

SYNTHETIC STUDIES IN THE
PREPARATION OF A VARIETY OF
SUBSTITUTED ACETYLENES

Thesis for the Degree of M. S.
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Jeffrey N. Smith
1971



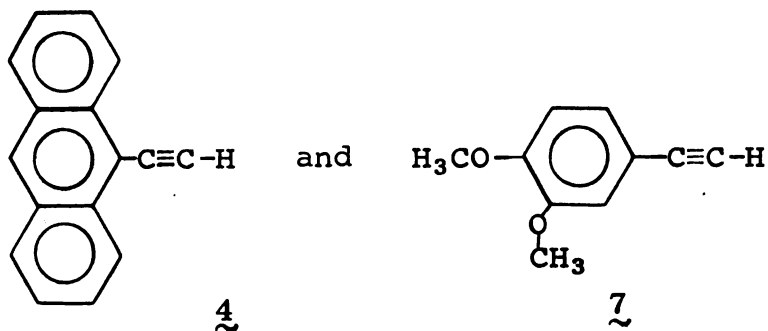
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SYNTHETIC STUDIES IN THE PREPARATION OF A VARIETY OF SUBSTITUTED ACETYLENES

Jeffrey N. Smith

The copper acetylides of two different electron-donating molecules (compounds 4 and 7)



were prepared. The attempted coupling reactions were performed with three different electron-withdrawing molecules: iodo-4-nitrobenzene, iodo-2,4-dinitrobenzene and picryl chloride.

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The various substituted acetylenes were evaluated and shown to exhibit charge transfer bands in the visible spectrum. Some interesting conclusions can be drawn, concerning the properties of these π -complexes.

SYNTHETIC STUDIES IN THE PREPARATION OF A VARIETY
OF SUBSTITUTED ACETYLENES

By

Jeffrey N. Smith

A THESIS

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To my wife, Betty, and to
the memory of my father

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The author wishes to express his sincere gratitude to Dr. Eugene LeGoff for his guidance and assistance throughout the course of this investigation.

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INTRODUCTION

The objective of this thesis is the synthesis of a variety of substituted acetylenes in an attempt to prepare a series of charge transfer complexes. A great deal of interest has been generated over the years by the molecular complexes formed by mixing certain aromatic hydrocarbons with a large variety of aromatic nitro-compounds^{1,2}.

The main spectral feature accompanying complex formation is the broad, intense absorption band in the ultra-violet or visible spectral region, due to the electronic transition from the ground state to the excited state. As the strength of the charge transfer complex is increased the energy gap for excitation is decreased and a higher wave length of absorption is observed, since the two are related inversely. The color of the complex will also become more intense as the energy gap is reduced.

This exploratory work was initiated to study the properties of charge transfer complexes and to relate these results to the future development of a linear, organic superconductor. A large volume of work has been generated on the preparations of organic semi-conductors³, but, to date, only theoretical predictions exist for organic superconductors.⁴

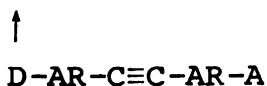
Two criteria are necessary for an organic molecule to exhibit conducting properties. The first being a high degree of electron delocalization within the molecule. The higher the electron mobility within the system, the smaller the energy gap is between the ground state and the excited state. The second requirement is the flow of electrons from one molecule to the next. Some low energy process is needed for this electron promotion.

The model which was, therefore, chosen for this study consisted of an acetylene substituted with an aromatic, electron donor on one end and a nitro-aromatic, electron acceptor on the other end.



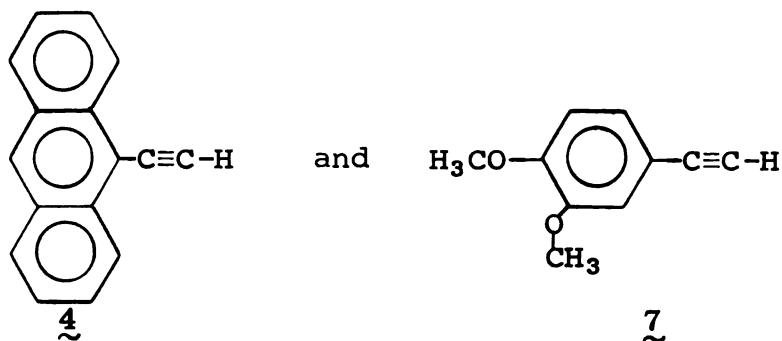
D - electron donor
 AR - aromatic molecule
 A - electron acceptor

The flow of electrons from one molecule to the next should be facilitated by this type of structure. The donor end of one molecule could line up with the acceptor end of another molecule to form the charge transfer complex.



The synthetic work entailed the preparation of the terminal acetylenes of the electron donor end and subsequent coupling of the acetylides with the electron acceptor end.

The electron donating molecules used were 9-anthrylacetylene (4) and 3,4-dimethoxy-phenylacetylene (7).



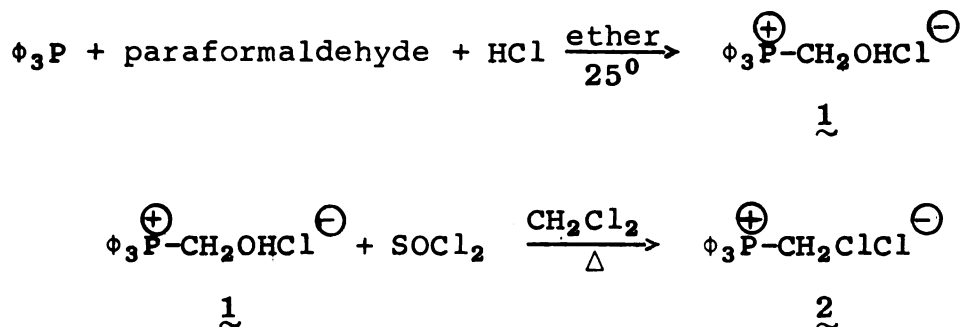
The copper acetylides of these molecules were prepared and then reacted with three different electron accepting halides: iodo-4-nitrobenzene, iodo-2,4-dinitrobenzene and picryl chloride.

From the observation of the visible spectral data, the preparation of some charge transfer complexes has succeeded. Some interesting conclusions can be drawn, concerning the properties of these complexes.

The results of this work are encouraging. The future preparation of an organic superconductor of this type is supported, however, further exploratory work is needed before a working model can be developed.

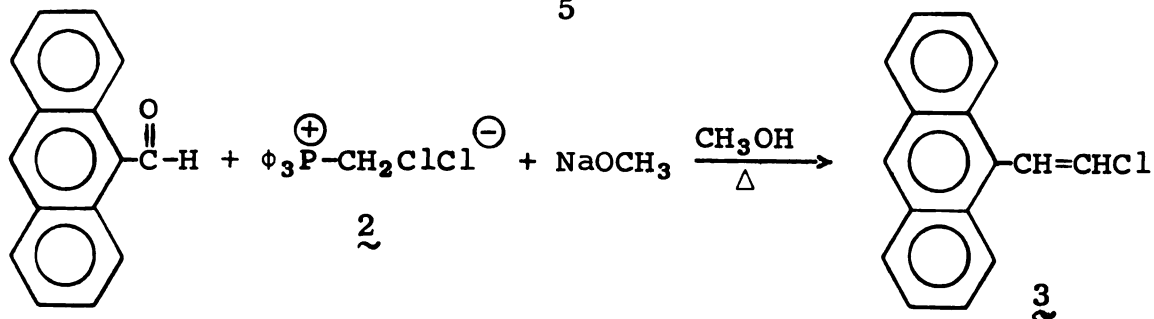
RESULTS

The preparation of the starting material, chloromethyl-triphenyl-phosphonium chloride (2), was easily accomplished by variations to the literature preparations described by Wittig⁵ and Köbrich.⁶



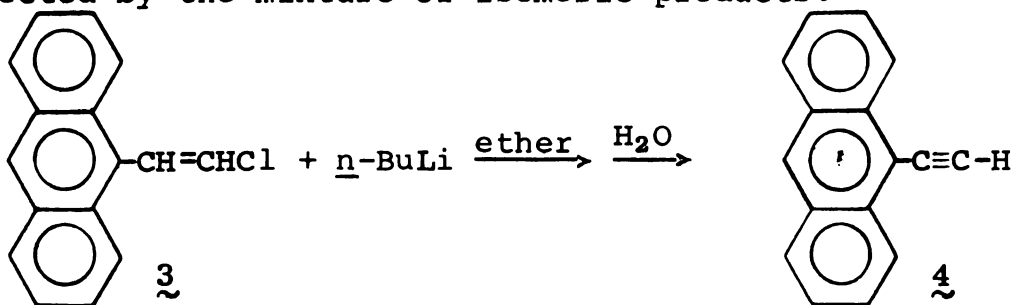
Simple treatment of triphenyl phosphine and paraformaldehyde with gaseous hydrogen chloride in ether at room temperature leads to hydroxymethyl-triphenyl-phosphonium chloride (1) in a 55% yield. This can be converted to compound (2) by treatment with thionyl chloride in methylene chloride under reflux in a 98% yield.

If the ylid of compound 2 is generated in the presence of 9-anthraldehyde by sodium methoxide, the normal Wittig type reaction will occur at the carbonyl to yield 9-(β -chlorovinyl)anthracene (3) in a 40% conversion.



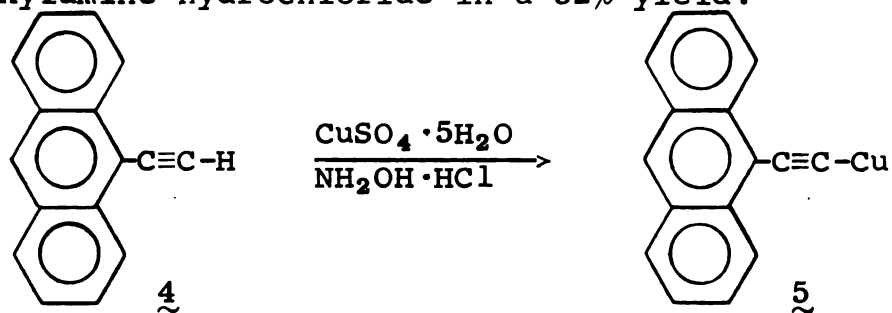
Both the cis and trans isomers of compound 3 were observed in this reaction. This can be shown through the nmr spectrum. Two proton bands, consisting of two AB quartets, are located at δ 6.40 (doublet, $J_{\text{trans}} = 14$ Hz) and δ 6.80 (doublet, $J_{\text{cis}} = 8$ Hz), the two lower doublets of each AB system are superimposed on the nine proton multiplet between δ 7.20-8.40 (aromatic)(Figure 1A). The cis isomeric product can be partially separated from the trans isomer by recrystallizing the mixture from methanol. An nmr spectrum of this material (Figure 1B) shows a decrease of the intensity of the doublet at δ 6.40, indicating partial fractional crystallization of the cis product.

Very careful thin layer chromatography with aluminum oxide and carbon tetrachloride produces a definite separation of the isomers. Further work on their ultimate separation, however, was not carried out, since conversion of compound 3 to the corresponding terminal acetylene is not affected by the mixture of isomeric products.



Dehydrohalogenation can be accomplished with n-butyl lithium as the base in an ether solution. Hydrolysis with water completes the reaction in a 95% yield.

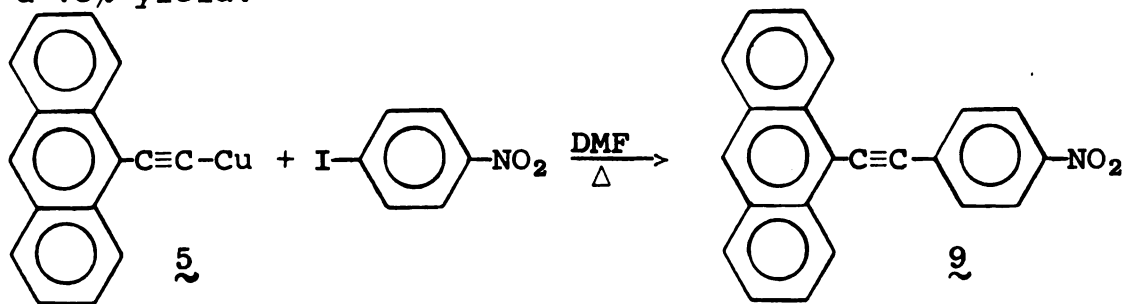
Through a procedure similar to that developed by Castro⁷ 9-anthrylacetylene (4) is converted to the corresponding copper acetylide (5) with cupric sulfate and hydroxylamine-hydrochloride in a 52% yield.

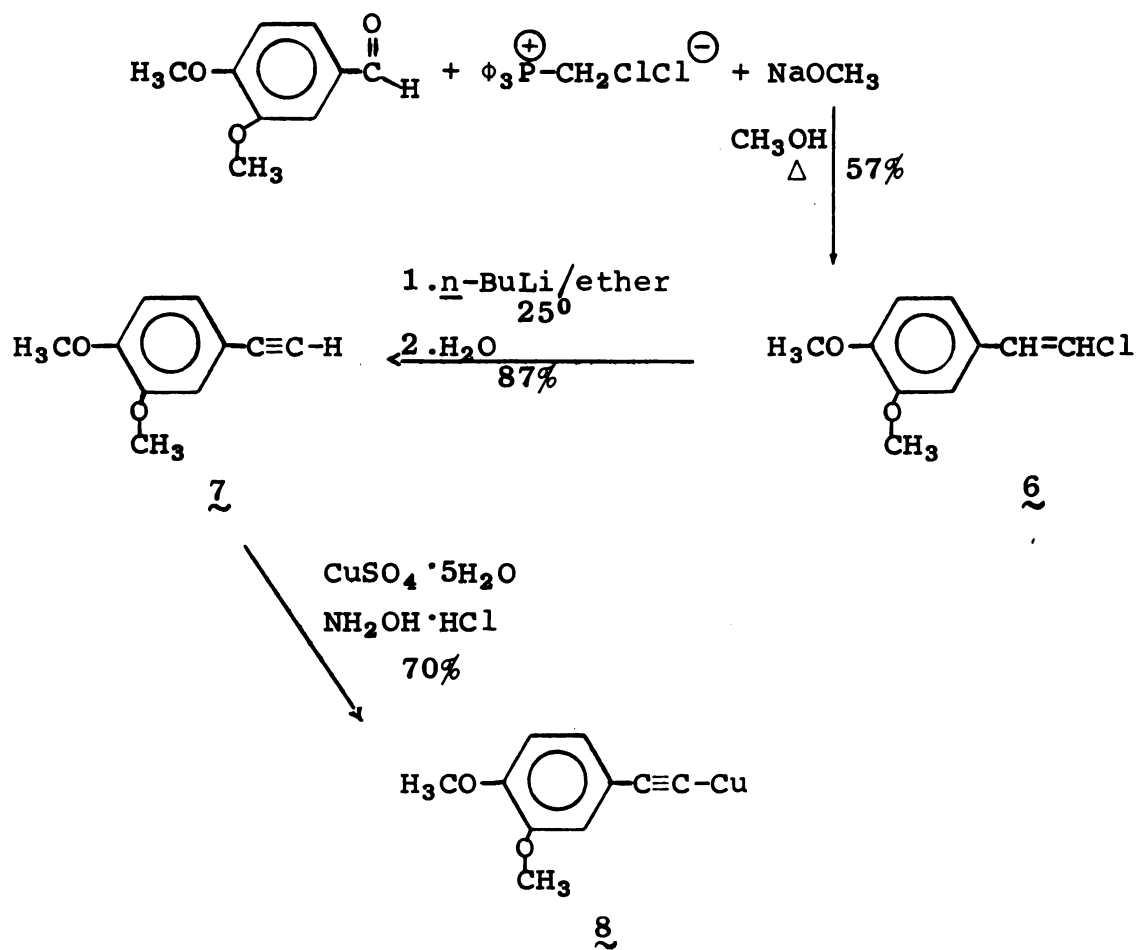


Similar work was carried out with another donor type molecule. The reaction sequence (Scheme I) with 1-substituted-3,4-dimethoxy-benzene was analogous to that of 9-substituted-anthracene, except for minor differences.

Now that the copper acetylides have been prepared the various coupling reactions can now be attempted. The procedures used were similar to those reported by Castro⁷ in his synthetic acetylene investigations.

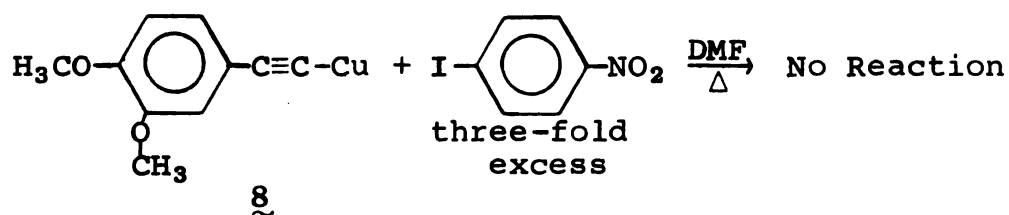
The reaction of iodo-4-nitrobenzene with compound 5 in dimethyl formamide at 120° was accomplished in 40 hours in a 73% yield.



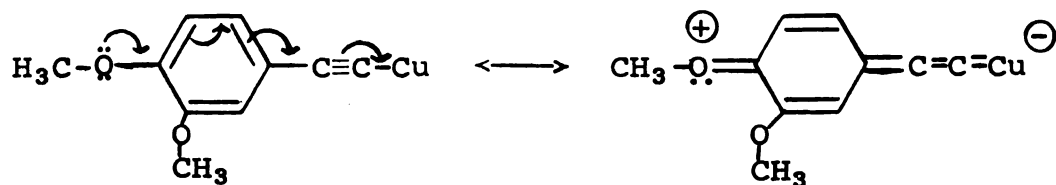


Scheme I.

The same reaction procedure was attempted with compound 8, but surprisingly, there was no reaction, even after three days of stirring at 120°. The insoluble copper acetylide was then removed from the reaction media by filtration and purified. The same conversion was attempted again with a three fold excess of iodo-4-nitrobenzene, but still no reaction was apparent.

