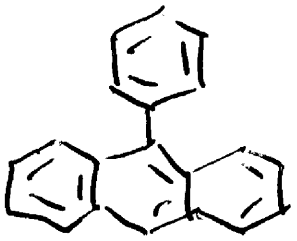
The absorption spectra of these compounds are graphed in Figure VII. The strong absorption of biphenyl (VI) occurs at 240 mu. This absorption is enhanced in 4,4'-dimethylbiphenyl (IX) due to the interaction of the para-methyl groups with the conjugated system. The spectrum of 3,3'-dimethylbiphenyl (VIII) is similar to that of biphenyl since meta-substituents cannot interact with the conjugated system. There is a decrease in absorption intensity for 2,2' dimethylbiphenyl (VII) due to the steric hindrance of the two ortho-methyl groups around the pivot bond. Although absorption is also decreased in the spectrum of 2,2',4,4'-tetramethylbiphenyl (X), interaction of the para-methyl groups with the conjugated system counteracts the steric hindrance of the ortho-methyl groups to a degree. Finally, 2,2',4,4', 6,6' hexamethylbiphenyl (XI), with four ortho-methyl substituents, shows the smallest absorption intensity of this series of compounds.

The relationship between restricted rotation and absorption spectra was extended to aryl substituted aromatic compounds by Jones (78). This author reports that 9-phenylanthracene (XII), 9,10-di-(α-naphthyl)-anthracene (XIV), and 9,9' dianthyrl (XV) have spectra which are almost

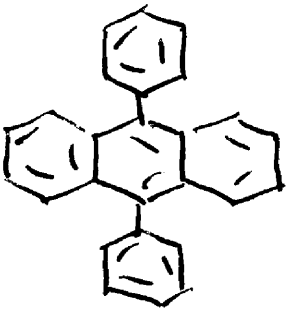
FIGURE VII


20
15
10
5
ε × 10⁻³
IX
VI
VIII
X
VII
XI
240
260
280
300
320
Wavelength, mμ
Ultraviolet Absorption of
Substituted Diphenyls
VI. Diphenyl
VII. 2,2'-Dimethyl
VIII. 3,3'-Dimethyl
IX. 4,4'-Dimethyl
X. 2,2',4,4'-Tetramethyl
XI. Dimesityl

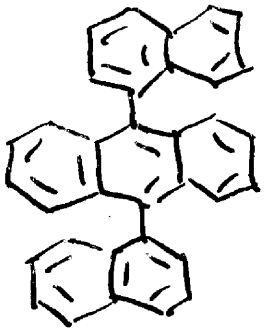
identical with that of anthracene. Molecular models show that an aryl substituent at the 9- or 10-carbon atoms in anthracene interferes with the ortho-hydrogens at the 1- and 8-positions of the anthracene nucleus. This results in steric hindrance to free rotation



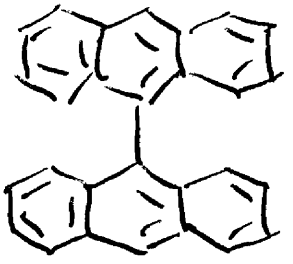
XII



XIII



XIV



XV

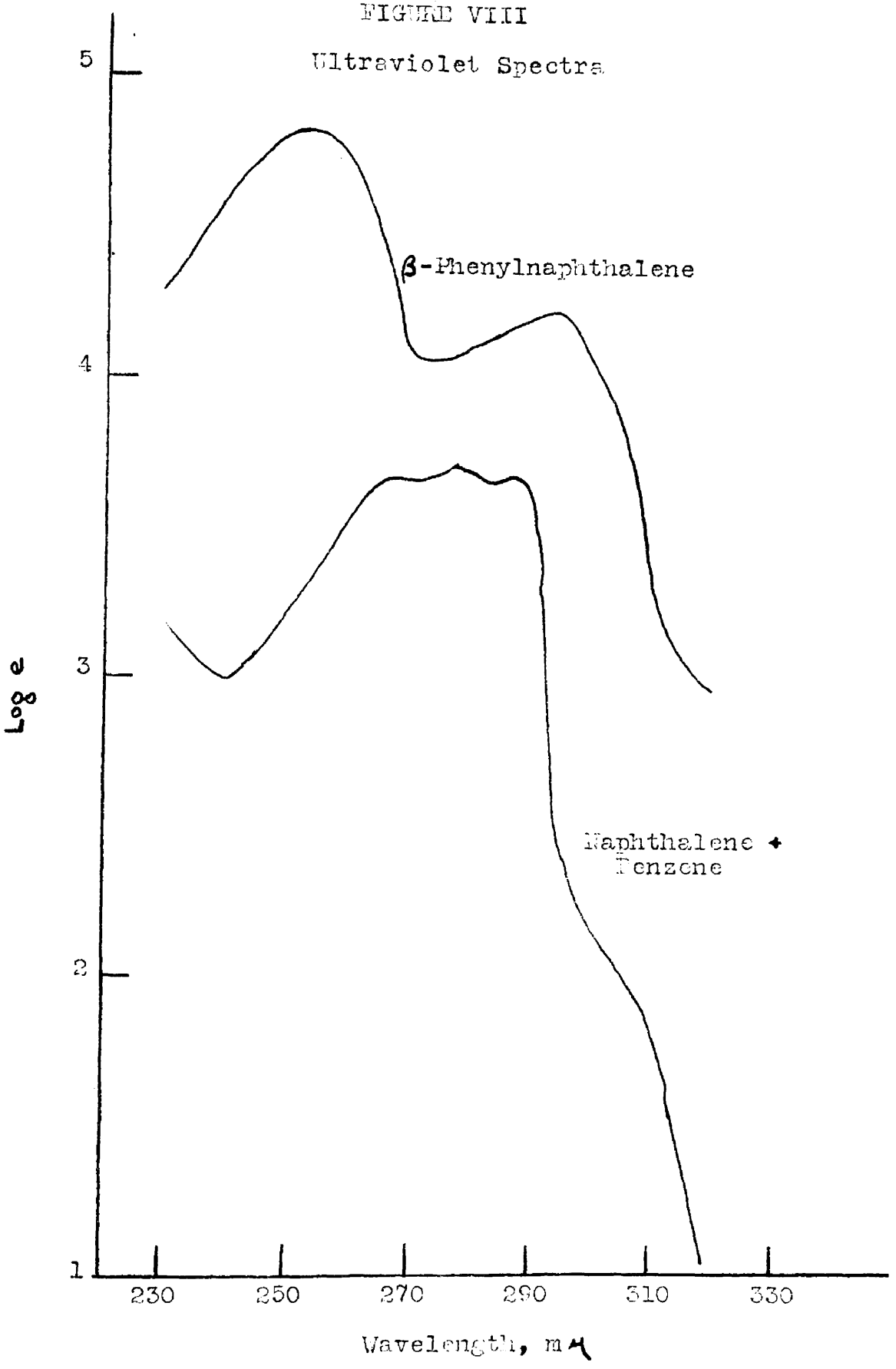
about the pivot bond.

The same author showed that β-phenylnaphthalene (XVI) has a more intense absorption spectrum than naphthalene or benzene (Figure VIII).

XVI

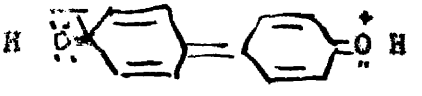
FIGURE VIII

Ultraviolet Spectra



In this instance, there is no steric hindrance to rotation around the pivot bond.

Williamson and Rodebush (72), in 1941, published the results of their study of the effect of substituent groups on biphenyl absorption. A partial list of their data is recorded in Table VI, and some interesting observations were made from these data. The 2,2'-substituted biphenyls show a decreased absorption at longer wavelengths of light than do the corresponding 3, 3'- or 4,4'-substituted biphenyls. This is in accord with the principle of steric inhibition to resonance between the two rings. It is also notable that 4,4'-dihydroxybiphenyl has a greater intensity of absorption than the corresponding 3,3'-isomer. This illustrates the fact that para-hydroxy groups have the ability to extend the resonating system



by formation of polar excited states as indicated above.

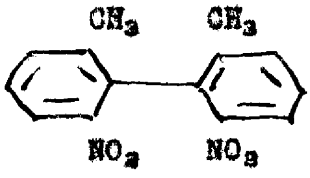
TABLE VI

EFFECT OF SUBSTITUENTS ON BIPHENYL ABSORPTION

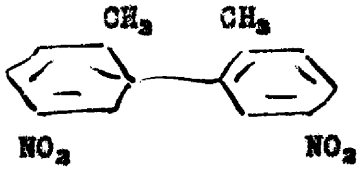
Biphenyl Compound	λ_{max}, mu	ϵ_{max}
2,2'-dimethoxy	277	6,000
4,4'-dimethoxy	263	21,700
2,2'-dihydroxy	285	6,000
3,3'-dihydroxy	255	12,000
4,4'-dihydroxy	265	22,400
2,2'-dicarboxy	280	2,200
3,3'-dicarboxy	243	20,000
4,4'-dichloro	260	21,700

The effect of amino and nitro groups on biphenyl absorption was investigated, in 1942, by Sherwood and Calvin (73). Their results confirmed and extended the previous work of Rodebush.

Nothing more was published concerning biphenyl absorption for several years until Pickett and her co-workers (74) reinitiated research in this important field. They examined the absorption spectra of a series of nitro- and aminobitolyls. A comparison of the absorption curves (Figure IX) of 6,6'-dinitro-2,2'-bitolyl (XVII) and 5,5'-dinitro-2,2'-bitolyl (XVIII) was in accord with the already established theory, the latter

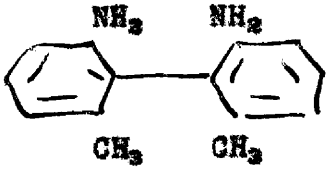


XVII

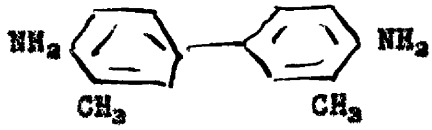


having the more intense absorption with a shift to longer wavelengths.

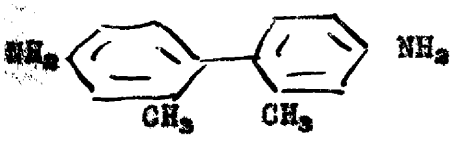
Further, these authors also recorded the absorption curves of four diaminobitolyl compounds (XIX-XXII).