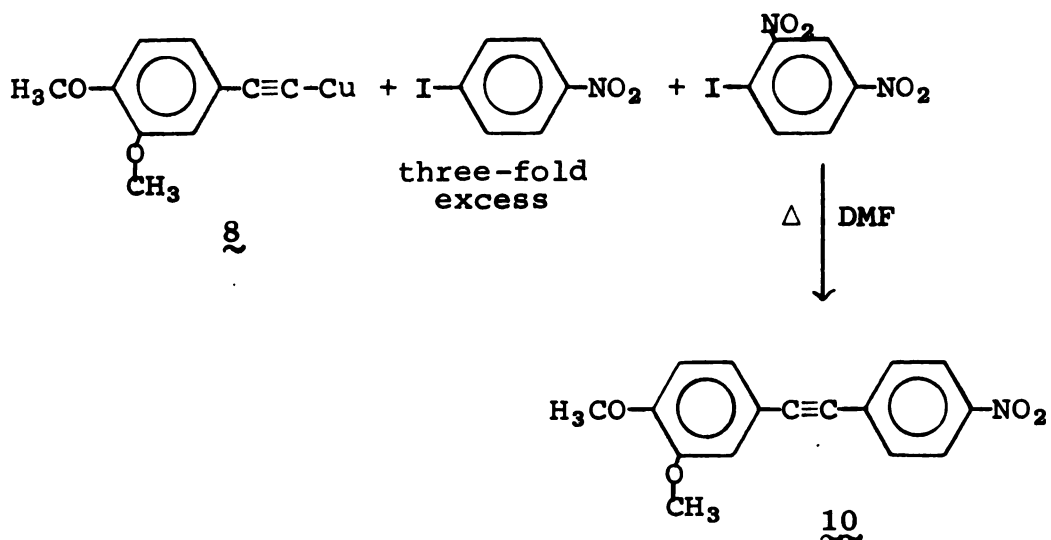


A possible explanation of the lower reactivity of the copper acetylide of 3,4-dimethoxyphenylacetylene (8) over that of the copper acetylide of 9-anthrylacetylene (5), would be the added amount of electron donation from the unshared electron pairs on the para methoxy oxygen. Delocalization of the electrons through the phenyl ring and the triple bond would be expected to strengthen the C-Cu bond significantly and thus retard the reaction.

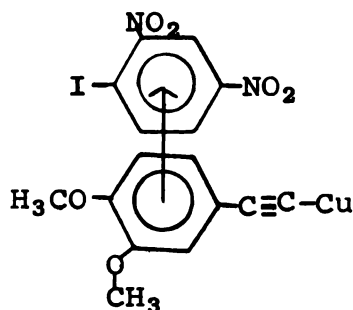


The vacant d-orbitals on the copper could accommodate the extra electrons to strengthen the C-Cu bond through back-bonding.

Instead of isolating the copper acetylide again from the reaction mixture, another electron accepting type molecule was added directly to the suspension. Iodo-2,4-dinitrobenzene was chosen because the added nitro group in the ortho position will withdraw electron density from the reaction center and, therefore, facilitate the reaction. An immediate reaction occurred with this addition, observable by the production of a dark red solution and the disappearance of the copper acetylide. Quite surprisingly, the mononitro coupled product (10) was recovered instead of the dinitro coupled product in a 65% yield.



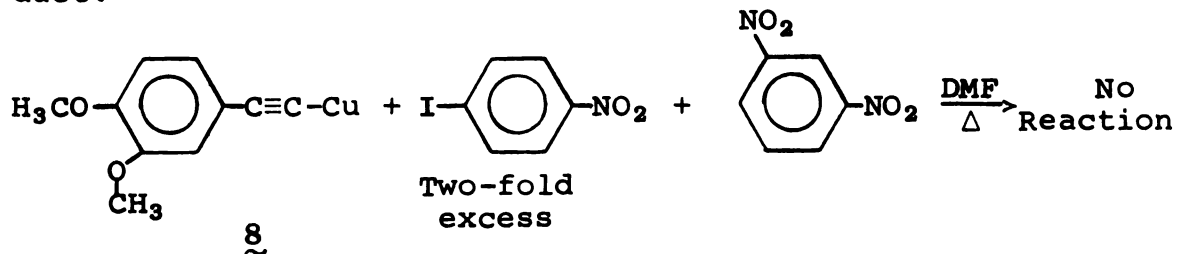
A preliminary explanation of this phenomena comes from the possibility of a π -complex forming between compound 8 and the electron-withdrawing, iodo-2,4-dinitrobenzene.



If electrons are removed by this π -complex, the amount of electron donation from the unshared electron pairs on the para oxygen would be decreased; the C-Cu bond strength would subsequently be weakened. This would lead to a more favored reaction.

The formation of the product could be governed by either the steric hindrance of the ortho nitro group or by the statistical factor of a three fold excess of the iodo-4-nitrobenzene.

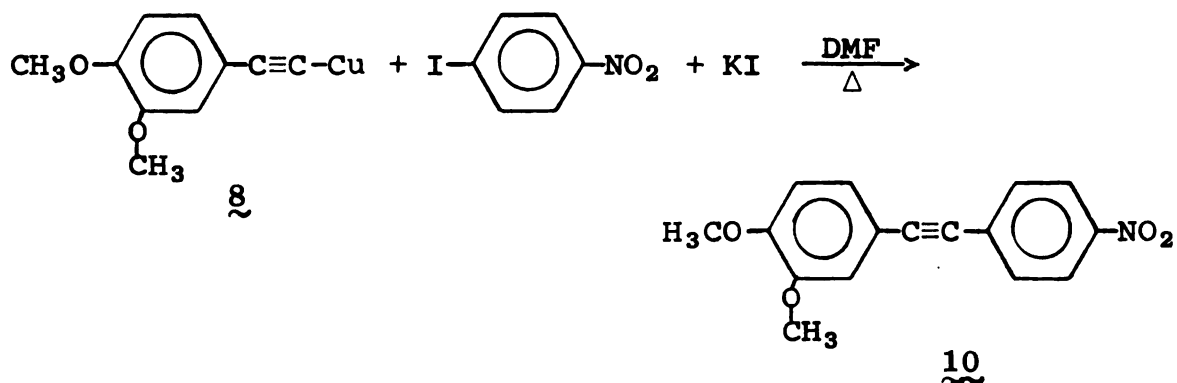
An experiment was designed to test this theory. The reaction was repeated substituting meta-dinitrobenzene for iodo-2,4-dinitrobenzene. If the π -complex is a real species, the reaction should proceed to the expected product.



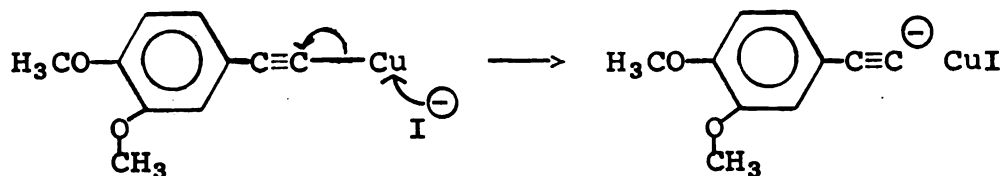
Since no reaction occurs under the conditions previously used, the π -complex theory was disproven.

Since the mechanism does not proceed through a π -complex, some other unknown complex must be forming with the acetylide to weaken the C-Cu bond.

To determine if free iodide will complex with the copper acetylide to weaken the C-Cu bond, the same reaction was run with potassium iodide as a catalyst. It was found that the reaction did go and in a good yield (75%), but a catalytic amount was not enough; a full equivalent was needed for the reaction to go to completion.



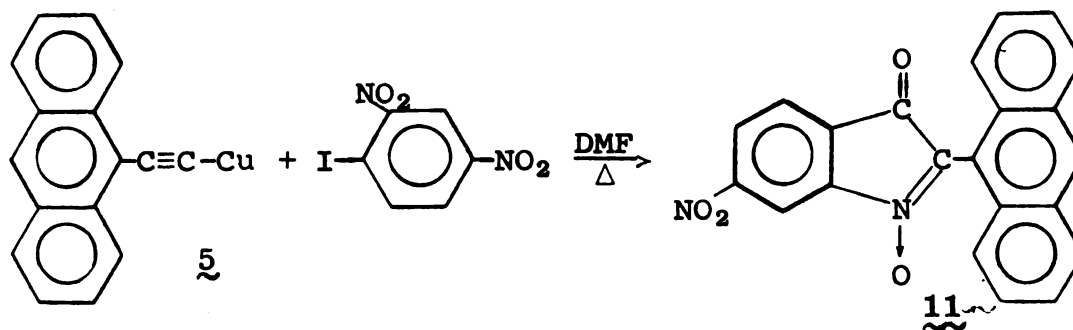
Apparently the iodide is complexing with the copper to weaken the C-Cu bond and help locate the negative charge on the carbon atom.



This localization of the charge would increase the nucleophilicity of the carbon atom of the acetylene to promote the reaction.

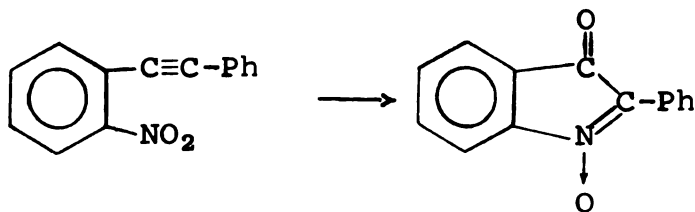
This explanation, however, does not explain why the iodo-2,4-dinitrobenzene will also catalyze the reaction. In that system no free iodide should be present. Apparently, it must be complexing with the copper in some unknown fashion to facilitate the reaction. Further work to determine the actual mechanisms of these catalysts was not investigated.

The next objective is to prepare the respective dinitro coupled products. Iodo-2,4-dinitrobenzene was then reacted with compound 5 under the normal conditions in dimethyl formamide at 120° and allowed to stir for three hours. Disappearance of the copper acetylide was observed with the production of a dark red solution. Analysis of the reaction product produced another surprise.



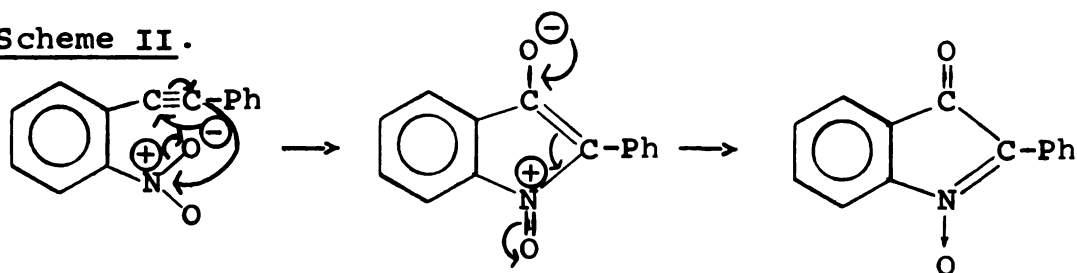
Instead of the expected dinitro coupled product, the corresponding rearranged, green isatogen was isolated in a 54% yield.

After searching the literature, it was discovered that ortho-nitro-acetylene compounds rearrange in the presence of sunlight and a variety of solvents (mainly chloroform and pyridine) to their respective isatogens.^{8,9,10}

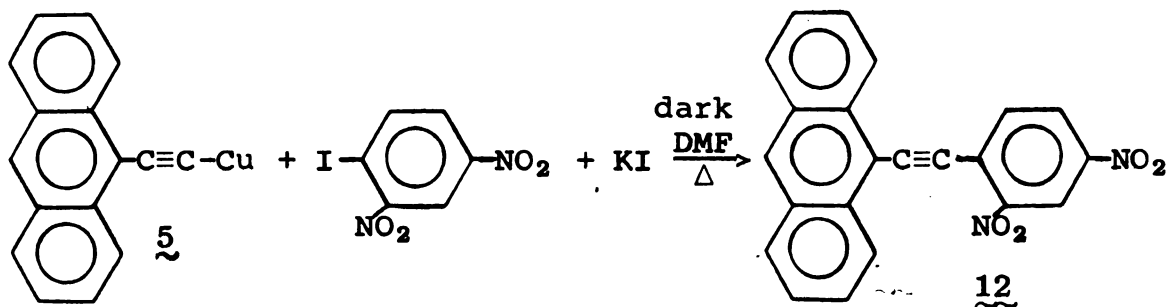


The mechanism for this rearrangement has not been investigated, but can be postulated to be as shown in Scheme II.

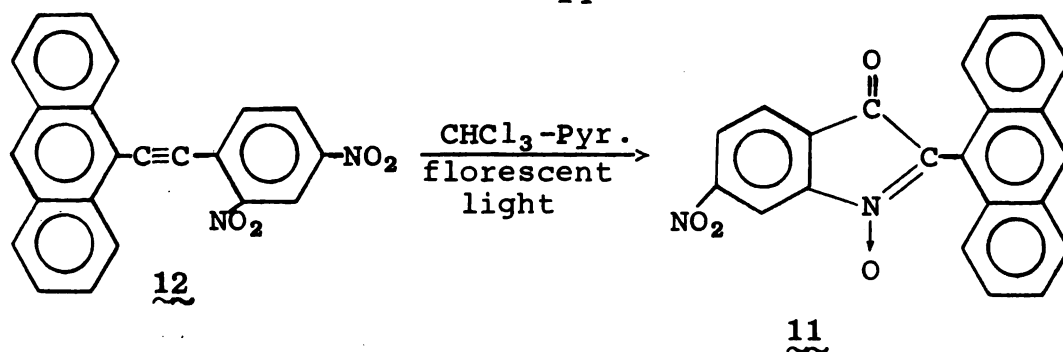
Scheme II.



In order to avoid this complication, the identical reaction was run in the dark with potassium iodide as a catalyst. The isatogen formation was halted and a yield of 78% was observed for the production of compound 12.

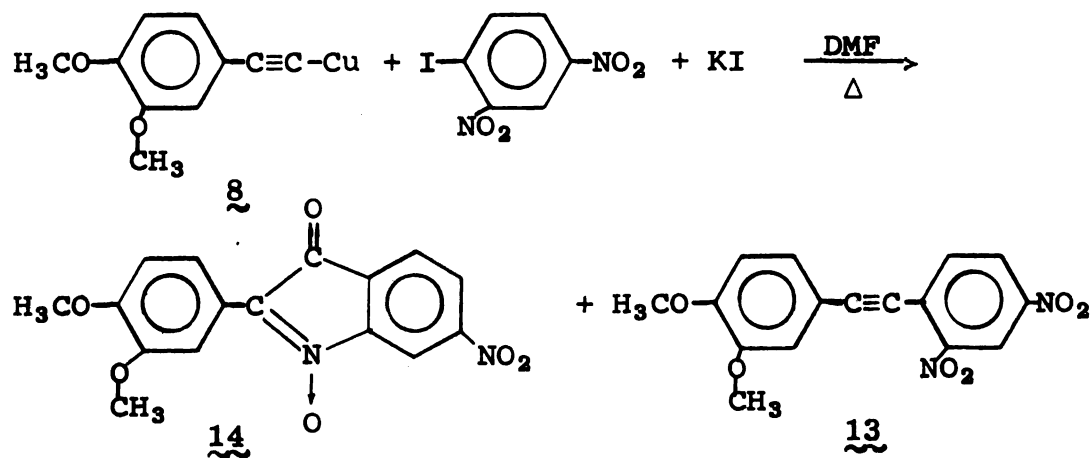


If this dark red compound (12) is then put in a solution of pyridine and chloroform and allowed to stir in the presence of a florescent light bulb for one day, a 50% conversion is obtained to the isatogen (11).

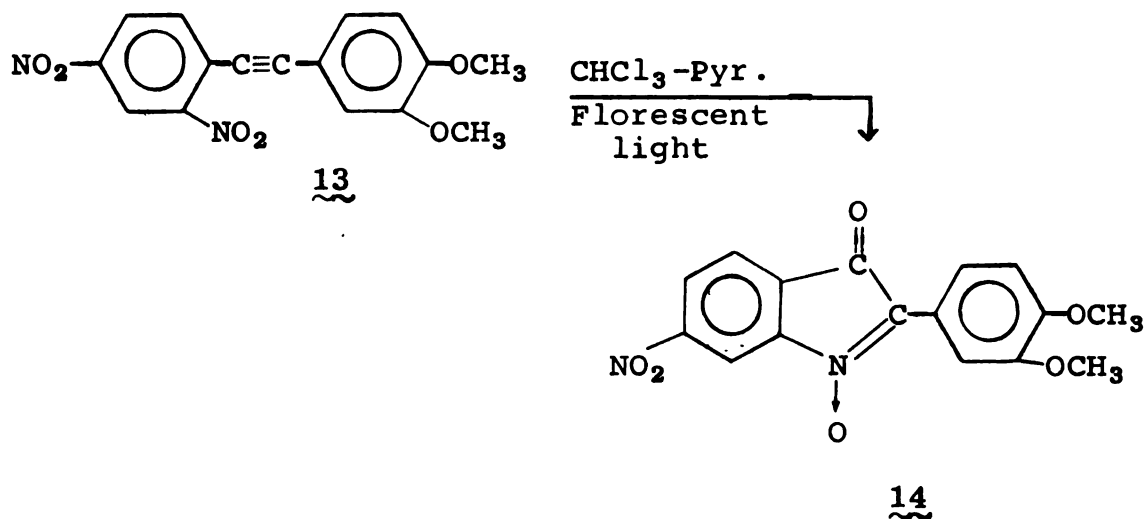


A characteristic difference is observed in the infrared spectrum. An acetylene stretch ($\text{C}\equiv\text{C}$) occurring at 2200 cm^{-1} for compound 12 is observed (Figure 7), while the spectrum of compound 11 has no acetylene stretch, but instead, a carbonyl absorption ($\text{C}=\text{O}$) at 1700 cm^{-1} (Figure 9).

This same type of photochemical rearrangement is observed in the reaction of compound 8 with iodo-2,4-dinitrobenzene, however, not as much isatogen is formed. If the reaction is performed under normal conditions with potassium iodide as the catalyst, both the acetylene (13) and the isatogen (14) are isolated.

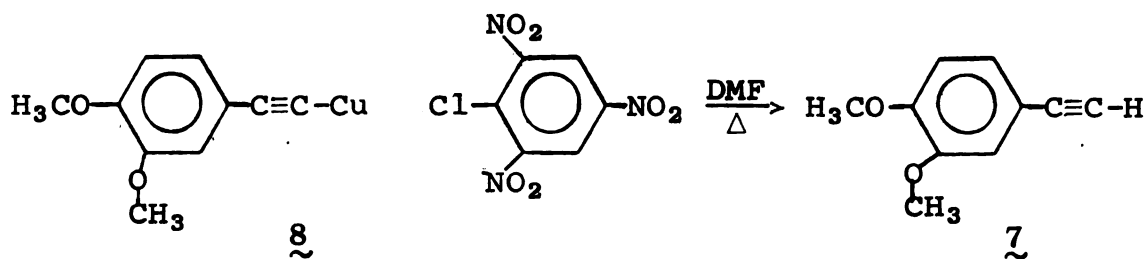


If the same reaction is run in the dark only the orange acetylene (13) is recovered in a 69% yield. Similarly, the conversion of the acetylene (13) to the violet isatogen (14), can be accomplished by allowing compound 13 to stir in the presence of a florescent light bulb for two days. The product can be isolated in a 50% yield.

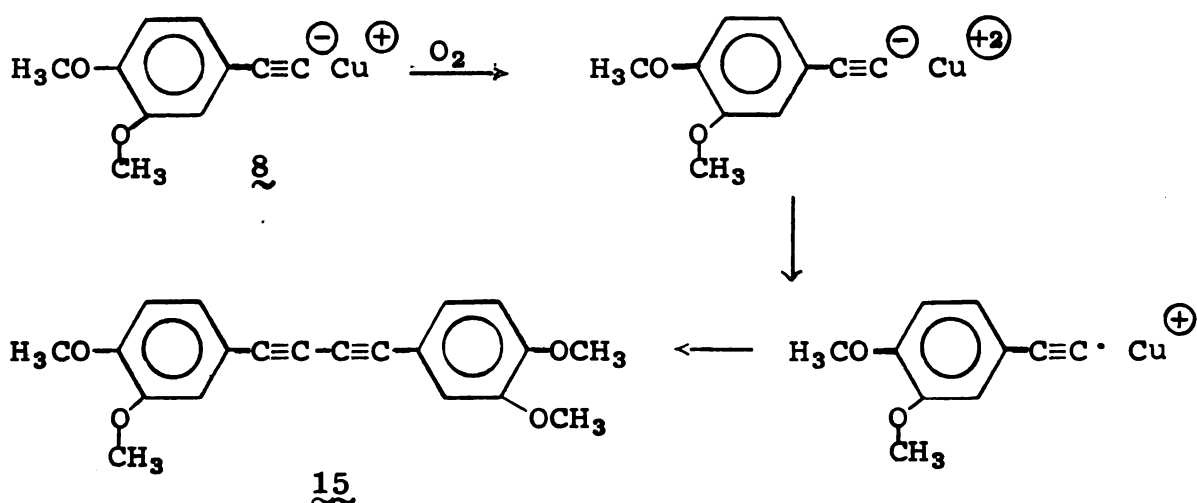


Conversion of the acetylenes to the isatogens is also observed in the solid state, so extreme precaution is necessary to keep the acetylene protected from light.

Now that the preparations had been worked out for the mono and dinitro coupled products, the trinitro products were desired. Initial experiments were performed with compound 8 and picryl chloride in dimethyl formamide at 120°. The reaction was complete in one hour but the expected coupled product was not obtained.

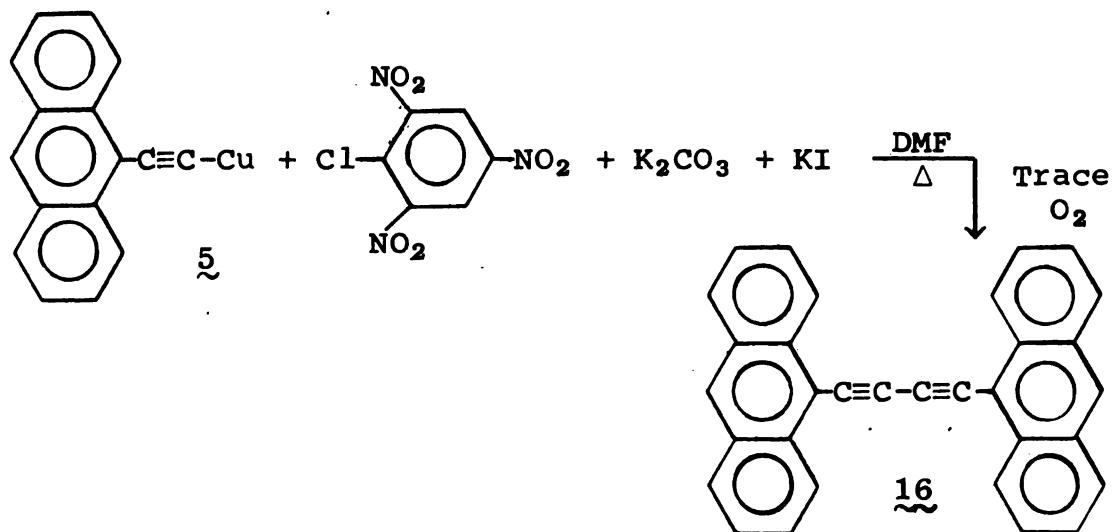


The terminal acetylene was the product isolated. Apparently, the copper acetylide is being hydrolyzed during the reaction. This could be caused by either picric acid in the picryl chloride or from water in the dimethyl formamide. Another trial of the reaction was attempted with special precautions made to recrystallize the picryl chloride (ethanol) and to dry the dimethyl formamide (molecular sieves, type 4A). In addition potassium carbonate was added to the reaction mixture to remove any residual source of protons and potassium iodide was added to catalyze the reaction. The same results as the preceding experiment were observed, however. It was also discovered through further experimentation that trace amounts of oxygen in the system will cause dimerization to the diacetylene (15)!¹



Therefore, mixtures of compounds 7 and 15 will be obtained, if care is not taken to remove all oxygen from the reaction vessel.

The same type of results were obtained in the reaction of compound 5 with picryl chloride.



The terminal acetylene (4) can be isolated, if all oxygen is removed from the system.

The possible reason for this strange behavior could be due to the steric hindrance to formation of the coupled product. The two ortho nitro groups are probably blocking the entry of the copper acetylide. The nucleophilic acetylide then abstracts a proton, possibly from the solvent, to complete the reaction.

DISCUSSION

Now that the various model compounds have been prepared, they must be evaluated to determine if charge transfer or π -complexes have been formed.

The formation of a charge transfer complex can easily be determined through the ultra-violet and visible spectra. If a long wave length of absorption exists for the various substituted acetylenes and isatogens, which is not present in either the electron donor or acceptor molecules, a charge transfer complex is indicated. This absorption is due to the electronic transition from the ground state of the complex to the excited state.^{1,2}

The highest wave length of absorption for the various substituted acetylenes and isatogens are presented in Table I. The respective absorptions for the individual donor and acceptor molecules are listed in Table II. By comparing the various visible spectral data, it can be clearly shown that charge transfer or π -complexes are being formed by these molecules. None of the selected donor or acceptor components approach the higher wavelengths of the charge transfer bands present in these systems.

Some substitutions have been made in Table II for the spectral data of some unavailable compounds. For instance,

Table I. Collected data on the various coupled acetylenes and isatogens.

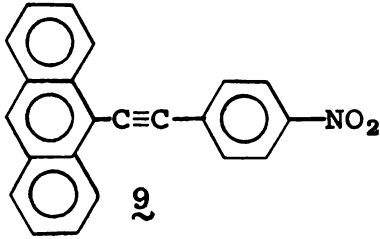
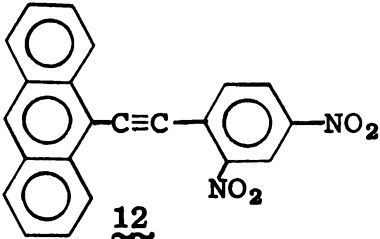
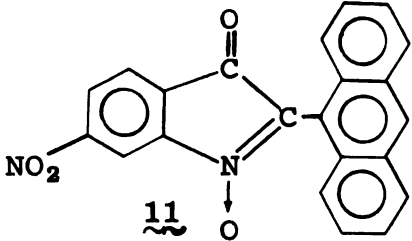
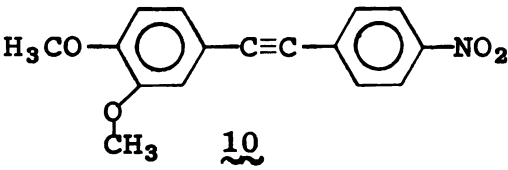
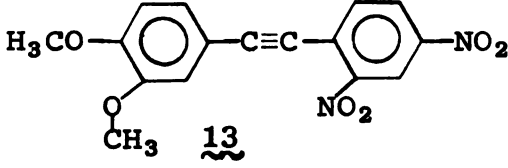
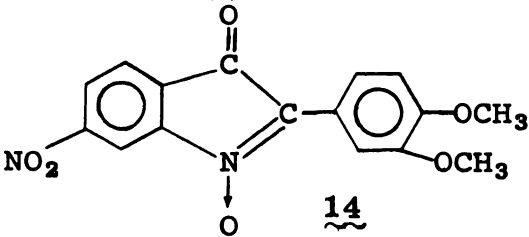
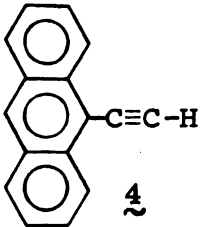
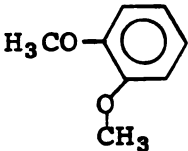
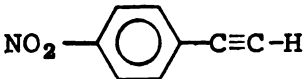
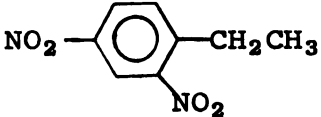
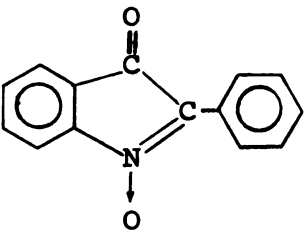
Structure	Color	Solvent	Charge Transfer Band (mμ)
 <chem>c1ccc2c(c1)ccc3c2C#Cc4ccc([N+](=O)[O-])cc4</chem> <u>9</u>	Orange	95% Ethanol	430
 <chem>c1ccc2c(c1)ccc3c2C#Cc4cc([N+](=O)[O-])ccc4[N+](=O)[O-]</chem> <u>12</u>	Red	CH ₂ Cl ₂	476
 <chem>O=C1C(=O)N(C1c2ccc([N+](=O)[O-])cc2)c3c4ccccc4cc5ccccc35</chem> <u>11</u>	Green	CH ₂ Cl ₂	562
 <chem>COc1cc(OC)ccc1C#Cc2ccc([N+](=O)[O-])cc2</chem> <u>10</u>	Yellow	95% Ethanol	356
 <chem>COc1cc(OC)ccc1C#Cc2cc([N+](=O)[O-])ccc2[N+](=O)[O-]</chem> <u>13</u>	Orange	CH ₂ Cl ₂	403
 <chem>O=C1C(=O)N(C1c2ccc([N+](=O)[O-])cc2)c3cc(OC)c(OC)cc3</chem> <u>14</u>	Violet	CH ₂ Cl ₂	523

Table II. Collected ultra-violet spectral data on the various electron donor and acceptor components.¹²

Structure	Solvent	Highest Wave Length of Absorptions, mμ
	C ₆ H ₁₂	391
	95% Ethanol	274
	95% Ethanol	286
	95% Ethanol	241
	CCl ₄	438 ¹³

the ultra-violet spectra of 2,4-dinitro-phenylacetylene and 3,4-dimethoxy-phenylacetylene have not been recorded in the literature. Substitution of these with 1-ethyl-2,4-dinitrobenzene and 3,4-dimethoxy-benzene, respectively, have been shown to be representative by the data in Table III. A series of 9-substituted and unsubstituted anthracenes (Table III) exhibit similar ultra-violet spectral absorptions.

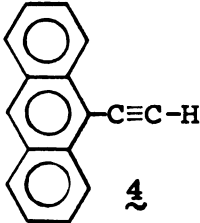
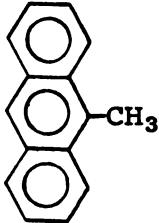
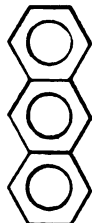
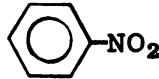
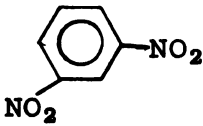
The model system for the isatogens (2-phenylisatogen) is not strictly correct, either; the best model would have another nitro group in the 6-position. This has been shown not to be a serious problem by a study of nitro-benzenes (Table III). The substitution of a nitro group in the meta position of nitrobenzene does not significantly change the absorption.

The color of the various complexes has been shown (see the Appendix) to arise from long tailing of the broad absorptions into the respective color regions and not from sharp absorptions. This can be attributed to the loose nature of binding in the ground state of the complex.^{1,2}

Three general conclusions can be drawn, if Table I is examined carefully.

1.) As the amount of electron withdrawing power is increased (nitro groups) within the molecule, the wavelength of the charge transfer band is increased. This tends to indicate the π -complex is strengthened as the amount of electron accepting ability is increased. The

Table III. Collected ultra-violet spectral data on some compounds used to study substituent effects on a few of the electron donor and acceptor molecules.

Structure	Solvent	Highest Wave Length of Absorptions, mμ
	C ₆ H ₁₂	391
	95% Ethanol	375.5
	95% Ethanol	274
	95% Ethanol	259
	95% Ethanol	235

energy gap between the ground state and the excited state is, therefore, decreased.

2. In all cases the 9-substituted-anthracenes absorb at higher wavelengths than the corresponding 1-substituted-3,4-dimethoxy-benzenes. Although the 1-substituted-3,4-dimethoxy-benzenes should be more electron donating, because of the unshared pairs of electrons on the methoxy oxygens, the 9-substituted anthracenes must overcome this effect through their extended conjugated systems.

3. Although the acetylene moiety has been destroyed in the isatogens, charge transfer complexes are still present. The formation of isatogens has increased the wavelength of absorption significantly in both cases. This is probably due to the presence of additional conjugation and the formation of a new chromophore. Charge transfer complexes in these systems seem extremely good.

It has, therefore, been shown that charge transfer complexes will form with these systems. Hopefully, this new knowledge will be useful for the future preparation of organic superconductors of this type.

EXPERIMENTAL

1. General Procedures

A. Spectra

Nuclear magnetic resonance spectra were determined on a Varian T-60 high resolution spectrometer with tetramethylsilane as a standard.

Infrared spectra were obtained on a Perkin-Elmer 237B Grating Infrared Spectrophotometer. Sodium chloride cells were used for all determinations.

Mass spectra were obtained using a Hitachi Perkin-Elmer Model RMU-6 low resolution instrument.

Ultraviolet and visible spectra were measured using 1 cm quartz cells on a Unicam Model SP-800 spectrophotometer.

B. Microanalysis

Microanalytical data were obtained from Spang Microanalytical Laboratory, Ann Arbor, Michigan and Water Quality Research Laboratory, Michigan State University.

C. Melting Points

Melting points were determined on a Thomas Hoover capillary melting point apparatus. All temperatures are uncorrected and recorded in degrees Centigrade.

2. Hydroxymethyl-triphenyl-phosphonium Chloride (1)^{5,6}

Triphenyl phosphine (26.2 g., 100 mmoles) was dissolved in 125 ml of anhydrous ether. Subsequent addition of 3.3 g (110 mmoles) of paraformaldehyde (trioxane) to the solution formed a suspension. Gaseous hydrogen chloride was passed slowly through the stirred mixture for a period of 3 hours at room temperature. The product precipitated as a white solid which was removed by filtration and washed with several portions of ether. Further purification involved reprecipitating the hydroxymethyl-triphenyl-phosphonium chloride (1) from methylene chloride with ether. This produced 18 g (55 mmoles) of pure, white product in a 55% yield: m.p. 192-194° [lit. m.p. 194-198°^{5,6}]. This white, powdery material is hygroscopic and should be dried in an oven for 10 hours at 90° under a vacuum (27 in Hg) for best results before further use.

3. Chloromethyl-triphenyl-phosphonium Chloride (2)^{5,6}

Thionyl chloride (11.3 g, 95 mmoles) was slowly dripped into a solution of 15.55 g (47.5 mmoles) of hydroxymethyl-triphenyl-phosphonium chloride (1) in 100 ml of methylene chloride. The reaction mixture was then refluxed

for 45 minutes, after which, the solvent was removed in the hood with a water aspirator. (Normal solvent removal with the rotary evaporator and a vacuum pump on the bench is not recommended because of the toxic effects of thionyl chloride.) The remaining residue was precipitated from a methylene chloride solution with ether. The white, powdery product (16.1 g, 46.5 mmoles) was isolated in a 98% yield: m.p. 256° [lit. m.p. 260-261°^{5,6}]. The product is hydroscopic and should be dried in an oven for 10 hours at 90° under a vacuum (27 in Hg) for best results before further use.

4. 9-(β -Chlorovinyl)anthracene (3) [The procedure used was similar to that described by Wittig⁵.]

Under a nitrogen atmosphere 3.47 g (10 mmoles) of chloromethyl-triphenyl-phosphonium chloride (2) was dissolved in 75 ml of dry methanol. Sodium methoxide (0.54 g, 10 mmoles) was then added to the solution. After the mixture was refluxed for fifteen minutes, 2.06 g (10 mmoles) of 9-anthraldehyde in 10 ml of methylene chloride was added dropwise. The reaction mixture was then refluxed for one hour and subsequently neutralized with 0.5 g of ammonium chloride. After the reaction mixture was cooled the solvent was removed and the residue taken up in ether and water. The ether portion was extracted with water, dried (MgSO_4) and the solvent stripped off under vacuum with a rotary evaporator. The residue which resulted was

chromatographed on dry column alumina (50 g, 27 mm column) with carbon tetrachloride. The first yellow band off the column contained the desired product. When the solvent had been stripped away, a yellow oil was obtained, which crystallized upon standing for half an hour. The 9-(β -chlorovinyl)anthracene (3) was then recrystallized from methanol to yield 0.96 g (4 mmoles) of nice, yellow crystals (40%): m.p. 79-81⁰; nmr spectrum (CCl_4), 2H band consisting of two AB quartets at δ 6.40 ($J_{\text{trans}} = 14 \text{ Hz}$) and δ 6.80 ($J_{\text{cis}} = 8 \text{ Hz}$), the lower two doublets of each AB system are superimposed on a 9H multiplet between δ 7.2-8.4 (aromatic), Figure 1; infrared spectrum (CS_2) cm^{-1} , 1612 (C=C), 725 (C-Cl) and 707 (9-substituted anthracene), Figure 2; mass spectrum (70 eV) m/e , 238(P) and 203(P-Cl).

Anal. Calcd. for $\text{C}_{16}\text{H}_{11}\text{Cl}$: C, 80.50; H, 4.61.

Found: C, 80.23; H, 4.45.

This reaction has also been performed with n-butyl lithium as the base in an ether or tetrahydrofuran solution at room temperature, but the yields were much lower.

5. 9-Anthrylacetylene (4) [The procedure used was similar to that described by Köbrich⁶ and Staab¹⁵.]¹⁴

To 100 ml of anhydrous ether [previously dried through an aluminum oxide (basic) column] 1.45 g (6.1 mmoles) of 9-(β -chlorovinyl)anthracene (3) was dissolved under a nitrogen atmosphere. n-Butyl lithium (8 ml, 1.5M solution in hexane, 12 mmoles) was added dropwise to the solution

over half an hour. Formation of a white precipitate (LiCl) was noticed after approximately half of the n-butyl lithium had been added. The reaction mixture was allowed to stir one hour at room temperature and was then hydrolyzed with 30 ml of water. The ether portion was then extracted with water and dried (CaCl₂). The ether was removed and the yellow oil which remained was chromatographed on dry column alumina (20 g, 17 mm column) with carbon tetrachloride. The first yellow band off the column contained the desired product. When the solvent was stripped away, a yellow oil was isolated, which crystallized when allowed to stand for half an hour. This was then recrystallized from petroleum ether (30-60°) to yield 1.17 g (5.8 mmoles) of nice, yellow crystals (95%): m.p. 71-73° [lit m.p. 73-75°¹⁴]; nmr spectrum (CCl₄), δ 3.80 (singlet, 1H) and a 9H multiplet between δ 7.25-8.75 (aromatic), Figure 3; infrared spectrum (CCl₄) cm^{-1} , 3275 (C $\equiv$ C-H) and 2080 (C $\equiv$ C), Figure 4. Care must be taken with this compound because it tends to self-polymerize under ambient conditions. Storage at 0° is recommended for best results.