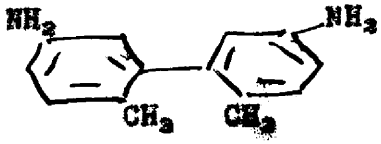
XIX



XX



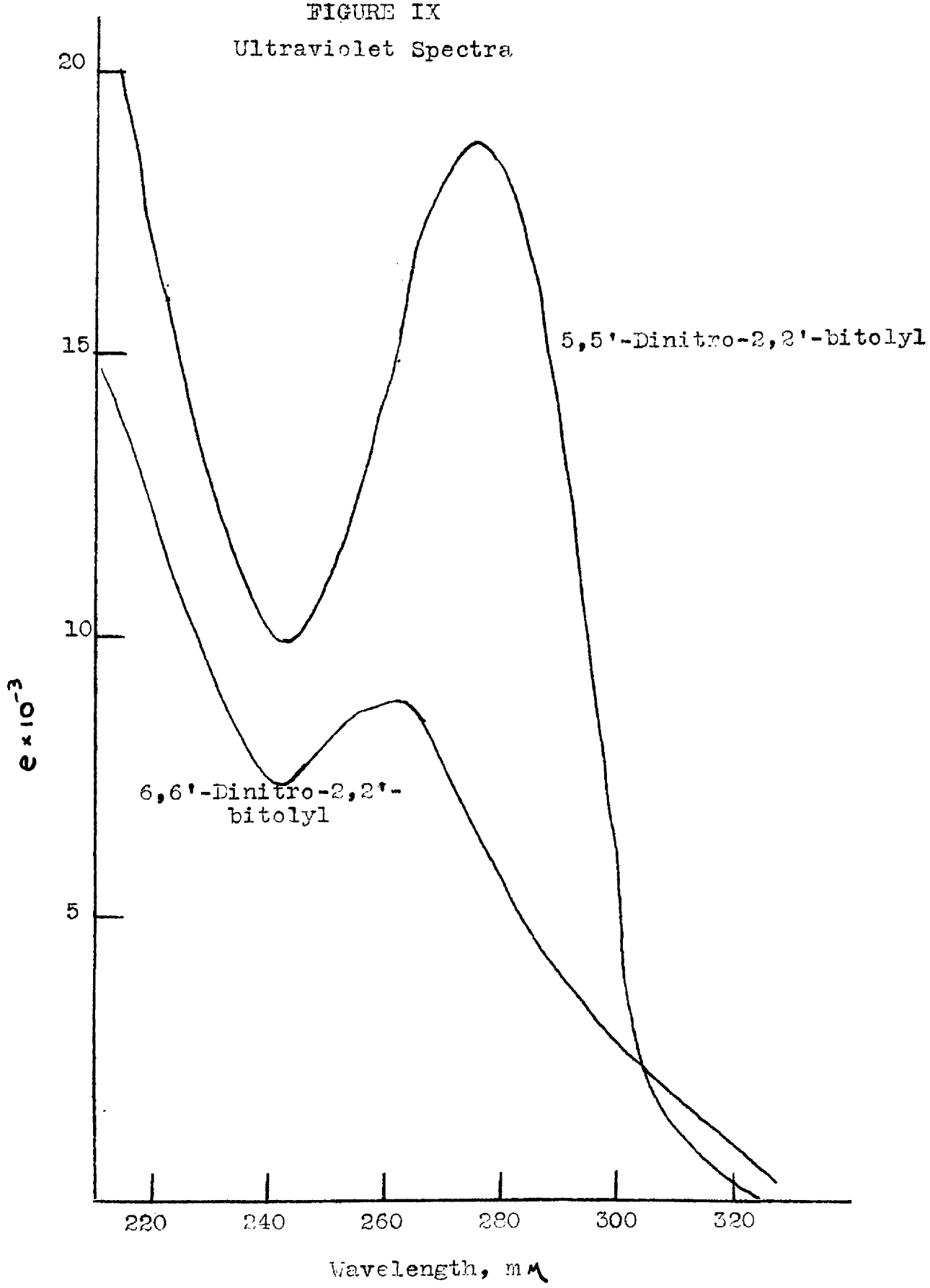
XXI



XXII

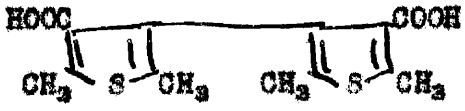
FIGURE IX

Ultraviolet Spectra

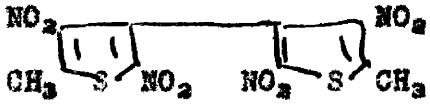


The 4,4' diamino-3,3'-bitolyl (XX) was found to have the greatest absorption intensity since rotation is practically unhindered. Correspondingly, 6,6'-diamino-2,2'-bitolyl (XIX) had the smallest absorption because the four ortho-substituents prevented rotation around the pivot bond. The 4,4'-diamino-2,2'-bitolyl (XXI) showed a greater absorption than 5,5'-diamino-2,2'-bitolyl (XXII) due to the extension of the conjugated system by a shift of an electron pair from the nitrogen in the para-position, similarly to that previously discussed in the case of 4,4'-dihydroxybiphenyl.

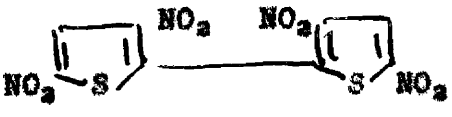
As recently as 1955, Jean and Nord (76) investigated restricted rotation and absorption spectra in the sulfur heterocyclic bithienyl series. The ultraviolet absorption curves of four of these compounds are recorded in Figure X. The 3,3'-dinitro-5,5'-diacetyl-2, 2'-bithienyl (XXVI) has a high intensity



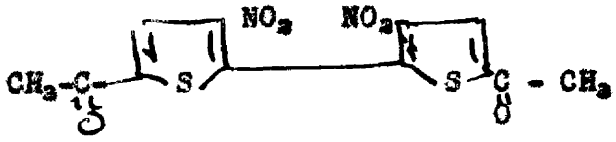
XXIII



XXIV



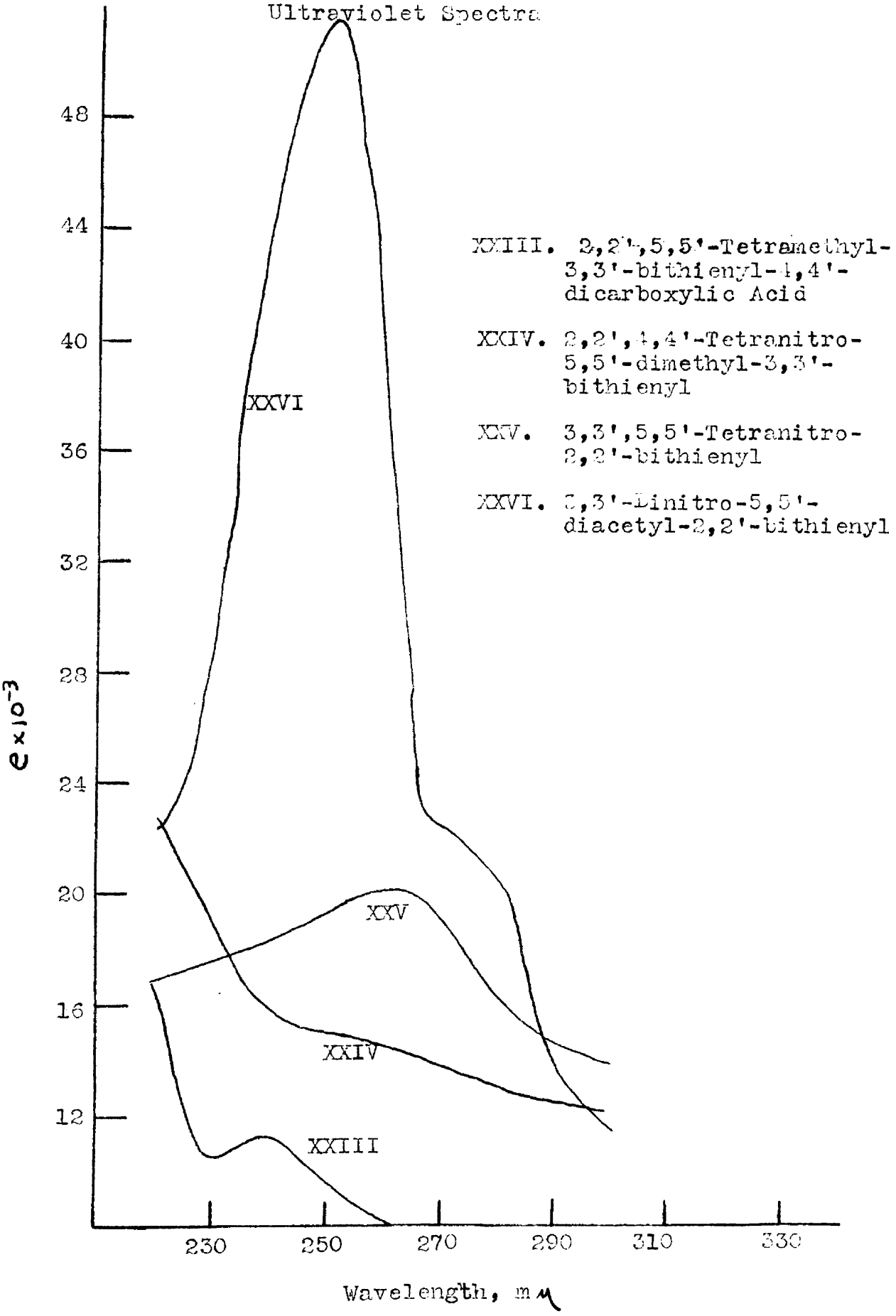
XXV



XXVI

absorption due to conjugation between the two thiophene rings. Thus, steric hindrance does not occur to any appreciable extent. An analogous explanation can be made to account for the similar although reduced absorption spectra of the 3,3',5,5'-tetranitro-2,2'-bithienyl compound

FIGURE X


Ultraviolet Spectra
48
44
40
36
32
28
24
20
16
12
ε x10⁻³
XXVI
XXV
XXIV
XXIII
230
250
270
290
310
330
Wavelength, mμ
XXIII. 2,2',5,5'-Tetramethyl-3,3'-bithienyl-4,4'-dicarboxylic Acid
XXIV. 2,2',4,4'-Tetranitro-5,5'-dimethyl-3,3'-bithienyl
XXV. 3,3',5,5'-Tetranitro-2,2'-bithienyl
XXVI. 3,3'-Dinitro-5,5'-diacetyl-2,2'-bithienyl

(XXV). However, 2,2',4,4'-tetranitro-5,5'-dimethyl-3,3'-bithienyl (XXIV) and 2,2',5,5'-tetramethyl-3,3'-bithienyl-4,4'-dicarboxylic acid show very negligible absorption due to the four ortho-substituents restricting rotation around the pivot bond and thus preventing coplanarity of the two heterocyclic rings. Jean and Nord also conclude that none of the 2,2'-bithienyls examined by them gave indications of sufficient restriction of rotation about the pivot bond to permit their resolution into enantiomorphic isomers.