6. Copper Acetylide of 9-Anthrylacetylene (5)[The procedure used was similar to that described by Castro.⁷]

Under a nitrogen atmosphere 1.92 g (7.7 mmoles) of hydrated cupric sulfate was dissolved in 25 ml of 28% ammonium hydroxide, after which, 100 ml of water was added.

Hydroxylamine-hydrochloride (1.07 g, 15 mmol) was then added as a solid and the dark blue solution became lighter. 9-Anthrylacetylene (4) (1.55 g, 7.7 mmol) was then added to the stirred, reaction mixture in 25 ml of tetrahydrofuran, dropwise. The formation of an orange solid was observed immediately. After the acetylene had all been added, the suspension was stirred for an additional fifteen minutes at room temperature and filtered. The product was washed several times with water, methanol and ether, successively. The bright, orange copper acetylide (1.06 g, 4.4 mmol) was isolated in a 52% yield. Due to the insolubility of the product in all solvents, no physical tests were performed. Unreacted 9-anthrylacetylene (4) can be recovered from the washings for further use.

7. 1-(4-Nitrophenyl) 9-anthrylacetylene (9) [The procedure used was similar to that described by Castro.⁷]

To 40 ml of dry (dried over molecular sieves, type 4A) and oxygen-free dimethyl formamide, 0.3 g (1.13 mmol) of the copper acetylide of 9-anthrylacetylene (5) was suspended. Iodo-4-nitrobenzene (0.9 g, 3.6 mmol) in 5 ml of dimethyl formamide was added dropwise to the reaction mixture under a nitrogen atmosphere. The contents were then heated at 120° for 40 hours. Slowly the copper acetylide disappeared and the solution became dark red. The solution was then cooled and poured into an evaporating dish and allowed to

remain on the steam bath in the hood until the solvent had been removed (half an hour). Minimum exposure to dimethyl formamide is desirable. The product was extracted from the remaining residue with chloroform and the insoluble material filtered away. Stripping off the solvent left a yellow solid, which was chromatographed on silicic acid (50 g, 27 mm column) with carbon tetrachloride. A red band moving slowly down the column contained the desired coupled product. After the carbon tetrachloride was removed, the solid material was crystallized from methanol to give 0.265 g (0.825 mmole) of orange needles in a 73% yield: m.p. 212-213°; compound 9 was too insoluble for an nmr spectrum; infrared spectrum (CHCl_3) cm^{-1} , 2175 ($\text{C}\equiv\text{C}$) and 1520, 1335 (NO_2), Figure 5; mass spectrum (70 eV) m/e , 323(P) and 277 (P- NO_2); λ_{max} (95% ethanol) $\text{m}\mu$, 252 (ϵ 85,300), 296 (ϵ 11,900), 312 (ϵ 10,100), 414 (ϵ 18,650) and 430 (ϵ 18,550), Figure 6.

Anal. Calcd. for $\text{C}_{22}\text{H}_{13}\text{NO}_2$: C, 81.73; H, 4.02

Found: C, 81.52; H, 4.11.

8. 1-(2,4-Dinitrophenyl) 9-Anthrylacetylene (12) [The procedure used was similar to that described by Castro⁷]

Under a nitrogen atmosphere and in the dark 0.1 g (0.378 mmole) of the copper acetylide of 9-anthrylacetylene (5) was suspended in 35 ml of dry and deoxygenated dimethyl formamide. To this reaction mixture was added a solution of 0.11 g (0.378 mmole) of 1-iodo-2,4-dinitrobenzene and

0.063 g (0.378 mmole) of potassium iodide in 10 ml of dimethyl formamide. The contents were then heated at 120° for one hour. The disappearance of the copper acetylide and the formation of a darkly colored, red solution was observed. The solvent was driven off and the product extracted from the remaining solid material with chloroform. After the insoluble material was filtered away, the solution was concentrated and cooled to 0°. The product crystallized as red cubes. Further recrystallizations were needed for a pure product. A 78% yield was obtained in which 0.11 g (0.3 mmole) of product was obtained: m.p. 279-280°; compound 12 was too insoluble for an nmr spectrum; infrared spectrum (CHCl_3) cm^{-1} , 2175 ($\text{C}\equiv\text{C}$) and 1540, 1350 (NO_2), Figure 7; mass spectrum (70 eV) m/e , 368(P), 322(P- NO_2) and 276(P-2 NO_2); λ_{max} (CH_2Cl_2) $\text{m}\mu$, 255.5 (ϵ 104,500), 330 (ϵ 5,260), 375 (ϵ 6,590), 387 (ϵ 6,780) and 476 (ϵ 5,410), Figure 8. As discussed in the RESULTS, ortho-nitro-acetylenes rearrange in the presence of light to their corresponding isatogens. Since the preparation of an analytically, pure sample of compound 12 is difficult to obtain, because of this sensitivity, the elemental analysis was not attempted. The corresponding isatogen (11), however, is stable to light and can easily be purified. Since the elemental analysis for compound 11 has been performed and shown to be correct, the structure of compound 12 is subsequently supported.

9. 2-Anthryl-6-nitro-3H-indol-3-one-N-oxide (11)

To 3 ml of chloroform and 5 ml of pyridine 0.1 g (0.3 mmole) of 1-(2,4-dinitrophenyl) 9-anthrylacetylene (12) was dissolved. The red solution was stirred in the hood at room temperature for one day under a florescent light bulb. The reaction media slowly changed color to a reddish-green. The residue remaining, after stripping off the solvent, was chromatographed on silicic acid (8 g, 14 mm column) with chloroform. The green isatogen eluted from the column slowly, but was very pure. After the chloroform was removed, a dark green solid (0.05 g, 0.15 mmole) was recovered, indicating approximately a 50% conversion from the acetylene: m.p. 225-226⁰; compound 11 was too insoluble for an nmr spectrum; infrared spectrum (CHCl₃) cm^{-1} , 1710 (C=O), and 1525, 1340 (NO₂), but no C≡C stretch, Figure 9; mass spectrum (70 eV) m/e , 366(P), 322(P-NO₂) and 294(322-CO); λ_{max} (CH₂Cl₂) $m\mu$, 254.3 (ϵ 84,400), 332 (ϵ 4,550), 348 (ϵ 5,250), 370 (ϵ 6,650), 385 (ϵ 6,600) and 562 (ϵ 491), Figure 10.

Anal. Calcd. for C₂₂H₁₂N₂O₄: C, 71.74; H, 3.26.

Found: C, 71.72; H, 3.44.

10. 1-(β -Chlorovinyl)-3,4-dimethoxy-benzene (6) [The procedure used was similar to that described by Wittig⁵]

Under a nitrogen atmosphere 3.47 g (10 mmoles) of chloromethyl-triphenyl-phosphonium chloride (2) was dissolved

in 75 ml of dry methanol. Sodium methoxide (0.54g, 10 mmoles) was then added to the solution. After refluxing for 15 minutes, 1.66 g (10 mmoles) of 3,4-dimethoxy-benzaldehyde in 10 ml of methanol was added dropwise. The reaction mixture was then refluxed for one hour and subsequently neutralized with 0.5 g of ammonium chloride. After the reaction mixture was cooled, the solvent was removed and the residue taken up in ether and water. The ether portion was extracted with water, dried (CaCl_2) and the solvent stripped off under vacuum with a rotary evaporator. The yellow oil which remained was distilled with a fractionating column to give a clear oil, however, further purification was needed. The product was then chromatographed on silicic acid (50 g, 27 mm column) with methylene chloride. The first band off the column contained the 1-(β -chlorovinyl) 3,4-dimethoxy-benzene (6) in good purity. Removal of the solvent yielded 1.42 g (5.65 mmoles) of the product (56.5%) as a clear oil: b.p. 91° (0.1 mm); nmr spectrum (CDCl_3), δ 3.85 (singlet, 6H) and a 5H multiplet between δ 6.10-7.50 (aromatic and vinyl), Figure 11; infrared spectrum (CS_2) cm^{-1} , 1600 (C=C), 1260 (C-O-C), 930 (C=C-Cl) and 730 (C-Cl), Figure 12; mass spectrum (70 eV) m/e , 198(P) and 183(P- CH_3).

Anal. Calcd. for $\text{C}_{10}\text{H}_{11}\text{ClO}_2$: C, 60.45; H, 5.54.

Found: C, 60.18; H, 5.51.

11. 3,4-Dimethoxy-phenylacetylene (7) [The procedure used was similar to that described by Köbrich⁶ and Staab¹³]^{16,17}

To 100 ml of anhydrous ether [previously dried through an aluminum oxide (basic) column] 3.3 g (16.2 mmoles) of 1-(β -chlorovinyl) 3,4-dimethoxy-benzene (6) was dissolved under a nitrogen atmosphere. n-Butyl lithium (22.2 ml, 1.5M solution in hexane, 33.3 mmoles) was added dropwise to the solution over half an hour. Formation of a white precipitate (LiCl) was noticed after approximately half of the n-butyl lithium had been added. The reaction mixture was allowed to stir one hour at room temperature and was then hydrolyzed with 30 ml of water. The ether portion was then extracted with water and dried (MgSO₄). After removing the ether, the yellow oil which remained was chromatographed on silicic acid (50 g, 27 mm column) with methylene chloride. The first yellow band off the column contained the desired product. When the solvent was stripped away, a yellow oil was isolated, which crystallized upon standing for half an hour. This was then recrystallized from petroleum ether (30-60°) to yield 2.28 g (14 mmoles) of nice, yellow crystals (91%): m.p. 72-73° [lit. m.p. 73-74°^{16,17}]; nmr spectrum (CDCl₃), δ 3.00 (singlet, 1H), δ 3.85 (singlet, 6H), δ 6.80 (AB doublet, 1H, J = 9 Hz), δ 7.00 (AC doublet, 1 H, J = 2 Hz) and δ 7.15 (ABC doublet of doublet, 1H, J = 2 and 9 Hz), Figure 13; infrared spectrum (CHCl₃) cm^{-1} , 3300 (C=C-H), 2100 (C $\equiv$ C)

and 1260 (C-O-C), Figure 14.

12. Copper Acetylde of 3,4-Dimethoxy-phenylacetylene (8)

[The procedure used was similar to that described by Castro⁷.]

Under a nitrogen atmosphere 4.8 g (19.2 mmoles) of hydrated cupric sulfate was dissolved in 25 ml of 28% ammonium hydroxide, after which, 100 ml of water was added. Hydroxylamine-hydrochloride (2.65 g, 38.2 mmoles) was then added as a solid and the dark blue solution became lighter. 3,4-Dimethoxy-phenylacetylene (7) (3.1 g, 19.2 mmoles) was then added to the stirred reaction mixture in 25 ml of ethanol. The formation of a yellow solid was observed immediately. After the acetylene had all been added, the suspension was stirred for an additional 15 minutes at room temperature and filtered. The product was washed several times with water, methanol and ether, successively. The bright yellow copper acetylde (3.69 g, 16.4 mmoles) was isolated in an 86% yield. No physical tests were performed on this product because of its insolubility in all solvents. Unreacted 3,4-dimethoxy-phenylacetylene (6) can be recovered from the washings for further use.

13. 1-(4-Nitrophenyl) 3,4-dimethoxy-phenylacetylene (10)

[The procedure used was similar to that described by Castro⁷].

To 40 ml of dry (dried over molecular sieves, type 4A) and oxygen free dimethyl formamide 0.1 g (0.45 mmoles) of the copper acetylide of 3,4-dimethoxy-phenylacetylene (8) was added. Iodo-4-nitrobenzene (0.11 g, 0.45 mmole) and 0.075 g (0.45 mmole) of potassium iodide were dissolved in 10 ml of dimethyl formamide and added to the suspension under a nitrogen atmosphere. The reaction mixture was then heated to 120° for one hour. The color of the solution became dark red as the copper acetylide reacted. The solution was then cooled and poured into an evaporating dish and allowed to remain on the steam bath in the hood until the solvent had been removed. The product was extracted from the remaining residue with chloroform and the insoluble material filtered away. Stripping off the solvent left a yellow solid, which was chromatographed on silicic acid (20 g, 17 mm column) with chloroform. The second yellow band off the column contained the desired coupled product. After the chloroform was removed, the solid material was crystallized from ethanol to give 0.95 g (0.33 mmole) of yellow crystals (75%): m.p. 125.5-130.5°; nmr spectrum (CDCl₃), δ 3.95 (singlet, 6H), δ 6.90 (AB doublet, 1H, J = 9 Hz), δ 7.10 (AC doublet, 1H, J = 2 Hz), δ 7.25 (ABC doublet of doublet, 1H, J = 2 and 9 Hz) and an A'B' quartet

at δ 7.70, 8.25 (doublets, 4H , $J = 9$ Hz), Figure 15; infrared spectrum (CHCl_3) cm^{-1} , 2200 ($\text{C}\equiv\text{C}$), 1500, 1340 (NO_2) and 1275 ($\text{C}-\text{O}-\text{C}$), Figure 16; mass spectrum (70 eV) m/e , 283(P), 268(P- CH_3), 253(P-2 CH_3) and 237(P- NO_2); λ_{max} (95% ethanol) $m\mu$, 261 (ϵ 14,400) and 356 (ϵ 16,800), Figure 17.

Anal. Calcd. for $\text{C}_{16}\text{H}_{13}\text{NO}_4$: C, 67.84; H, 4.59; N, 4.95.

Found: C, 67.02; H, 4.54; N, 4.87.

14. 1-(2,4-Dinitrophenyl)-3,4-dimethoxy-phenylacetylene (13)

[The procedure used was similar to that described by Castro⁷].

Under a nitrogen atmosphere and in the dark 0.1 g (0.45 mmole) of the copper acetylide of 3,4-dimethoxy-phenylacetylene (8) was suspended in 35 ml of dry and deoxygenated dimethyl formamide. To this reaction mixture was added a solution of 0.13 g (0.45 mmole) of iodo-2,4-dinitrobenzene and 0.074 g (0.45 mmole) of potassium iodide in 10 ml of dimethyl formamide. The contents were heated at 120° for one hour. The disappearance of the copper acetylide and the formation of a darkly colored red solution was observed. The solvent was driven off and the product extracted with chloroform from the remaining solid material. After the insoluble material was filtered away, the solvent was stripped off and a silicic acid column (20 g, 17 mm column) was run with the residue, eluting with methylene chloride. The third yellow band off the column contained

the desired, coupled product. After the methylene chloride was removed the solid material was crystallized from methanol to give nice, orange crystals (0.101 g, 0.31 mmole) in a 69% yield: m.p. 137.5-138.5°; nmr spectrum (CDCl_3), δ 3.95 (singlet, 6H), δ 6.94 (AB doublet, 1H, $J = 9$ Hz), δ 7.14 (AC doublet, 1H, $J = 2$ Hz), δ 7.34 (ABC doublet of doublet, 1H, $J = 2$ and 9 Hz), δ 7.94 (A'B' doublet, 1H, $J = 9$ Hz), δ 8.49 (A'B'C' doublet of doublet, 1H, $J = 2$ and 9 Hz) and δ 9.00 (A'C' doublet, 1H, $J = 2$ Hz), Figure 18; infrared spectrum (CHCl_3) cm^{-1} , 2200 ($\text{C}\equiv\text{C}$), 1525, 1350 (NO_2) and 1260 ($\text{C}-\text{O}-\text{C}$), Figure 19; mass spectrum (70 eV) m/e , 328(P), 282(P- NO_2) and 236(P-2 NO_2); λ_{max} (CH_2Cl_2) $m\mu$, 259.5 (ϵ 20,000), 280.5 (ϵ 16,400), 321 (ϵ 8,910) and 403 (ϵ 18,100), Figure 20. As discussed in the RESULTS, ortho-nitro-acetylenes rearrange in the presence of light to their corresponding isatogens. Since the preparation of an analytically, pure sample of compound 13 is difficult to obtain, because of this sensitivity, the elemental analysis was not attempted. The corresponding isatogen (14), however, is stable to light and can easily be purified. Since the elemental analysis for compound 14 has been performed and shown to be correct, the structure of compound 13 is subsequently supported.

15. 2-(3,4-Dimethoxy-phenyl) 6-nitro-3H-indol-3-one-N-oxide (14)

To 3 ml of chloroform and 5 ml of pyridine 0.1 g (0.3 mmole) of 1-(2,4-dinitrophenyl) 3,4-dimethoxy-phenylacetylene (13) was dissolved. The orange solution was stirred in the hood for two days at room temperature under a fluorescent light bulb. The reaction media slowly changed color to red. The residue remaining, after the solvent was removed, was chromatographed on silicic acid (8 g, 14 mm column) with methylene chloride. The violet isatogen eluted from the column slowly, but was very pure. After the chloroform was removed, a dark purple solid (0.05 g, 0.15 mmole) was recovered, indicating approximately a 50% conversion from the acetylene: m.p. 226-227.5°; infrared spectrum (CHCl_3) cm^{-1} , 1700 (C=O), 1525, 1335 (NO_2) and 1260 (C-O-C), but no $\text{C}\equiv\text{C}$ stretch, Figure 21; mass spectrum (70 eV) m/e , 328(P), 382(P- NO_2) and 254(382-CO); λ_{max} (CH_2Cl_2) $m\mu$, 282 (ϵ 17,150), 322 (ϵ 10,050), 366 (ϵ 10,930) and 523 (ϵ 1,885), Figure 22.

Anal. Calcd. for $\text{C}_{16}\text{H}_{12}\text{N}_2\text{O}_6$: C, 58.54; H, 3.66.

Found: C, 58.70; H, 3.82.