DISCUSSION

The 3-arylthianaphthenes for which ultraviolet absorption curves were determined in this investigation are listed in Table VIII, together with the wavelengths and extinction coefficients of their absorption maxima. The individual curves for each of the arylthianaphthenes are shown in the Figures XI to XVII. In general, the spectra of these compounds are in accord with the theory previously discussed in the historical part of this thesis.

Before proceeding with the detailed discussion of these absorption spectra, it is necessary to assess the effect of the chlorine and carboxyl groups in the three similar 5-chloro-3-aryl-2-thianaphthenecarboxylic acids on the ultraviolet absorption curves of these compounds. This information is needed

in order to make an interpretive comparison of the absorption spectra of the 5-chloro-3-aryl-2-thianaphthenecarboxylic acids with the absorption spectra of the 3-arylthianaphthenes containing no functional group or halogen substituent.

With regard to the chlorine substituent, it has previously been shown (71) that chlorine exhibits only negligible resonance interaction with the aromatic ring in chlorobenzene. This is justified, on

FIGURE XI

Ultraviolet Spectrum of
Thianaphthene

3.7×10^{-5} M

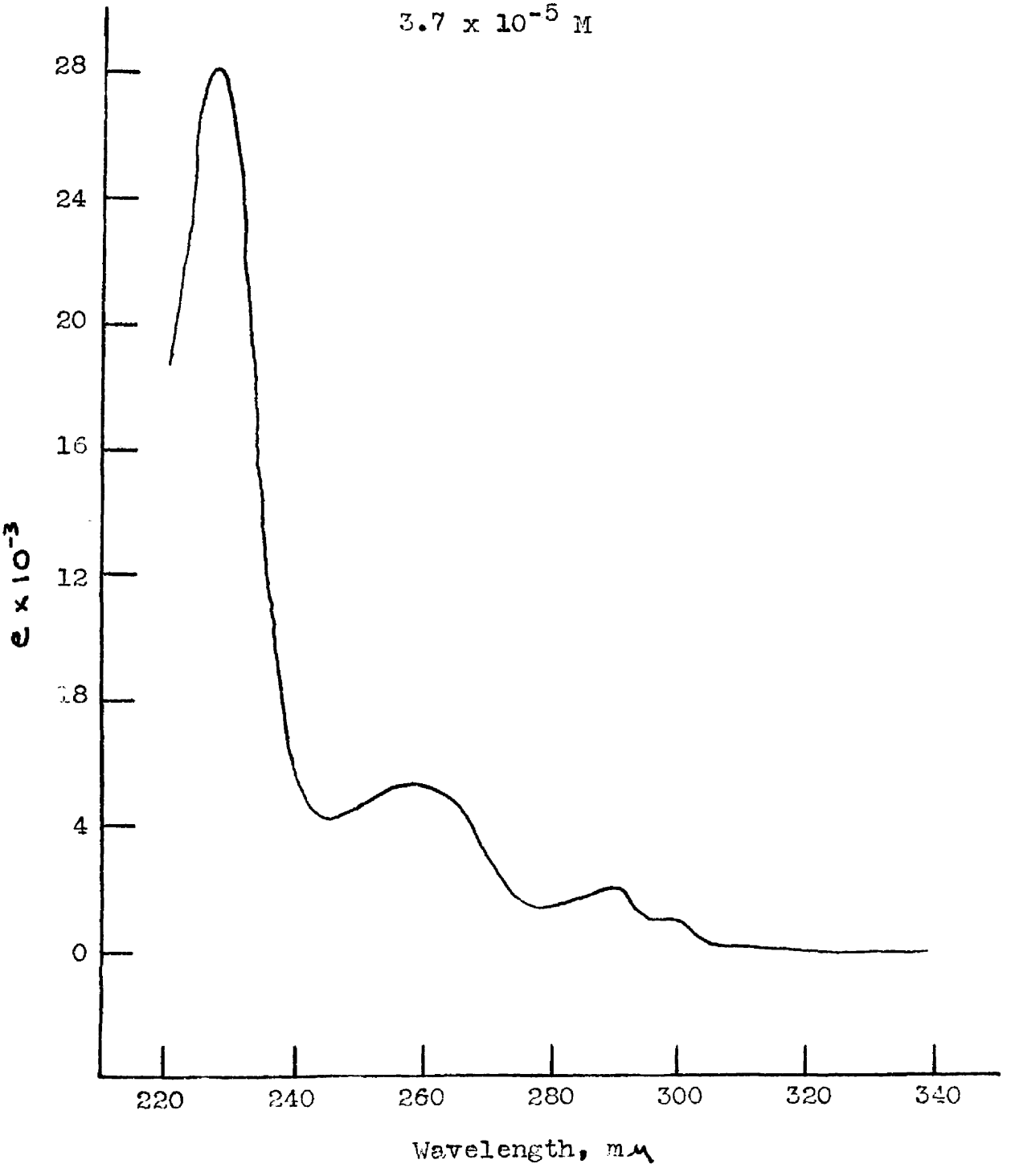


FIGURE XII
Ultraviolet Spectrum of
3-Phenylthianaphthene

3.8×10^{-5} M

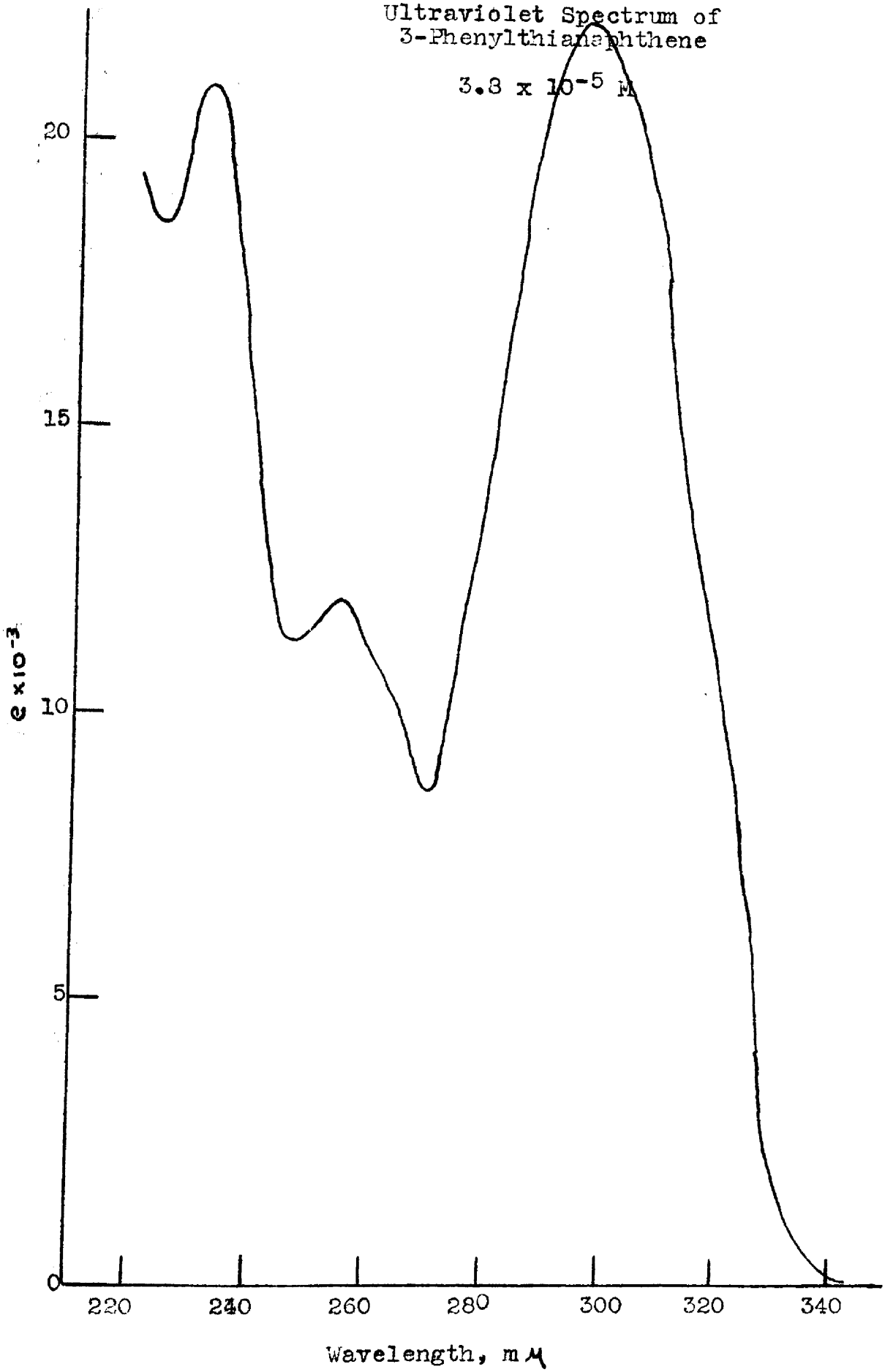


FIGURE XIII

Ultraviolet Spectrum of
3-(1'-Naphthyl)-thianaphthene

1.08×10^{-5} M

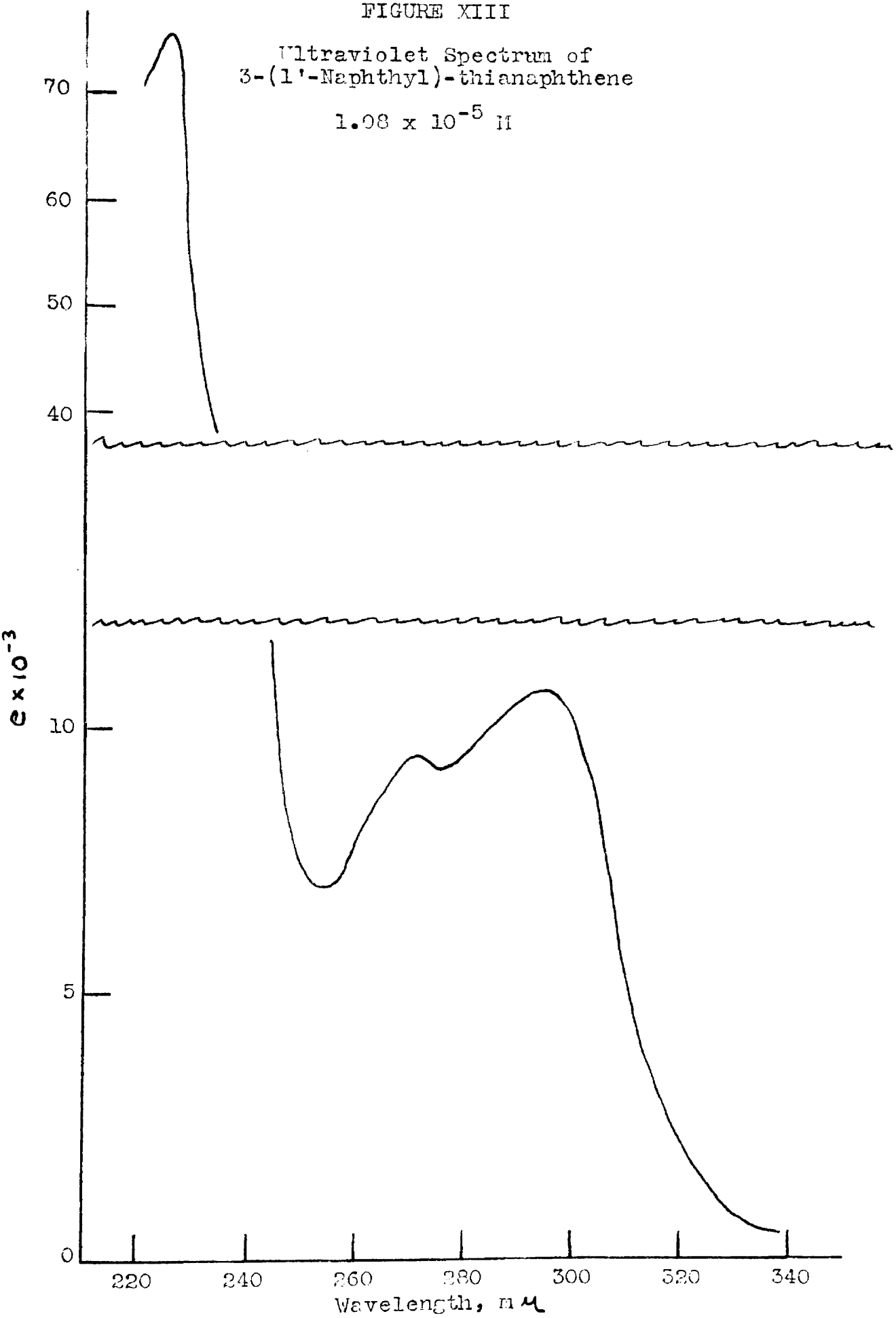


FIGURE XIV

Ultraviolet Spectrum of
3,3'-Bithianaphthene

1.24×10^{-5} M

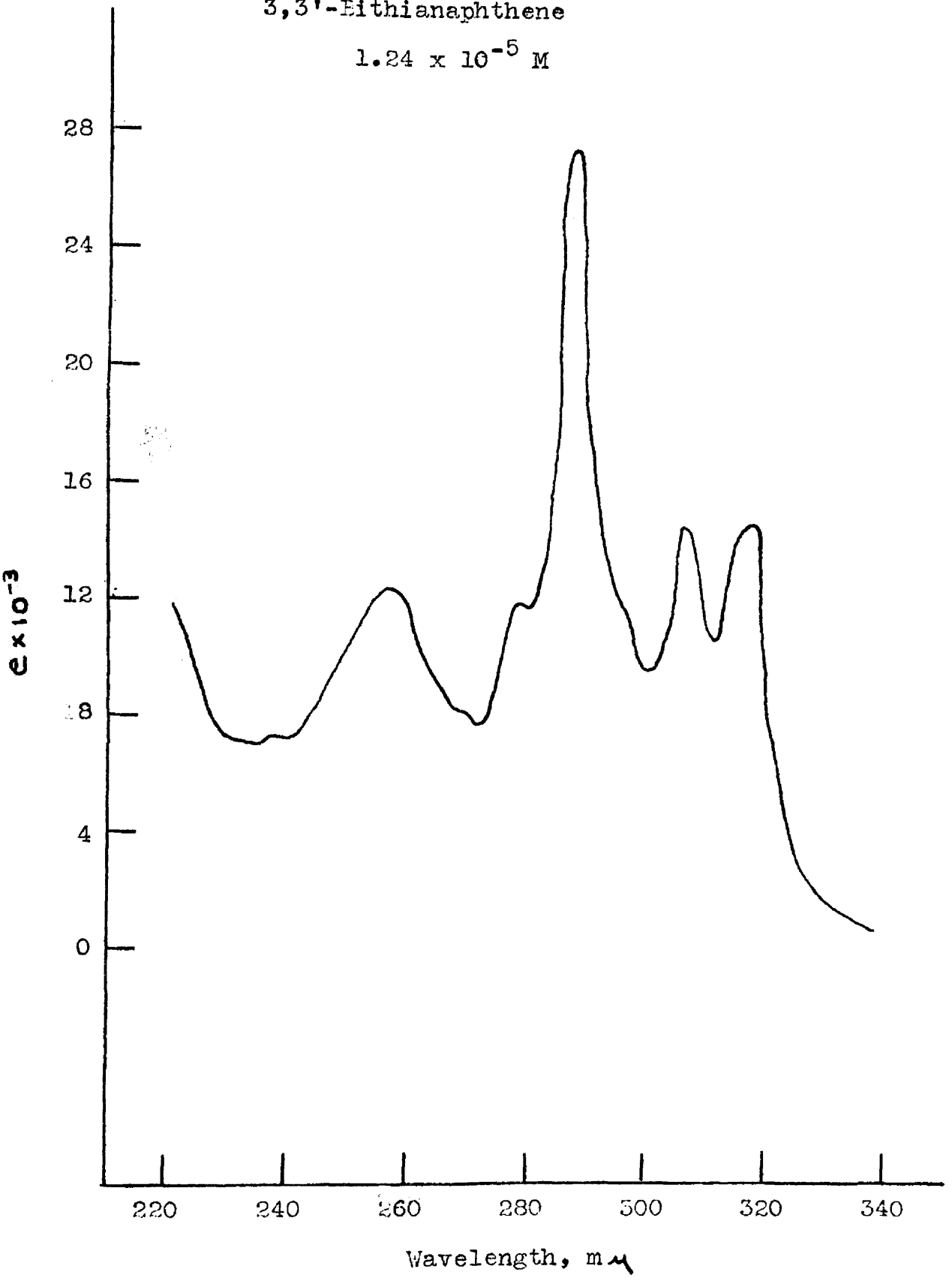


FIGURE XV

Ultraviolet Spectrum of
5-Chloro-3-phenyl-2-thianaphthenecarboxylic Acid

4.98×10^{-5} M

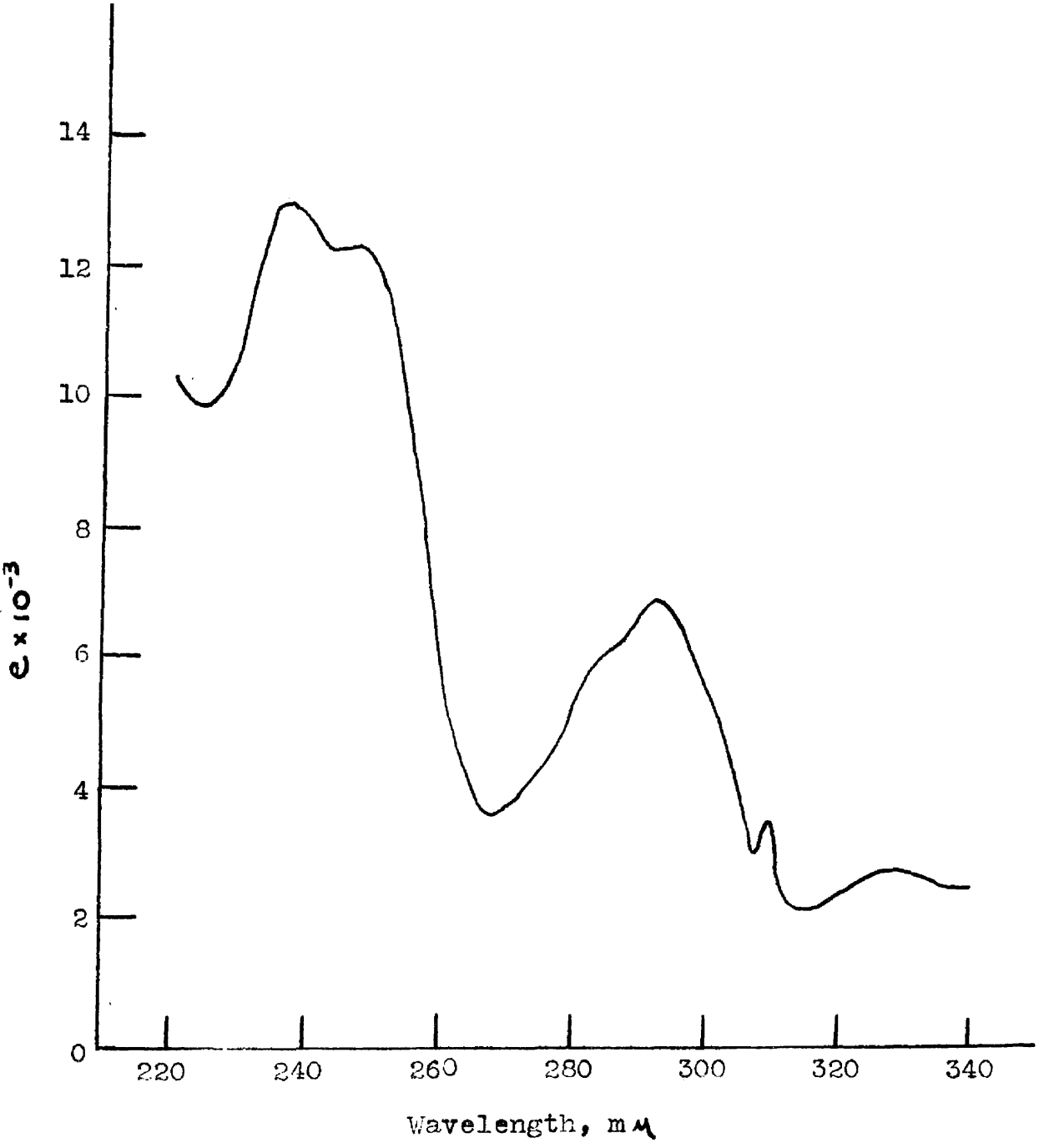


FIGURE XVI

5-Chloro-3-(2'-thienyl)-2-thianaphthenecarboxylic Acid

9.8×10^{-6} M

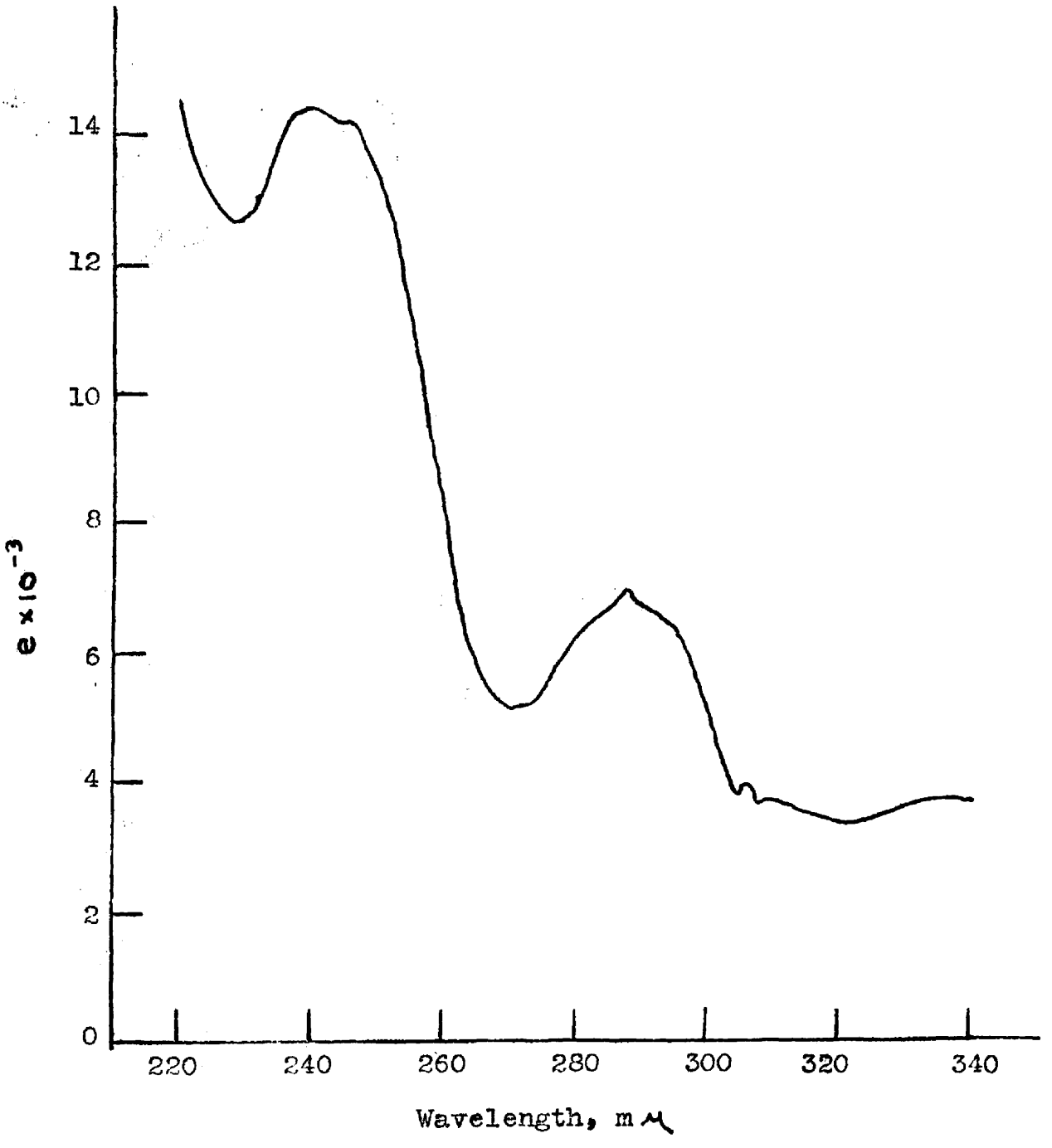
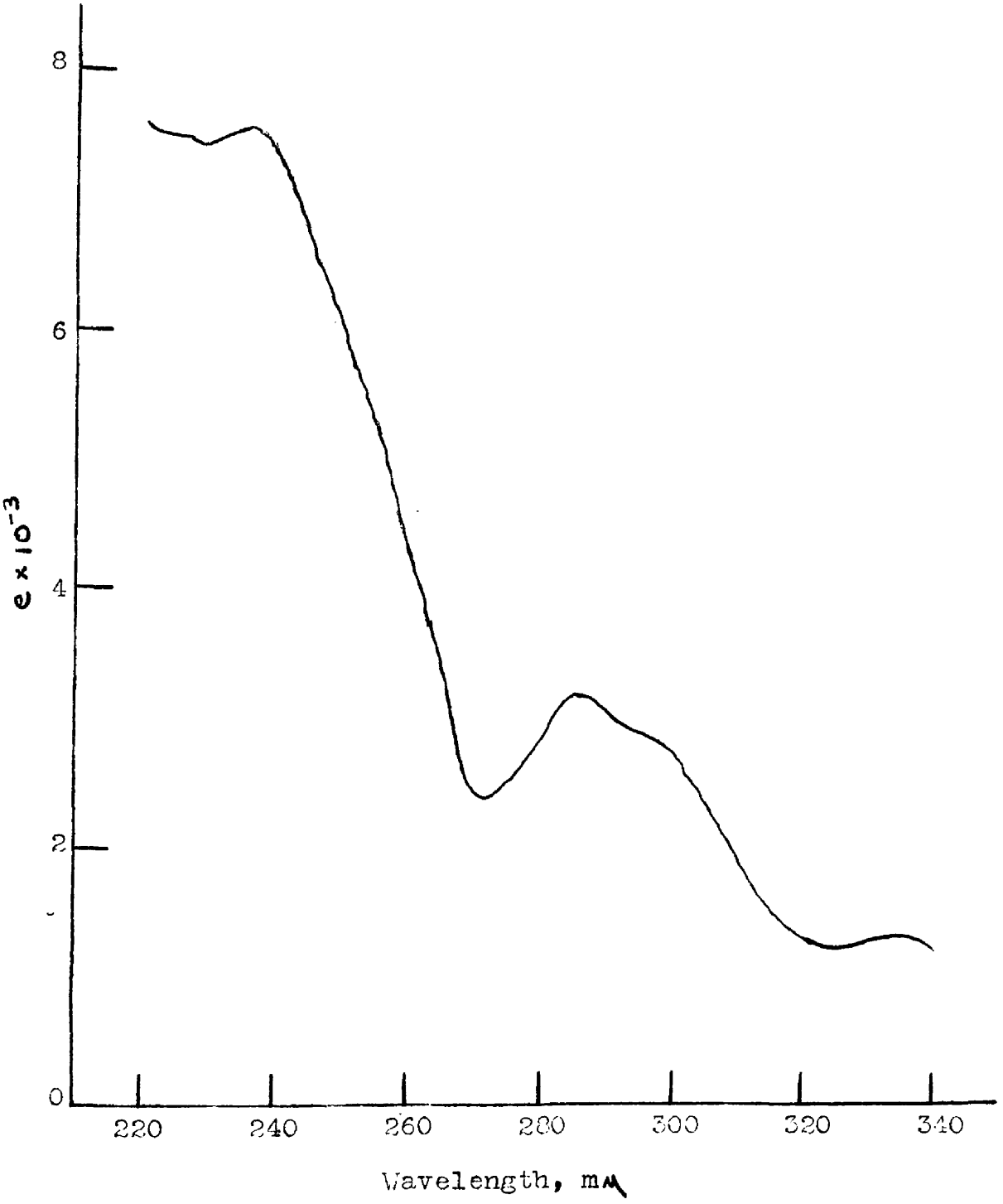


FIGURE XVII

Ultraviolet Spectrum of
5-Chloro-3-(o-carboxyphenyl)-2-thianaphthenecarboxylic Acid

4.5×10^{-5} M



theoretical grounds, by the comparatively small contribution, due to resonance, of the halogen to the excited state of the aromatic ring. Padhye and Desai (79) have compared the absorption spectrum of 5-chlorothianaphthene with that of thianaphthene. Their results show that the absorption spectra of these compounds are quite similar and that, therefore, chlorine must interact with the thianaphthene nucleus only to a minor degree causing a small shift of the absorption maxima to slightly longer wavelengths while the absorption intensities remain nearly identical.

On the other hand, the carboxyl function due to double bond character in its structure can interact with the aromatic ring and extend the resonance of the aromatic structure. This would be expected to have a very considerable effect on the absorption spectrum of such a molecule. O'Shaughnessy and Rodebush (71) have confirmed this in the case of biphenyl derivatives having carboxyl groups substituted ortho and para to the pivot bond. The presence of the carboxyl function shifted the characteristic absorption maximum of the biphenyl ring system to longer wavelengths and very considerably enhanced its absorption intensity.

The same effect would be expected to be operative in a 2-thianaphthenecarboxylic acid. The absorption spectra of several 2-thianaphthyl ketones have been recorded (80) and the shift to longer wavelengths accompanied by more intense absorption is observed. It is quite reasonable to assume that the carbonyl functions of the ketone and carboxylic acid will affect absorption spectra in a similar manner.