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APPENDIX

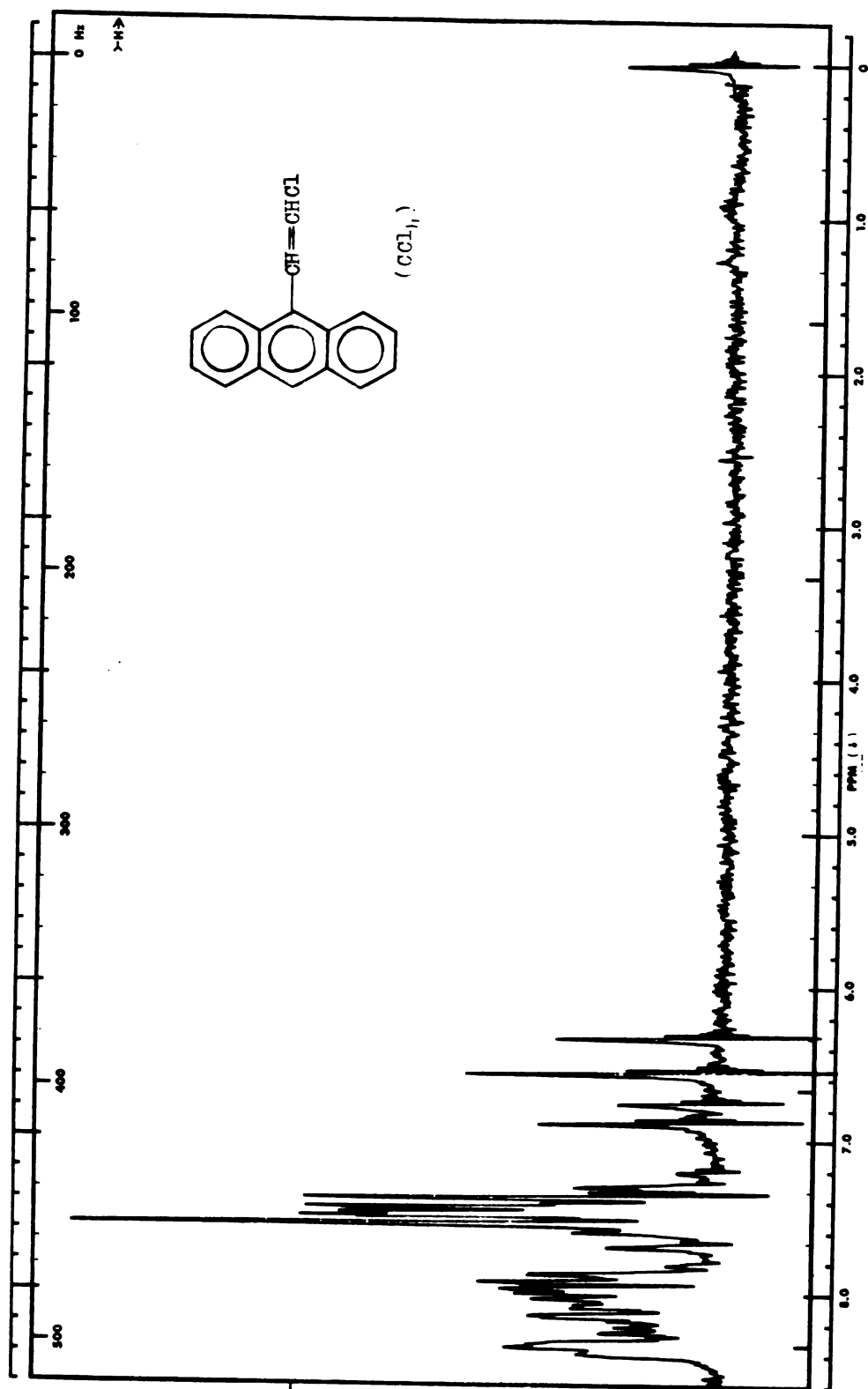


Figure 1A. Nmr spectrum of 9-(β-chlorovinyl) anthracene (3).

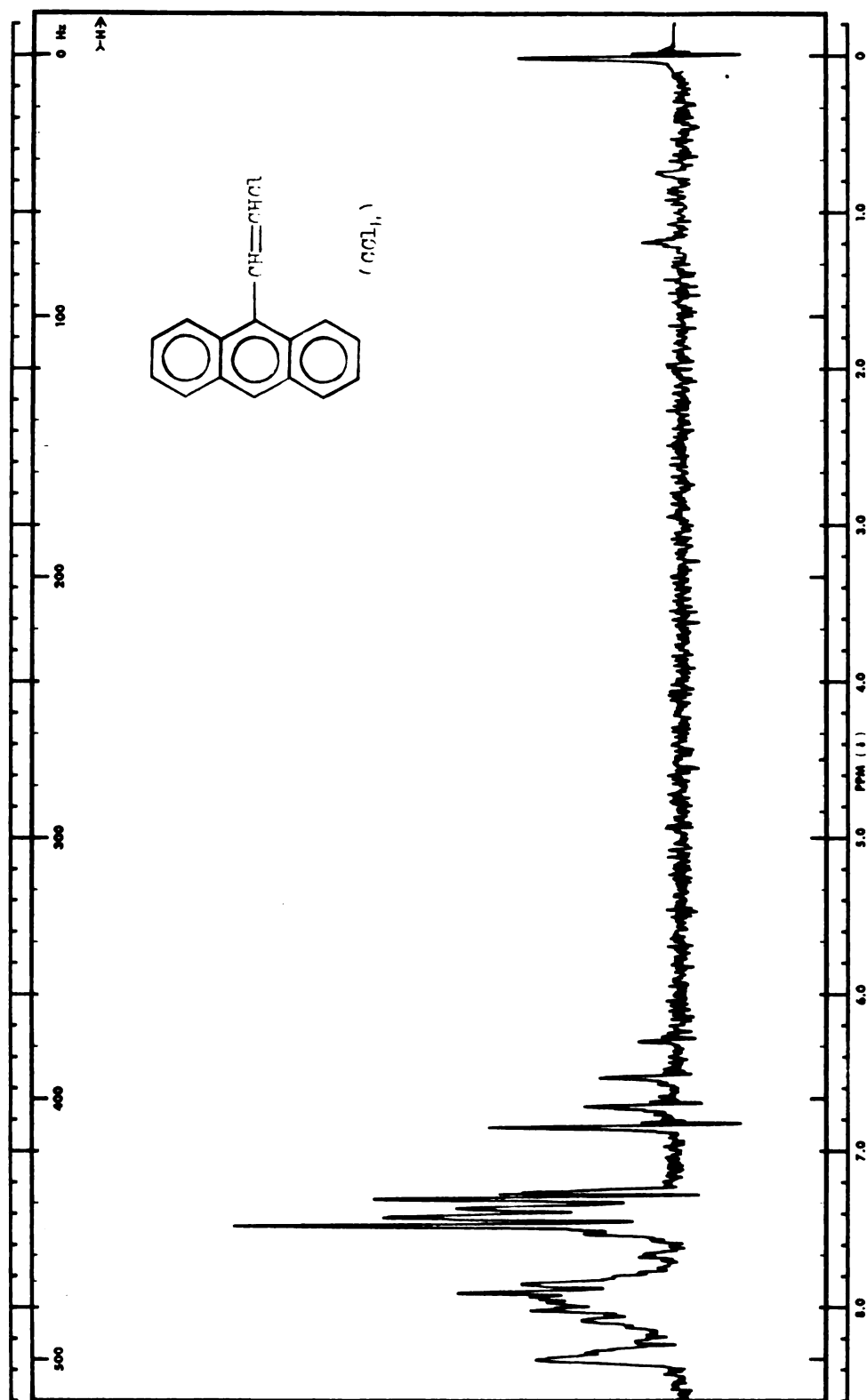


Figure 1B. Nmr spectrum of 9-(β-chlorovinyl) anthracene (3); recrystallized from methanol.

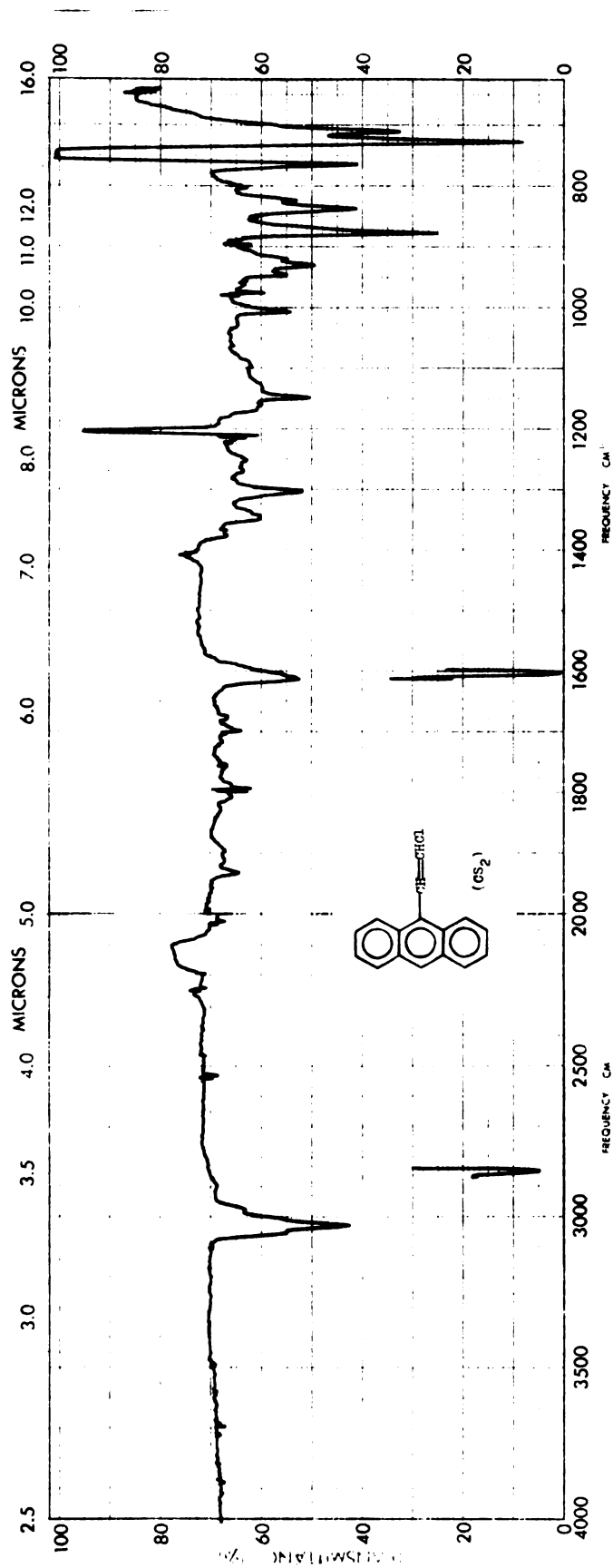


Figure 2. Infrared spectrum of 9-(β-chlorovinyl) anthracene (3).

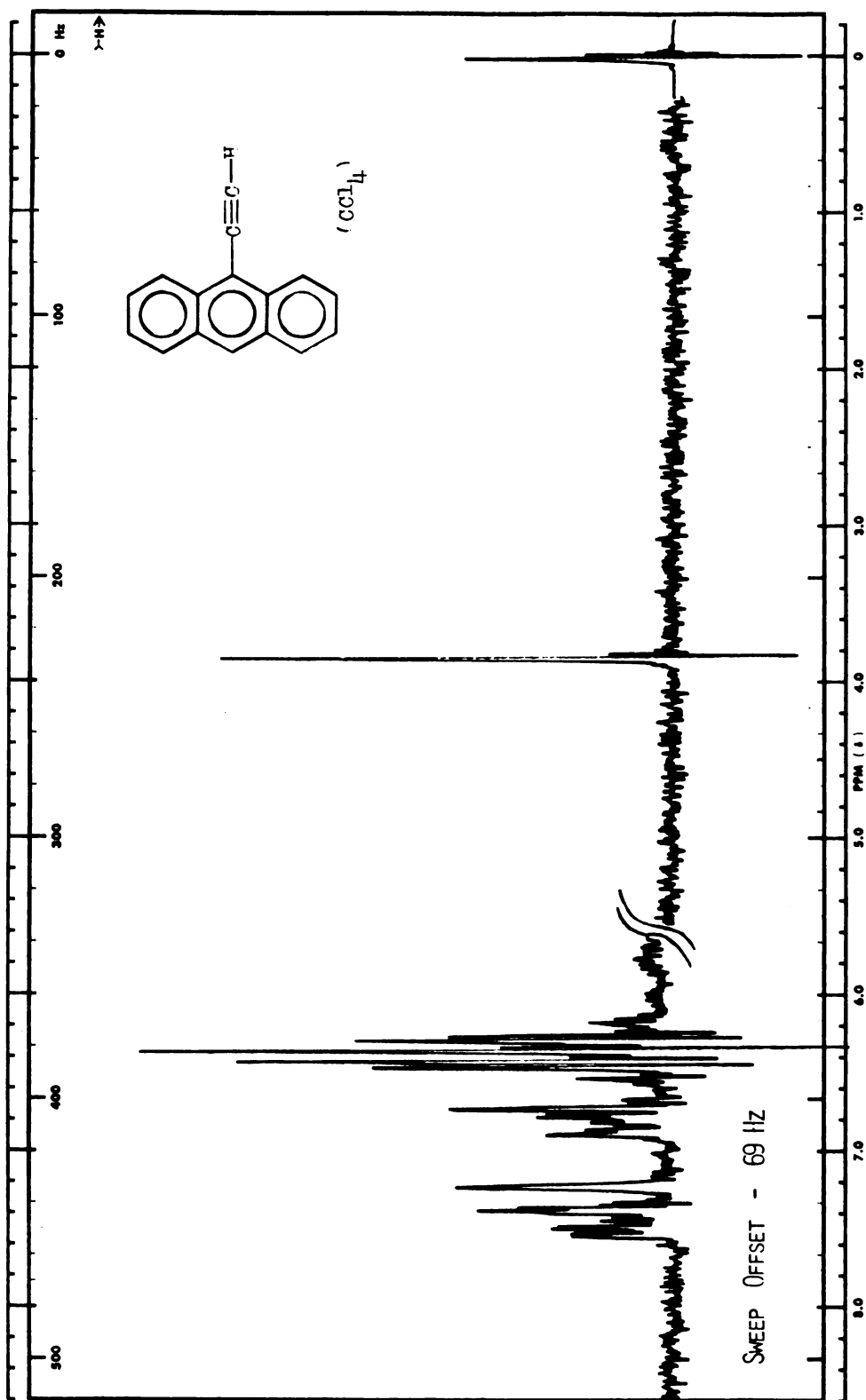


Figure 3. Nmr spectrum of 9-anthrylacetylene (4).

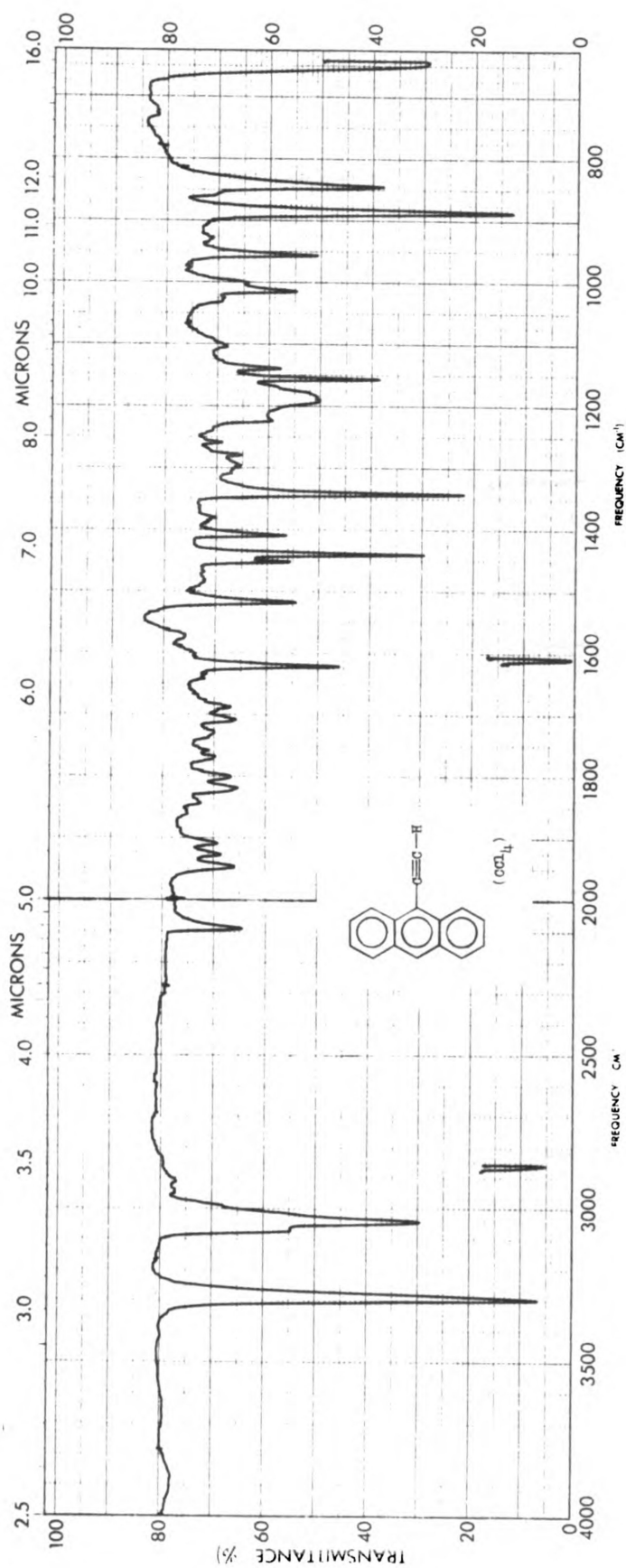


Figure 4. Infrared spectrum of 9-anthracetylene (4).

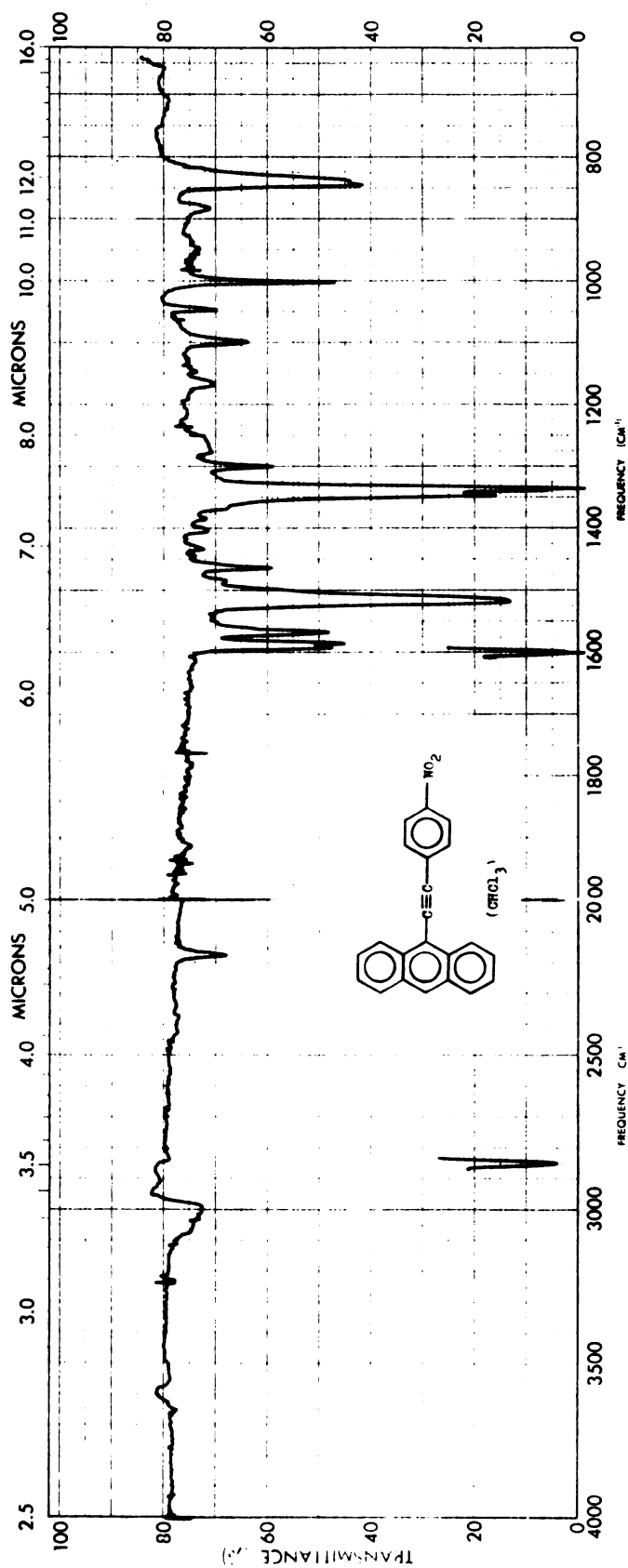


Figure 5. Infrared spectrum of 1-(4-nitrophenyl) 9-anthracetylene (9).