To aid in the discussion of the absorption spectra determined in the course of the present investigation, the curves of the compounds studied have been graphed together in Figure XVIII. The extinction coefficients have been converted to logarithms to facilitate inclusion of all the absorption curves on the same scale.

The absorption curve (Figure XVIII c, Figure XI) for thianaphthene has the fine structure which is characteristic of an unsubstituted aromatic compound. When the conjugated system is extended by substitution of a phenyl group in the 3-position of the thianaphthene nucleus, there is an increase in absorption intensity and a smoothing out of its fine structure (Figure XVIII d, Figure XII). The same phenomenon is observed in the spectrum of biphenyl as compared to benzene (68). However, 3-(1'-naphthyl)-thianaphthene (Figure XVIII e, Figure XIII) has a considerably lower absorption intensity than 3-phenylthianaphthene (Figure XVIII d, Figure XII). If steric hindrance were not operative, and thus were not preventing coplanarity of the naphthyl and thianaphthyl parts of the molecule, the naphthyl group would be expected to extend the total resonating system by a larger factor than a phenyl group and, as a result, enhance the absorption intensity to a greater degree. The reduction in absorption intensity can be attributed to the hindrance to free rotation about the pivot bond imposed by the hydrogen atoms in the 4- and 8'-positions, thus inhibiting coplanarity of the naphthyl and thianaphthyl group with a resulting loss in resonance.