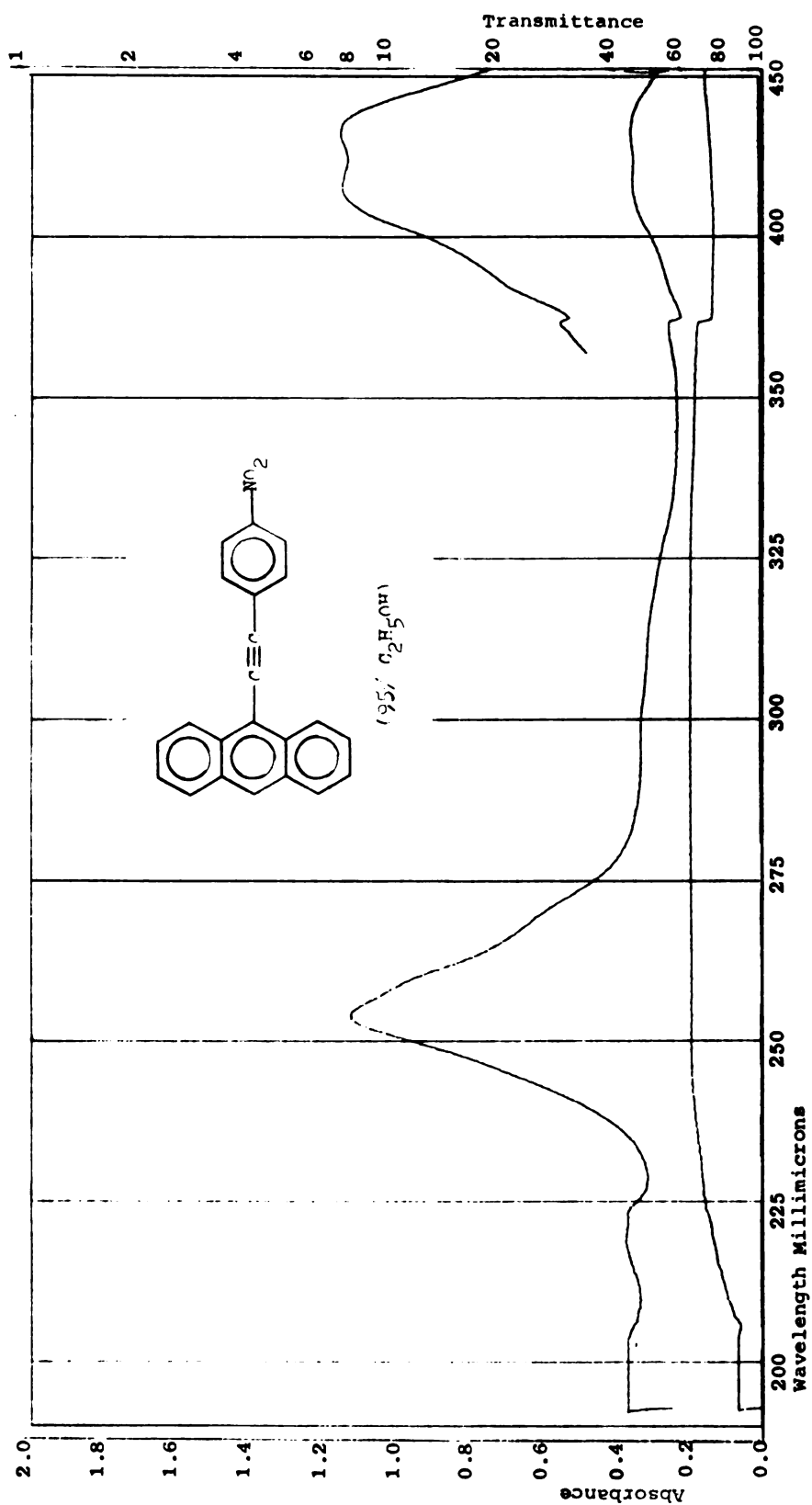


Figure 6. Ultra-violet and visible spectra of 1-(4-nitrophenyl) 9-anthryl-acetylene (9).

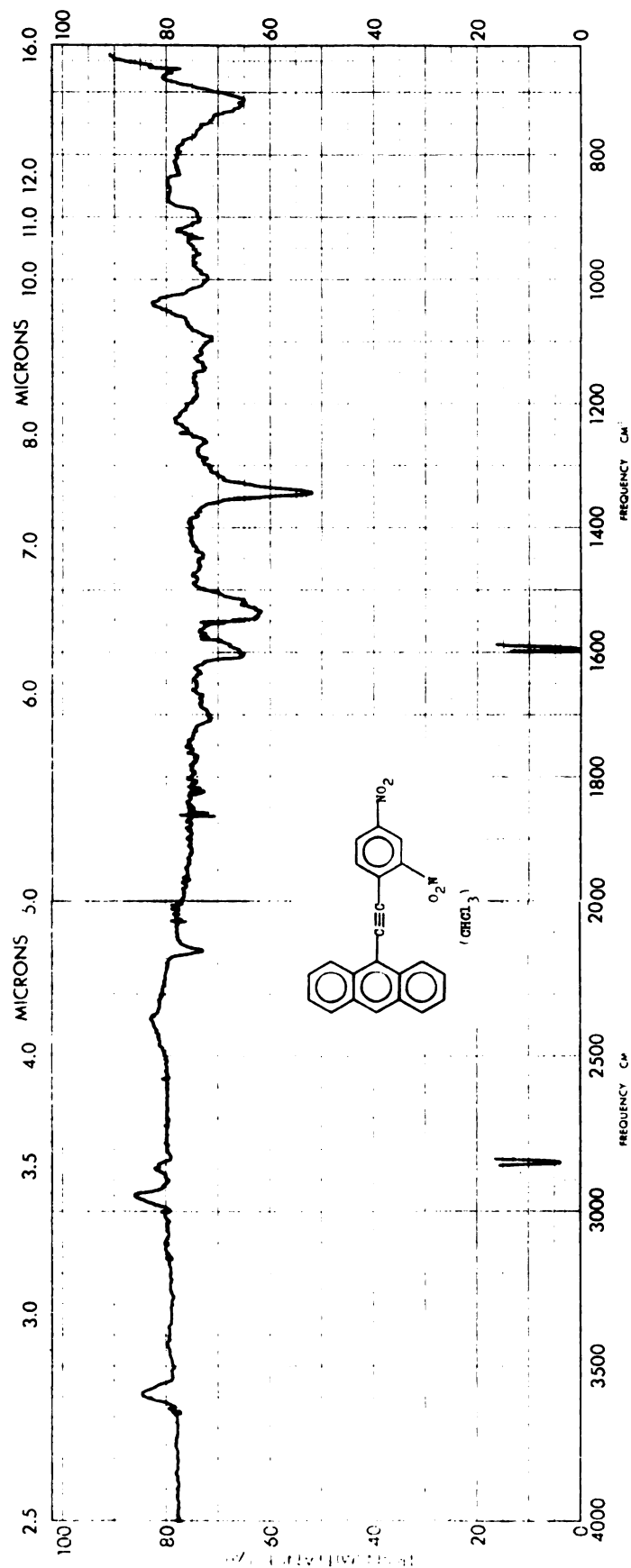


Figure 7. Infrared spectrum of 1-(2,4-dinitrophenyl) 9-anthracetylene (12).

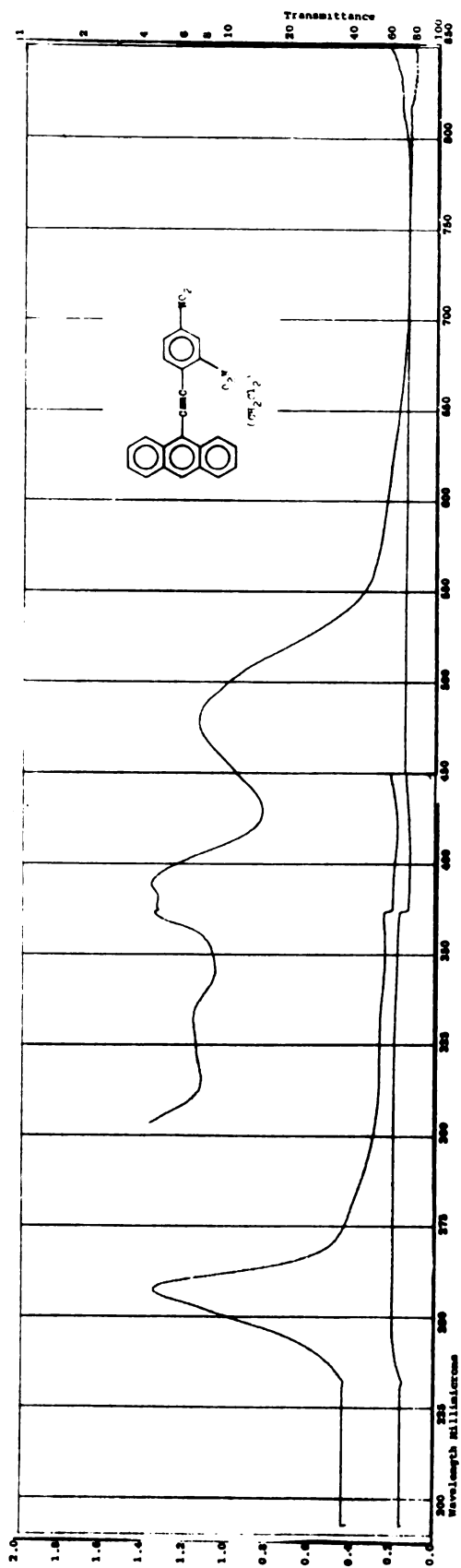


Figure 8. Ultra-violet and visible spectra of 1-(2,4-dinitrophenyl) 9-anthrylacetylene (12).

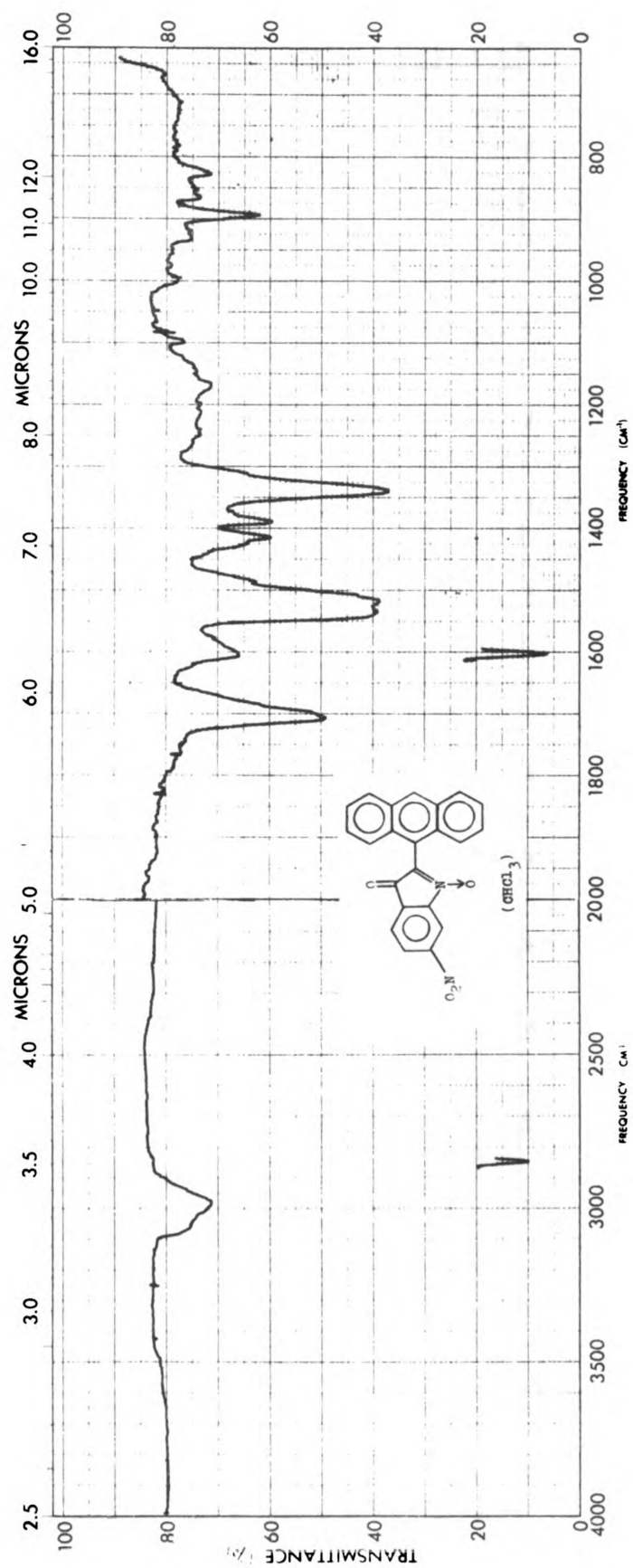


Figure 9. Infrared spectrum of 2-anthryl-6-nitro-3H-indol-3-one-N-oxide (11).

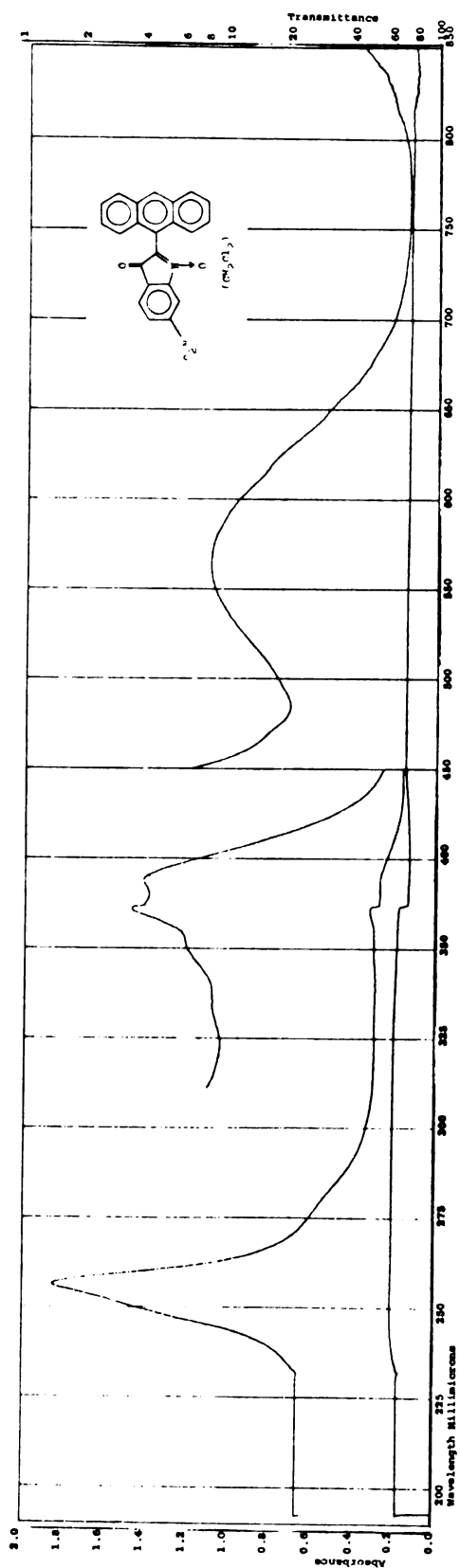


Figure 10. Ultra-violet and visible spectra of 2-anthryl-6-nitro-3H-indol-3-one-N-oxide (11).

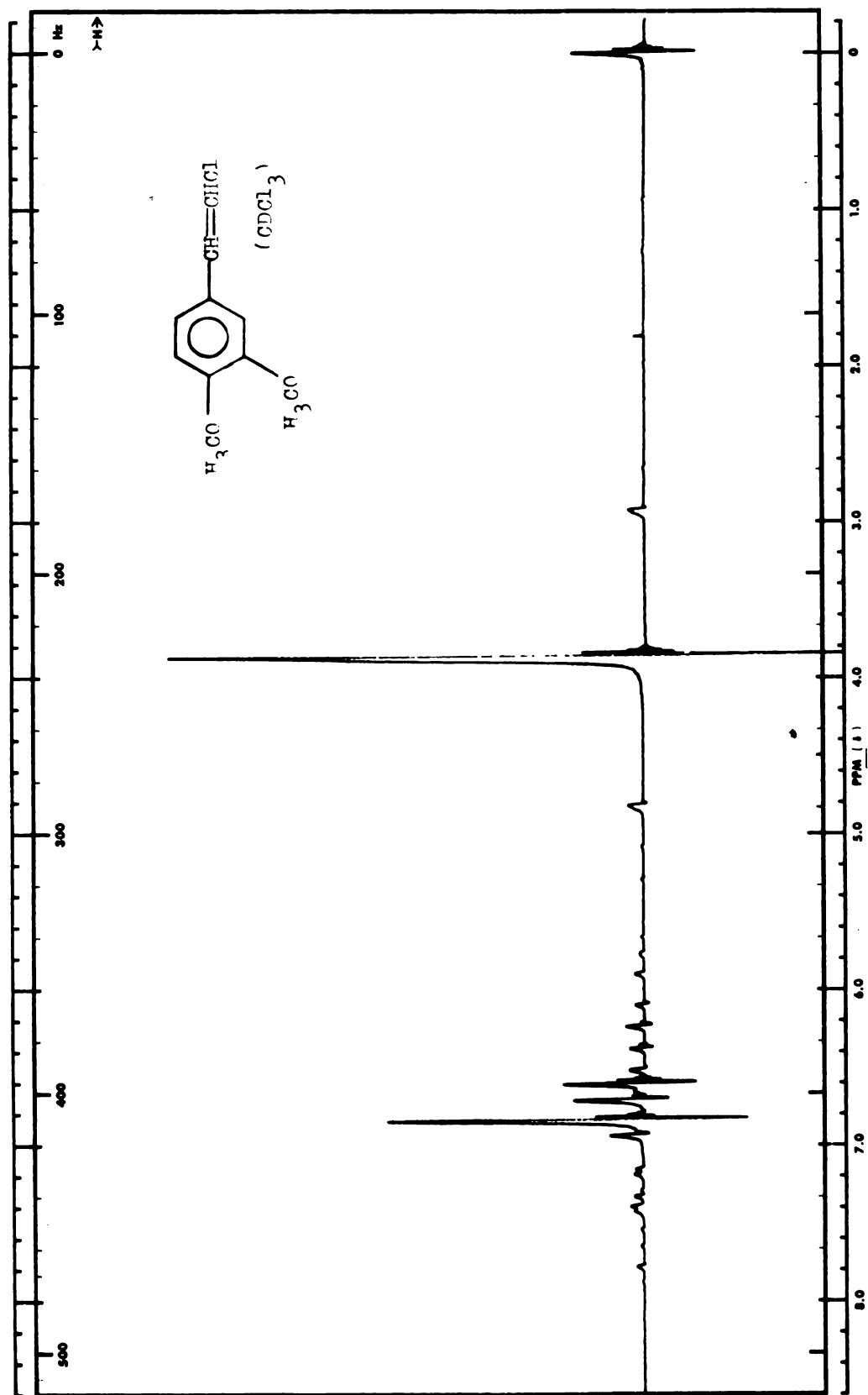


Figure 11. Nmr spectrum of 1-(β-chlorovinyl) 3,4-dimethoxybenzene (6).