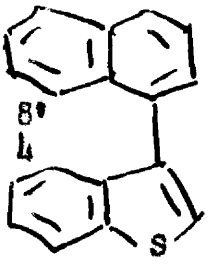


TABLE VII

ULTRAVIOLET ABSORPTION OF 3-ARYLTHIANAPHTHENES

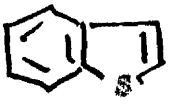
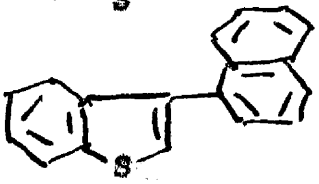
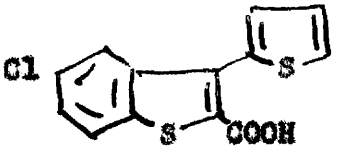
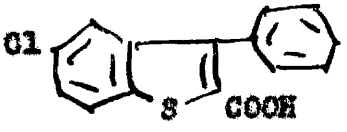
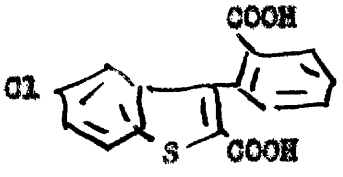
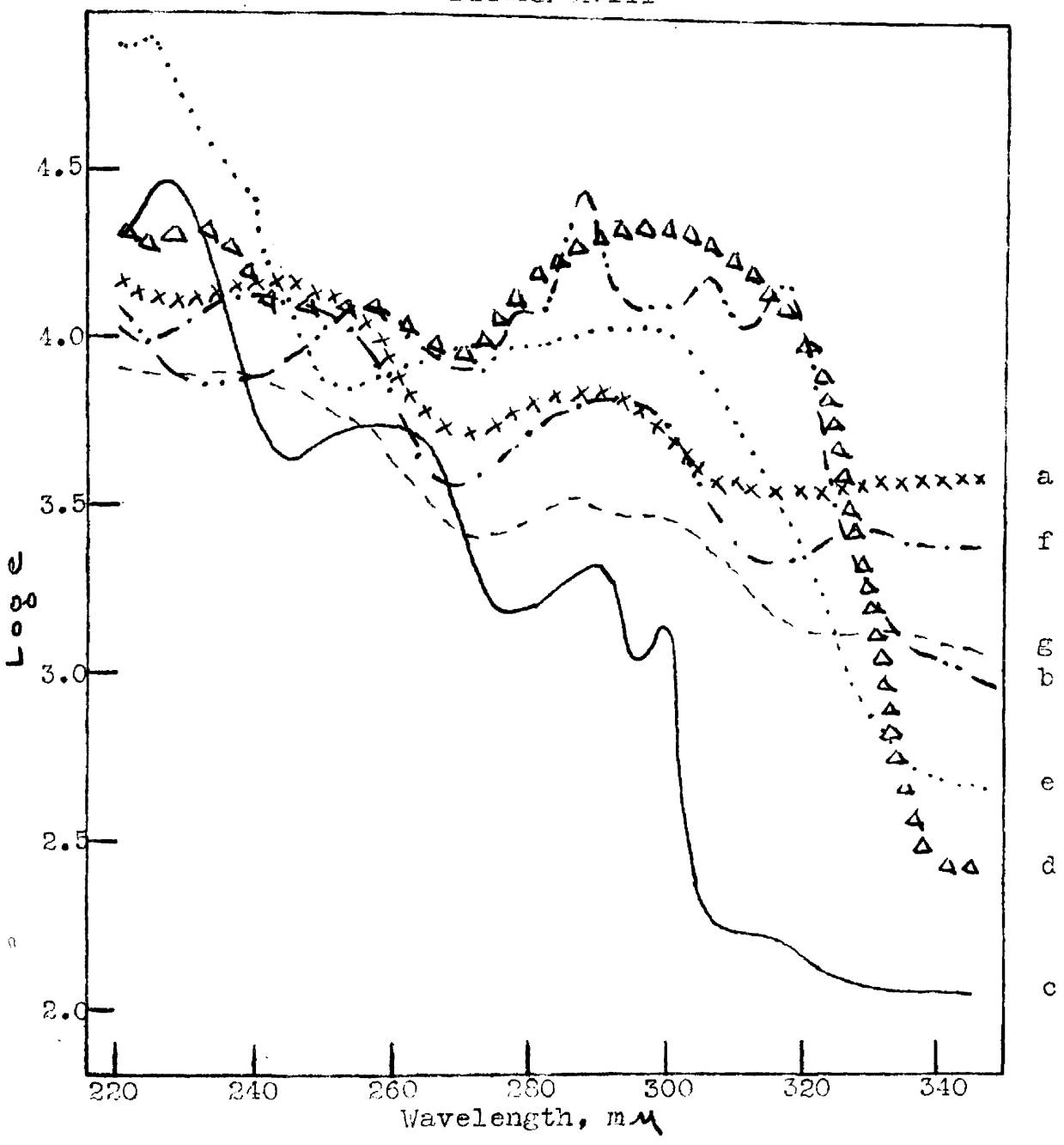
Compound	λ_{max}, mu	e x 10^{-3}	λ_{max}, mu	e x 10^{-3}
	227	28.4		
	256	12.5	288	27.8
	233	21.2	297	22.4
	225	76.5	295	10.9
	239	14.6	288	7.1
	236	13.1	294	7.0
	236	7.7	286	3.3

FIGURE XVIII



a. ××××××××× 5-Chloro-3-(2'-thienyl)-2-thianaphthenecarboxylic Acid

b. — — ·· — — 3,3'-Dithianaphthene

c. ——————— Thianaphthene

d. ΔΔΔΔΔ 3-Phenylthianaphthene

e. ..... 3-(1'-Naphthyl)-thianaphthene

f. —· —· — 5-Chloro-3-phenyl-2-thianaphthenecarboxylic Acid

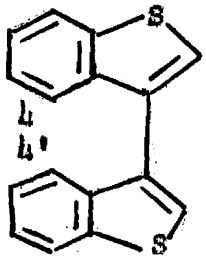
g. — — — — 5-Chloro-3-(o-carboxyphenyl)-2-thianaphthenecarboxylic Acid

Inspection of the absorption spectra of 5-chloro-3-(2'-thienyl)-2-thianaphthenecarboxylic acid (Figure XVIII a, Figure XVI) and 5-chloro-3-phenyl-2-thianaphthenecarboxylic acid (Figure XVIII f, Figure XV) reveal a very close similarity. The isoelectronic relationship between benzene and thiaphene would predict such a similarity in the spectra of these compounds. Both absorption curves show a reduced intensity compared to those compounds which are not substituted in the 2-position with respect to the pivot bond. This undoubtedly is a result of the steric inhibition to free rotation supplied by the carboxyl group which prevents coplanarity of the thienyl or phenyl group with the thianaphthyl group thereby reducing the resonance of the systems. As previously noted, the carboxyl group tends to enhance absorption due to its interaction with the aromatic ring. That the opposite occurs is a further indication that the carboxyl group is sterically inhibiting full resonance in these structures.

When a second carboxyl group is placed adjacent to the pivot bond, as in 5-chloro-3-(o-carboxyphenyl)-2-thianaphthenecarboxylic acid (Figure XVIII g, Figure XVII), the absorption maximum almost disappears. Thus, resonance through the pivot bond appears to be virtually non-existent due to the lack of coplanarity of the thianaphthyl and phenyl groups; such coplanarity being prevented by steric hindrance of the two carboxyl groups.

The absorption spectrum of 3,3'-bithianaphthene (Figure XVIII b, Figure XIV) is somewhat more difficult to fully explain. Although there is an increase in the absorption intensity as compared to that

of thianaphthene, the fine structure of the thianaphthene spectrum has been retained. Therefore, the spectrum of 3,3'-bithianaphthene may be interpreted to show an absorption curve approximately equivalent to twice the concentration of thianaphthene. Such a situation would preclude any very appreciable resonance through the pivot bond. This would strongly suggest that the hydrogen atoms at the 4- and 4'-positions are capable of imposing steric hindrance to free rotation about the pivot bond, resulting in non-coplanarity of the two thianaphthyl groups with the attendant loss in resonance.



This is an analogous situation to that found for 1,1'-binaphthyl by other authors (83) and to 3-(1'-naphthyl)-thianaphthene, discussed previously.

In conclusion, it can be stated, with a very reasonable degree of certainty, that 5-chloro-3-(o-carboxyphenyl)-2-thianaphthenecarboxylic acid and very probably 3,3'-bithianaphthene exist in a non-coplanar structure and the former should therefore be capable of optical resolution. However, it is not to be inferred that evidence for non-coplanarity is sufficient by itself for predicting the possibility of resolution in compounds where optical activity is due to restricted rotation.

EXPERIMENTAL

The ultraviolet absorption spectra were determined employing a Beckman Model DU Spectrophotometer equipped with equally matched, one centimeter, fused quartz cells. The solvent used in every case was Eastman Kodak C.P. grade cyclohexane which was further purified by passage through a column of silica gel. The matching of the quartz cells was frequently checked by comparing readings taken with cyclohexane alone in the cells.

The solutions were prepared by the volume dilution method and were all of the order of 10^{-5} M. The procedure used in preparing the solutions was as follows. A sample of 2×10^{-3} moles was accurately weighed out on an analytical balance and dissolved in 100 ml. of cyclohexane measured in a calibrated volumetric flask. A 5 ml. aliquot of this solution was then diluted to 100 ml. in a calibrated volumetric flask. An aliquot of the latter solution was transferred to a quartz cell.

Optical density readings were taken over a range of wavelengths from 220-340 mu at every 5 mu and at every 2 mu in the regions of abrupt change in absorption. The values for the optical density readings were converted to molar extinction coefficients by means of the equation,

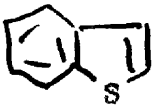
$$\epsilon = \frac{E}{Cl}$$

where ϵ is the molar extinction coefficient, E is the optical density, C is the concentration of the light absorbing species in moles per liter, and l is the length in centimeters of the light path in the

absorbing solution. Values for the logarithms of the molar extinction coefficients were then tabulated. The concentrations and readings for the individual compounds are listed in Tables VIII to XIV.