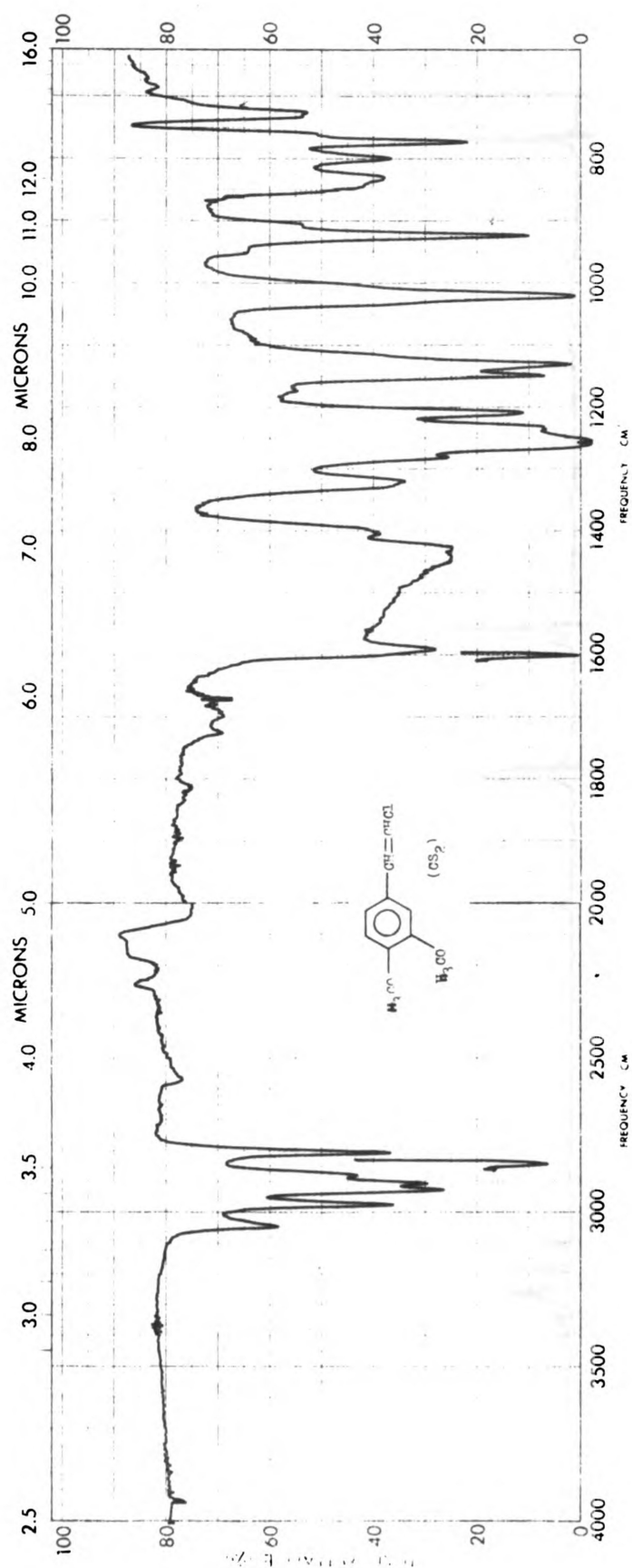


Figure 12. Infrared spectrum of 1-(β-chlorovinyl) 3,4-dimethoxybenzene (6).

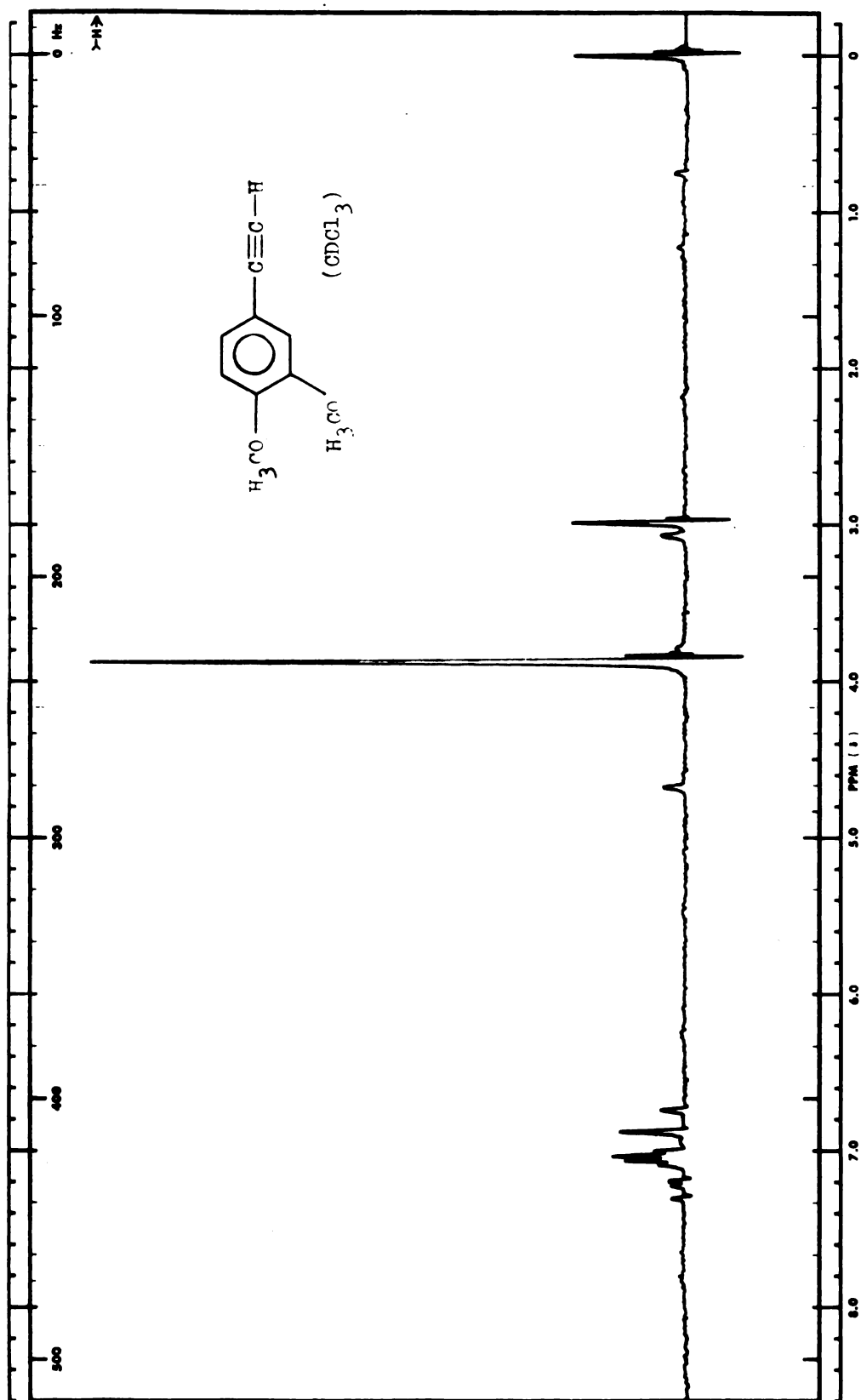


Figure 13. Nmr spectrum of 3,4-dimethoxy-phenylacetylene (7).

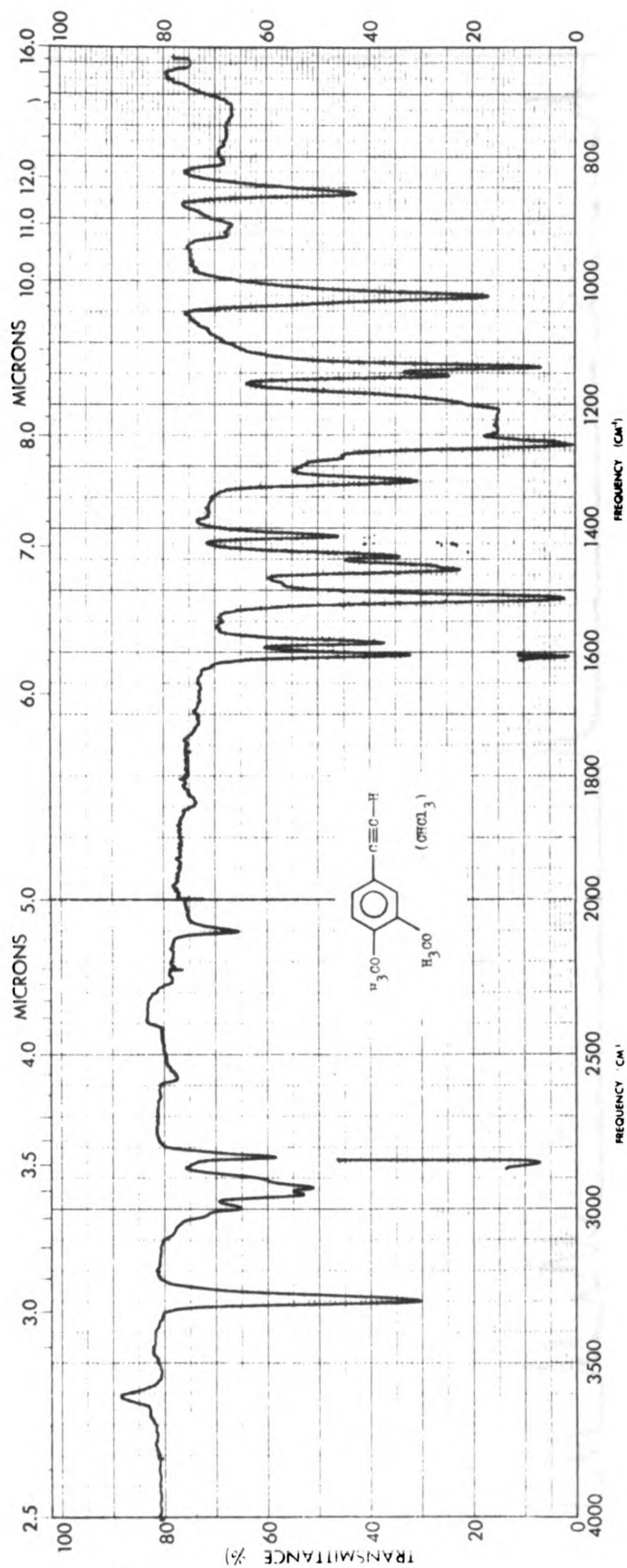


Figure 14. Infrared spectrum of 3,4-dimethoxy-phenylacetylene (7).

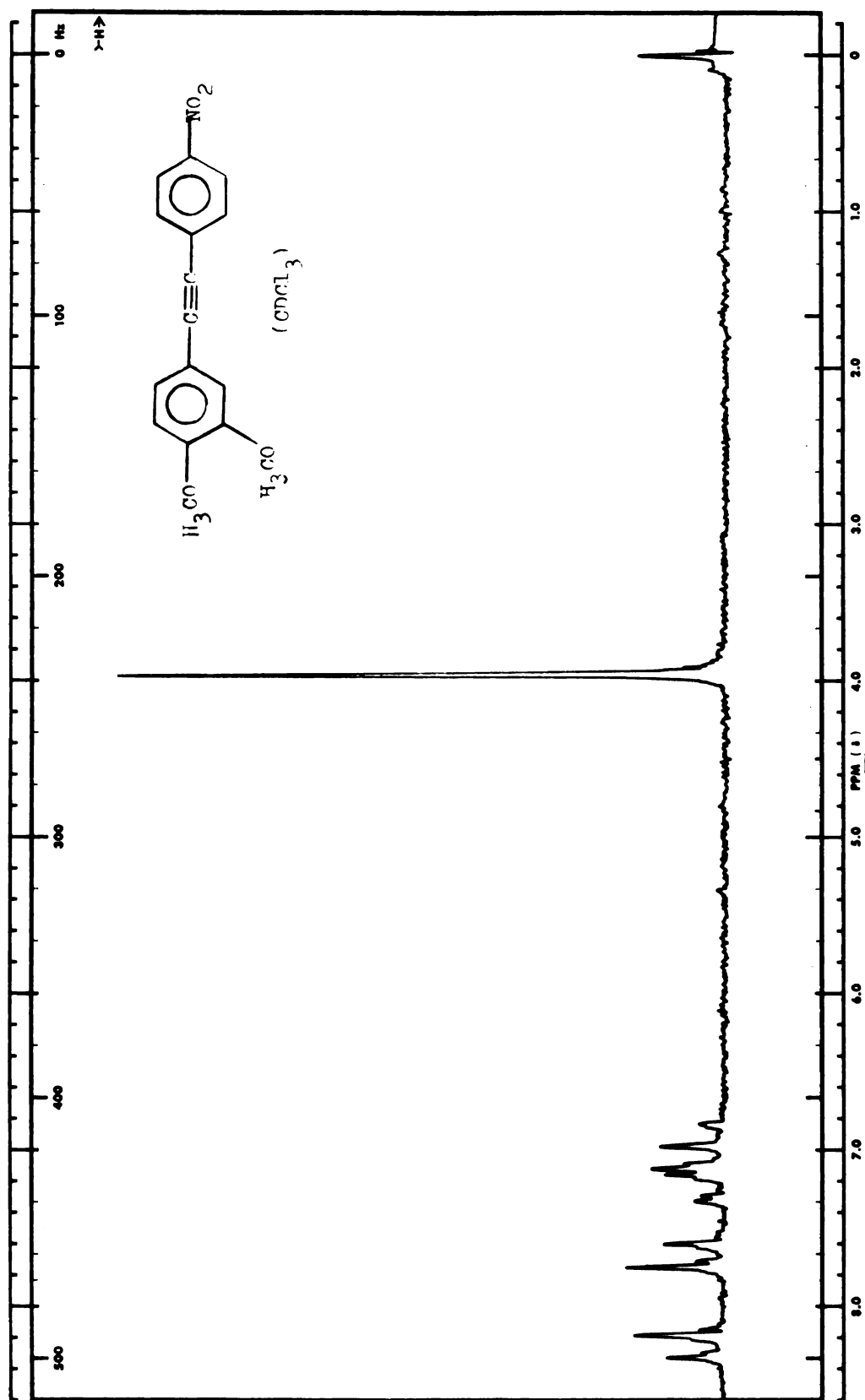


Figure 15. Nmr spectrum of 1-(4-nitrophenyl) 3,4-dimethoxy-phenylacetylene (10).

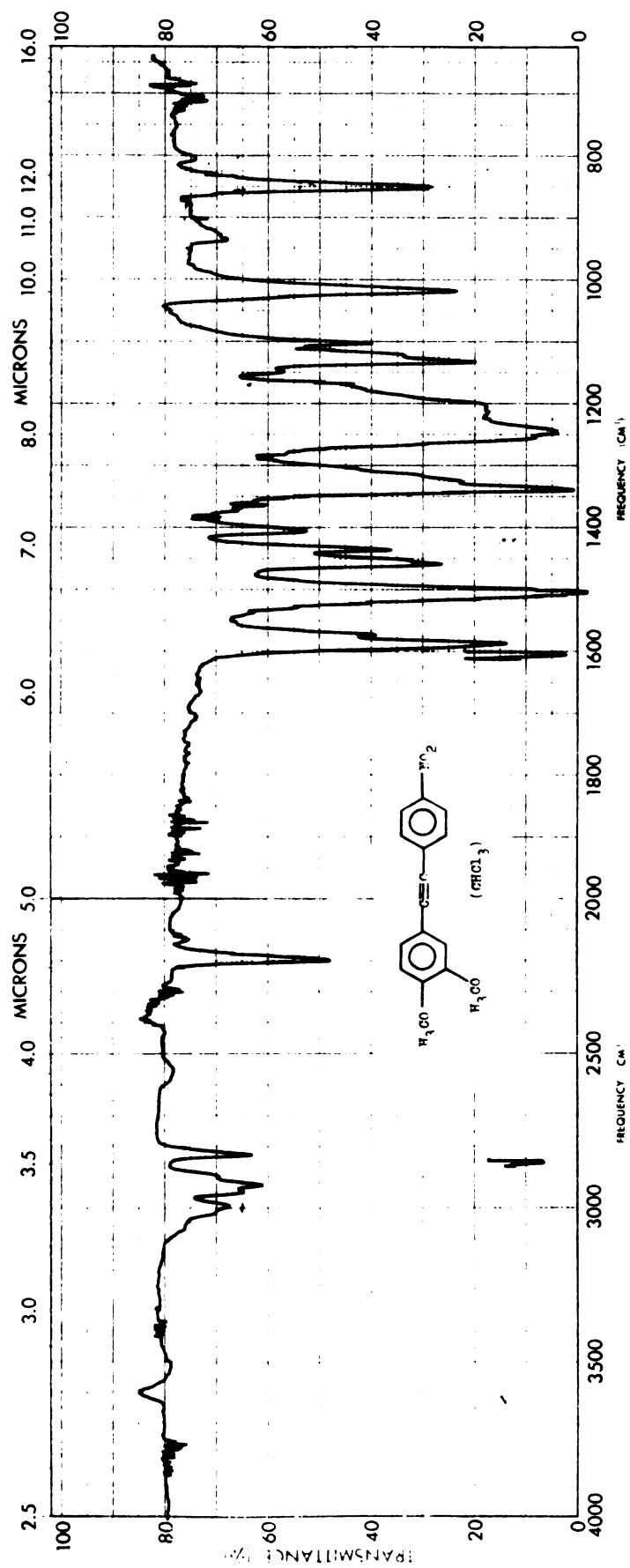


Figure 16. Infrared spectrum of 1-(4-nitrophenyl) 3,4-dimethoxy-phenylacetylene (10).