TABLE VIII

THIANAPHTHENE

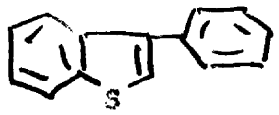


3.7×10^{-5} M

Wavelength, mu	E	$\epsilon \times 10^{-3}$	log ϵ
220	0.672	18.1	4.26
222	0.809	21.8	4.34
224	0.950	25.6	4.41
226	1.05	28.3	4.45
228	1.05	28.3	4.45
230	0.960	25.9	4.41
232	0.750	20.3	4.31
234	0.538	14.5	4.16
240	0.198	5.40	3.73
245	0.156	4.21	3.62
250	0.174	4.70	3.67
255	0.198	5.38	3.73
260	0.198	5.38	3.73
265	0.180	4.86	3.69
270	0.105	2.83	3.45
275	0.055	1.48	3.17
280	0.058	1.56	3.19
285	0.065	1.75	3.24
290	0.080	2.16	3.33
295	0.040	1.08	3.03
300	0.050	1.35	3.13
305	0.007	0.19	2.28
310	0.006	0.16	2.20
315	0.006	0.16	2.20
320	0.005	0.14	2.15
330	0.004	0.11	2.04
340	0.004	0.11	2.04

TABLE IX

3-PHENYLTHIANAPHTHENE

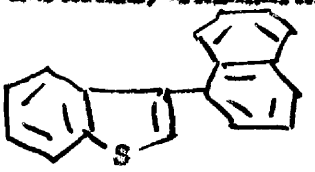


3.8×10^{-5} M

Wavelength, mu	E	$\epsilon \times 10^{-3}$	log ϵ
220	0.740	19.5	4.29
222	0.718	18.9	4.28
224	0.706	18.6	4.27
226	0.721	19.0	4.28
228	0.761	20.0	4.30
230	0.795	20.9	4.32
232	0.800	21.1	4.32
234	0.775	20.4	4.31
240	0.567	14.9	4.17
245	0.433	11.4	4.06
250	0.437	11.5	4.06
255	0.465	12.2	4.09
260	0.422	11.1	4.05
265	0.387	10.2	4.01
270	0.328	8.6	3.93
275	0.431	11.3	4.05
280	0.561	14.8	4.17
285	0.689	18.1	4.26
290	0.782	20.6	4.31
295	0.850	22.4	4.35
300	0.840	22.1	4.34
305	0.800	21.1	4.32
310	0.700	18.4	4.26
315	0.515	13.6	4.13
320	0.419	11.0	4.04
330	0.074	1.9	3.28
340	0.008	0.21	2.32

TABLE X

3-(1'-NAPHTHYL)-THIANAPHTHENE



1.08×10^{-5} M

Wavelength, mu	E	$\epsilon \times 10^{-3}$	log ϵ
220	0.770	71.3	4.85
222	0.790	73.1	4.86
225	0.827	76.5	4.88
228	0.641	59.4	4.77
230	0.533	49.4	4.69
235	0.365	33.8	4.53
240	0.250	23.1	4.36
245	0.123	11.4	4.06
250	0.078	7.2	3.86
255	0.076	7.0	3.85
260	0.086	8.0	3.90
265	0.095	8.8	3.94
270	0.104	9.6	3.98
275	0.101	9.3	3.97
280	0.105	9.7	3.99
285	0.110	10.2	4.01
290	0.115	10.6	4.03
295	0.118	10.9	4.04
300	0.114	10.6	4.03
305	0.091	8.4	3.92
310	0.059	5.5	3.74
315	0.039	3.6	3.56
320	0.025	2.3	3.36
325	0.014	1.3	3.11
330	0.008	0.74	2.87
340	0.005	0.46	2.66

TABLE XI

3,3'-BITRIANAPHTHENE

1.24×10^{-5} M

Wavelength, mu	E	$\epsilon \times 10^{-3}$	log ϵ
220	0.152	12.2	4.09
222	0.140	11.3	4.05
224	0.122	9.84	3.99
226	0.103	8.32	3.92
228	0.094	7.57	3.88
230	0.092	7.43	3.87
232	0.092	7.43	3.87
234	0.090	7.26	3.86
236	0.091	7.34	3.87
238	0.093	7.49	3.87
240	0.092	7.43	3.87
242	0.094	7.57	3.88
244	0.102	8.23	3.92
246	0.113	9.12	3.96
248	0.123	9.92	3.99
250	0.130	10.5	4.02
252	0.140	11.3	4.05
254	0.149	12.0	4.08
256	0.155	12.5	4.10
258	0.154	12.4	4.09
260	0.144	11.6	4.06
262	0.126	10.0	4.00
264	0.114	9.19	3.96
266	0.107	8.63	3.94
268	0.104	8.39	3.92
270	0.100	8.06	3.91
272	0.097	7.82	3.89
274	0.106	8.55	3.93
276	0.133	10.7	4.03
278	0.150	12.1	4.08
280	0.147	11.8	4.07
282	0.156	12.6	4.10
283	0.170	13.7	4.14
284	0.195	15.7	4.20
285	0.236	19.0	4.28
286	0.292	23.6	4.37

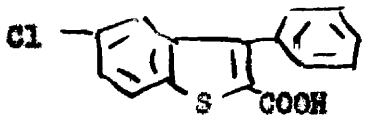
Continued next page

TABLE XI - Continued

Wavelength, mu	E	$\epsilon \times 10^{-3}$	log ϵ
287	0.340	27.4	4.44
288	0.345	27.8	4.44
289	0.300	24.2	4.38
290	0.243	19.6	4.29
292	0.178	14.3	4.16
294	0.160	12.9	4.11
296	0.147	11.9	4.08
298	0.130	10.5	4.02
300	0.120	9.69	3.99
302	0.125	10.1	4.00
304	0.154	12.4	4.09
305	0.170	13.7	4.14
306	0.184	14.9	4.17
308	0.170	13.7	4.14
310	0.140	11.3	4.05
312	0.133	10.7	4.03
315	0.177	14.3	4.16
318	0.185	14.9	4.17
320	0.140	11.3	4.05
322	0.092	7.45	3.87
325	0.040	3.22	3.51
330	0.023	1.85	3.27
335	0.015	1.21	3.08
340	0.013	1.05	3.02

TABLE XII

5-CHLORO-3-PHENYL-2-THIANAPHTHENECARBOXYLIC ACID



4.98×10^{-6} M

Wavelength, mu	E	$\epsilon \times 10^{-3}$	log ϵ
220	0.521	10.43	4.02
222	0.500	10.01	4.00
224	0.491	9.86	3.99
226	0.498	10.00	4.00
228	0.519	10.40	4.02
230	0.552	11.08	4.04
232	0.592	11.88	4.07
234	0.629	12.61	4.10
236	0.653	13.10	4.12
238	0.652	13.08	4.12
240	0.639	12.81	4.11
242	0.620	12.42	4.09
244	0.618	12.39	4.09
246	0.617	12.37	4.09
248	0.619	12.40	4.09
250	0.602	12.08	4.08
252	0.571	11.47	4.06
254	0.524	10.50	4.02
256	0.469	9.42	3.97
258	0.388	7.79	3.89
260	0.309	6.21	3.79
262	0.243	4.89	3.69
264	0.201	4.04	3.61
266	0.181	3.64	3.56
268	0.178	3.57	3.55
270	0.185	3.72	3.57
272	0.194	3.90	3.59
274	0.204	4.10	3.61
276	0.219	4.40	3.64
278	0.238	4.78	3.68
280	0.261	5.25	3.72
282	0.284	5.71	3.76
284	0.299	6.01	3.78
286	0.310	6.22	3.79
288	0.321	6.45	3.81
290	0.332	6.67	3.82

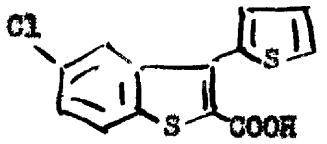
Continued next page

TABLE XII - Continued

Wavelength, mu	E	$\epsilon \times 10^{-3}$	log ϵ
292	0.346	6.94	3.84
294	0.348	6.99	3.84
296	0.334	6.20	3.83
298	0.313	6.29	3.79
300	0.284	5.70	3.76
302	0.249	5.00	3.69
304	0.213	4.28	3.63
306	0.178	3.57	3.55
308	0.149	2.99	3.48
310	0.126	3.53	3.40
312	0.112	2.24	3.35
316	0.104	2.09	3.32
320	0.112	2.24	3.35
324	0.124	2.49	3.39
328	0.134	2.69	3.43
332	0.134	2.69	3.43
336	0.129	2.59	3.41
340	0.125	2.51	3.39

TABLE XIII

5-CHLORO-3-(2'-THIENYL)-2-THIANAPHTHENECARBOXYLIC ACID



9.8×10^{-6} M

Wavelength, mu	E	$\epsilon \times 10^{-3}$	log ϵ
220	0.145	14.8	4.17
222	0.136	13.9	4.14
224	0.130	13.3	4.12
226	0.127	13.0	4.11
228	0.125	12.8	4.11
230	0.126	12.9	4.11
232	0.127	13.0	4.11
234	0.135	13.8	4.14
236	0.139	14.2	4.15
238	0.143	14.6	4.16
240	0.143	14.6	4.16
242	0.142	14.5	4.16
244	0.141	14.4	4.16
246	0.141	14.4	4.16
248	0.138	14.1	4.15
250	0.132	13.5	4.13
252	0.125	12.8	4.11
254	0.116	11.8	4.07
256	0.106	10.8	4.03
258	0.092	9.37	3.97
260	0.079	8.07	3.91
262	0.068	6.95	3.84
264	0.060	6.13	3.79
266	0.055	5.63	3.75
268	0.053	5.42	3.73
270	0.052	5.31	3.72
272	0.051	5.20	3.72
274	0.053	5.42	3.73
276	0.056	5.72	3.76
278	0.059	6.03	3.78
280	0.062	6.33	3.80
282	0.065	6.64	3.82
284	0.065	6.64	3.82
286	0.068	6.95	3.84
288	0.070	7.14	3.85

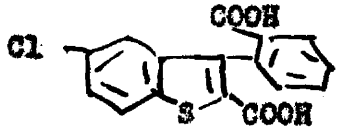
Continued next page

TABLE XIII- Continued

Wavelength, mu	E	$\epsilon \times 10^{-3}$	log ϵ
290	0.067	6.85	3.84
292	0.067	6.85	3.84
294	0.065	6.64	3.82
296	0.063	6.44	3.81
298	0.055	5.63	3.75
300	0.048	4.90	3.69
305	0.038	3.88	3.59
306	0.040	4.08	3.61
308	0.037	3.78	3.58
310	0.038	3.88	3.59
312	0.036	3.67	3.56
315	0.035	3.57	3.55
320	0.034	3.47	3.54
325	0.034	3.47	3.54
330	0.037	3.78	3.58
335	0.037	3.78	3.58
340	0.037	3.78	3.58

TABLE XIV

5-CHLORO-3-(o-CARBOXYPHENYL)-2-THIANAPHTHENECARBOXYLIC ACID



4.5×10^{-6} M

Wavelength, mu	E	e x 10^{-3}	log e
220	0.345	7.66	3.88 (4)
222	0.342	7.61	3.88 (1)
224	0.340	7.57	3.88 (-1)
226	0.340	7.57	3.88 (-1)
228	0.338	7.53	3.88 (-3)
230	0.338	7.53	3.88 (-3)
232	0.340	7.57	3.88 (-1)
234	0.342	7.61	3.88 (+1)
236	0.344	7.65	3.88 (+4)
238	0.342	7.61	3.88 (+1)
240	0.334	7.44	3.87
242	0.325	7.23	3.86
244	0.315	7.00	3.85
246	0.300	6.67	3.82
248	0.287	6.38	3.80
250	0.271	6.02	3.78
252	0.255	5.67	3.75
254	0.245	5.45	3.74
256	0.236	5.24	3.72
258	0.219	4.88	3.69
260	0.200	4.45	3.65
262	0.174	3.87	3.59
264	0.149	3.31	3.52
266	0.130	2.89	3.46
268	0.119	2.66	3.42
270	0.111	2.47	3.39
272	0.110	2.44	3.39
274	0.112	2.49	3.40
276	0.116	2.58	3.41
278	0.122	2.71	3.43
280	0.127	2.82	3.45
282	0.135	3.00	3.48
284	0.142	3.16	3.50
286	0.147	3.27	3.51
288	0.145	3.23	3.51

Continued next page

TABLE XIV - Continued

Wavelength, mu	E	e x 10^{-3}	log e
290	0.140	3.11	3.49
292	0.135	3.00	3.48
294	0.132	2.94	3.47
296	0.131	2.91	3.46
298	0.129	2.87	3.46
300	0.126	2.80	3.45
302	0.121	2.69	3.43
304	0.112	2.49	3.40
306	0.105	2.33	3.37
308	0.098	2.18	3.34
310	0.088	1.95	3.29
315	0.069	1.53	3.18
320	0.060	1.33	3.12
325	0.057	1.27	3.10
330	0.059	1.31	3.12
335	0.060	1.33	3.12
340	0.057	1.27	3.10

SUMMARY

1. The ultraviolet absorption curves of 3,3'-bithianaphthene and five 3-arylthianaphthenes have been determined.

2. These absorption curves have been interpreted according to a theory of steric hindrance to free rotation about the pivot bond of the two aromatic rings.

REFERENCES

1. F. G. Bordwell and W. H. McKellin, J. Am. Chem. Soc., 72, 1985 (1950).

2. W. Steinkopf, "Die Chemie des Thiophens," Theodore Steinkopff, Dresden and Leipzig, 1941, Edwards Brothers, Ann Arbor, 1944.

3. D. K. Fukushima, "Heterocyclic Compounds," Vol. II, ed. R. C. Elderfield, John Wiley and Sons, New York, N. Y., 1951.

4. H. D. Hartough and S. L. Meisel, "Compounds with Condensed Thiophene Rings," Interscience Publishers, New York, N. Y., 1954.

5. V. Meyer, Ber., 19, 1432 (1886).

6. A. Biedermann, Ber., 19, 1615 (1886).

7. L. Gattermann and A. E. Lockhart, Ber., 26, 2808 (1893).

8. C. Chmelewsky and P. Friedlander, Ber., 46, 1903 (1913).

9. A. Bezdrick, P. Friedlander and P. Koenigner, Ber., 41, 227 (1908).

10. F. Arndt, A. Kirsh and P. Nachtwey, Ber., 59B, 1078 (1926).

11. R. V. Moore and B. S. Greenfelder, J. Am. Chem. Soc., 69, 2008 (1947).

12. C. Hansch and W. A. Blondon, J. Am. Chem. Soc., 70, 1561 (1948).

13. C. Hansch and F. Hawthorne, J. Am. Chem. Soc., 70, 2495 (1948).

14. J. Boes, Apothekerztg., 17, 565 (1902); Centr., 1902, II, 804.

15. R. Weissgerber and O. Kruber, Ber., 53B, 1551 (1920).

16. D. A. Shirley and M. D. Cameron, J. Am. Chem. Soc., 74, 664 (1952).

17. E. G. G. Werner, Rec. trav. chim., 68, 509 (1949).

18. F. Krollpfeiffer and H. Hartmann, Ann., 563, 15 (1949).

19. F. Krollpfeiffer, K. L. Schneider, and A. Wissner, Ann., 566, 139 (1950).

20. Buu-Hoi and P. Cagniant, Ber., B76, 1269 (1943).

21. Buu-Hoi and P. Cagniant, Rec. trav. chim., 67, 64 (1948).

22. A. V. Sunthankar and B. D. Tilak, Proc. Indian Acad. Sci., 32, Sect. A., 396 (1950).

23. K. Rabindran and B. D. Tilak, Current Science, 20, 205 (1951).

24. M. W. Farrar and R. Levine, J. Am. Chem. Soc., 72, 4433 (1950).

25. A. W. Horton, J. Org. Chem., 14, 760 (1949).

26. R. Gaertner, J. Am. Chem. Soc., 74, 4950 (1952).

27. K. Fries, H. Heering, E. Hemmecke, and G. Siebert, Ann., 527, 83 (1937).

28. A. Schonberg and A. vonVargha, Ber., B64, 1390 (1931).

29. M. C. Kloetzel, J. E. Little, and D. M. Frisch, J. Org. Chem., 18, 1511 (1953).

30. H. Staudinger and J. Siegwart, Helv. Chim. Acta, 3, 840 (1920).

31. K. Fries and E. Hemmecke, Ann. 470, 1 (1929).

32. Buu-Hoi and Nguyen-Hoán, J. Chem. Soc., 251 (1951).

33. Buu-Hoi and Nguyen-Hoán, Rec. trav. chim., 68, 441 (1949).

34. A. W. H. Barton and E. W. McClelland, J. Chem. Soc., 1574 (1947).

35. D. A. Shirley and M. D. Cameron, J. Am. Chem. Soc., 72, 2788 (1950).

36. Buu-Hoi and P. Cagniant, Rec. trav. chim., 62, 719 (1943).

37. Buu-Hoi and P. Cagniant, Bull. soc. chim. France, 123 (1946).

38. S. L. Meisel, G. C. Johnson, and H. D. Hartough, J. Am. Chem. Soc., 72, 1910 (1950).

39. F. Ullmann and J. Korselt, Ber., 40, 642 (1907).

40. A. E. Senear, M. M. Rapport, and J. B. Koepfli, J. Biol. Chem., 167, 232 (1947).

41. K. Brand and W. Groebe, J. prakt. chem. 108, 1 (1924).

42. C. J. Miller and S. Smiles, J. Chem. Soc., 127, 231 (1925).

43. J. von Braun, Ber., 38, 180 (1905).

44. P. Chevin and J. Gunthart, Bull. soc. chim., 12, 105 (1945).

45. Buu-Hoi and Nguyen-Hoán, Rec. trav. chim., 68, 5 (1949).

46. J. Szmuskovicz and E. J. Modest, J. Am. Chem. Soc., 725, 71 (1950).

47. Buu-Hoi and J. Lecocq, Compt. rend., 222, 1441 (1946).

48. R. Gaertner, J. Am. Chem. Soc., 74, 4950 (1952).

49. R. T. Van Vleck, U. S. Pat. 2,557,708 (1951); Chem. Abstracts, 46, 731 (1952).

50. E. C. Kleiderer and R. Adams, J. Am. Chem. Soc., 55, 4219 (1933).

51. H. Gilman and M. Lichtenwalter, J. Am. Chem. Soc., 61, 957 (1939).

52. J. Thompson, Org. Syn., 20, 94 (1940).

53. K. E. Ungnade and D. V. Nightingale, J. Am. Chem. Soc., 66, 1218 (1944).

54. N. Zelinsky, Ber., 30, 1541 (1897).

55. A. M. Hutchison and S. Smiles, J. Chem. Soc., 101, 570 (1912).

56. P. Friedlander, Ber., 39, 1060 (1906).

57. R. B. Carlin, J. Am. Chem. Soc., 67, 930 (1945).

58. F. Ullmann, Ann., 332, 38 (1904).

59. P. E. Fanta, Chem. Rev., 38, 139 (1946).

60. J. Krizewsky and E. E. Turner, J. Chem. Soc., 115, 559 (1919).

61. L. Mascarelli, B. Longo, and A. Rivera, Gazz. chim. ital., 68, 33 (1938); Chem. Abstracts, 32, 4565 (1938).

62. W. Steinkopf, R. Leitsmann, and K. H. Hofmann, Ann., 546, 180 (1941).

63. J. B. Senderens, Compt. rend., 154, 778 (1912).

64. K. von Auwers and W. Thiess, Ber., B53, 2285 (1920).

65. L. Ruzicka, J. Meyer, and M. Mingazzini, Helv. Chim. Acta., 5, 363 (1922).

66. L. Gattermann, Ber., 25, 3531 (1892).

67. J. A. Blanchette and E. V. Brown, J. Am. Chem. Soc., 73, 2779 (1951).

68. L. W. Pickett, G. F. Walter, and France, J. Am. Chem. Soc., 58, 2296 (1936).

69. M. Pestemer and S. Mayer-Pitsch, Monatsh., 70, 104 (1937).

70. M. Calvin, J. Org. Chem., 4, 256 (1939).

71. M. T. O'Shaughnessy and W. H. Rodebush, J. Am. Chem. Soc., 62, 2906 (1940).

72. B. Williamson and W. H. Rodebush, J. Am. Chem. Soc., 63, 3018 (1941).

73. D. W. Sherwood and M. Calvin, J. Am. Chem. Soc., 64, 1350 (1942).

74. L. W. Pickett, M. Groth, S. Duckworth, and J. Cunliffe, J. Am. Chem. Soc., 72, 44 (1950).

75. M. Crawford and I. F. B. Smith, J. Chem. Soc., 4133 (1952).

76. G. N. Jean and F. F. Nord, J. Org. Chem., 20, 1370 (1955).

77. O. Bastiansen, Acta. Chem. Scand., 3, 408 (1942).

78. R. N. Jones, J. Am. Chem. Soc., 63, 1658 (1941).

79. M. R. Radhye and S. R. Desai, Trans. Faraday Soc., 49, 1386 (1953).

80. P. Ramart-Lucas and M. Martynoff, Compt. rend., 236, 2247 (1953).

81. J. H. Gardner and P. Borgstrum, J. Am. Chem. Soc., 51, 3375 (1929).

82. F. C. Whitmore, C. J. Stehman, and J. M. Herndon, J. Am. Chem. Soc., 55, 3807 (1933).

83. R. A. Friedel, M. Orchin, and L. Reggel, J. Am. Chem. Soc., 70, 199 (1948).