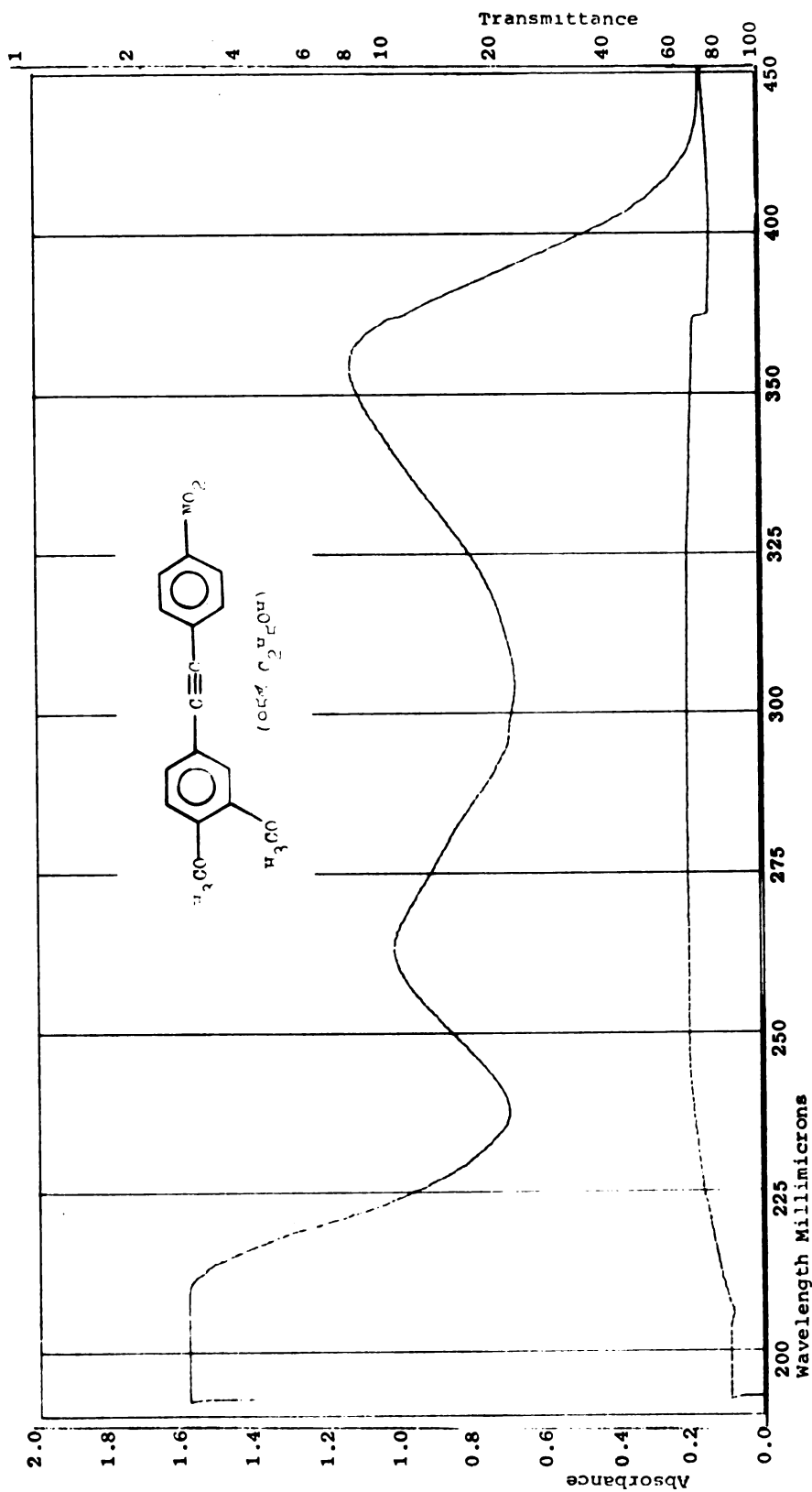


Figure 17. Ultra-violet and visible spectra of 1-(4-nitrophenyl) 3,4-dimethoxy-phenylacetylene (10).

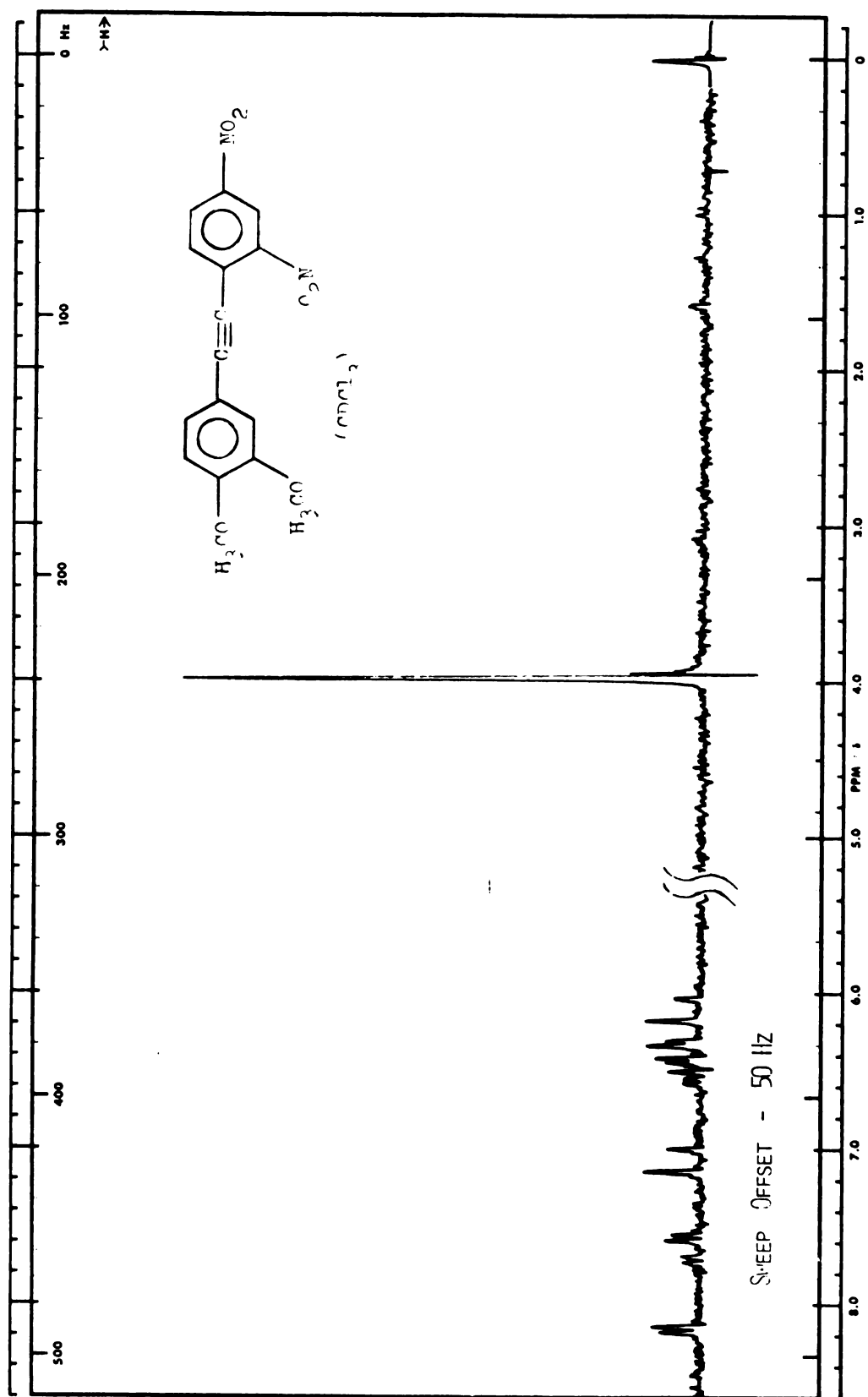


Figure 18. Nmr spectrum of 1-(2,4-dinitrophenyl)-3,4-dimethoxy-phenylacetylene (13).

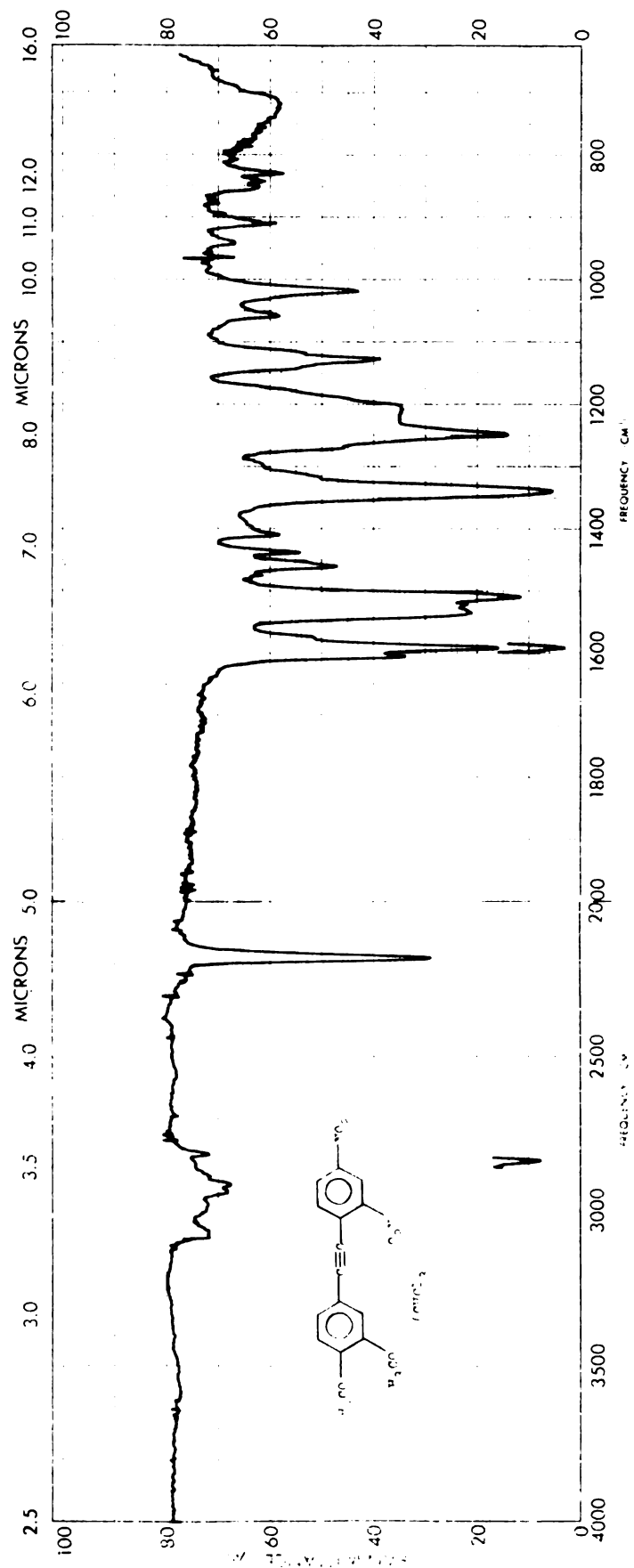


Figure 19. Infrared spectrum of 1-(2,4-dinitrophenyl)-3,4-dimethoxy-phenylacetylene (13).

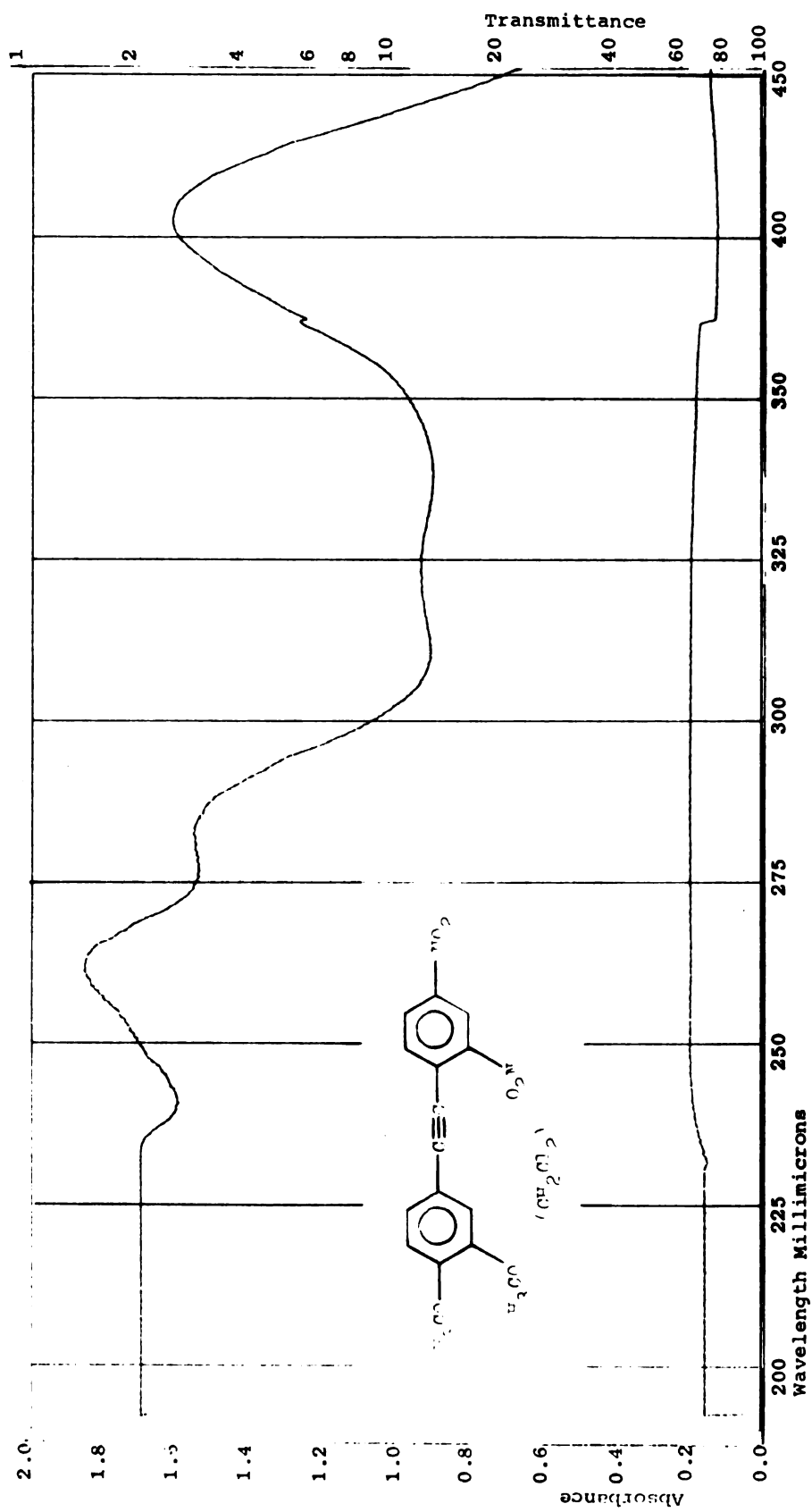


Figure 20. Ultra-violet and visible spectra of 1-(2,4-dinitrophenyl) 3,4-dimethoxy-phenylacetylene (13).

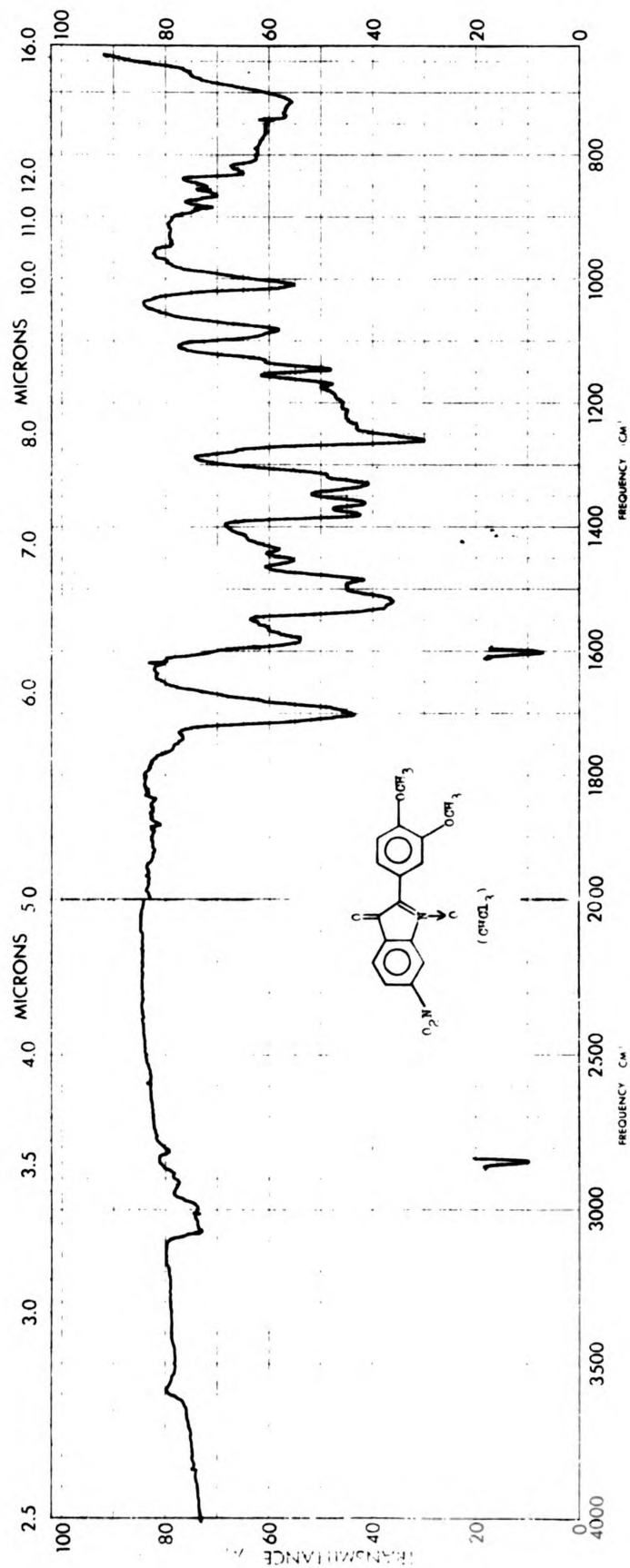


Figure 21. Infrared spectrum of 2-(3,4-dimethoxyphenyl) 6-nitro-3H-indol-3-one-N-oxide (14).

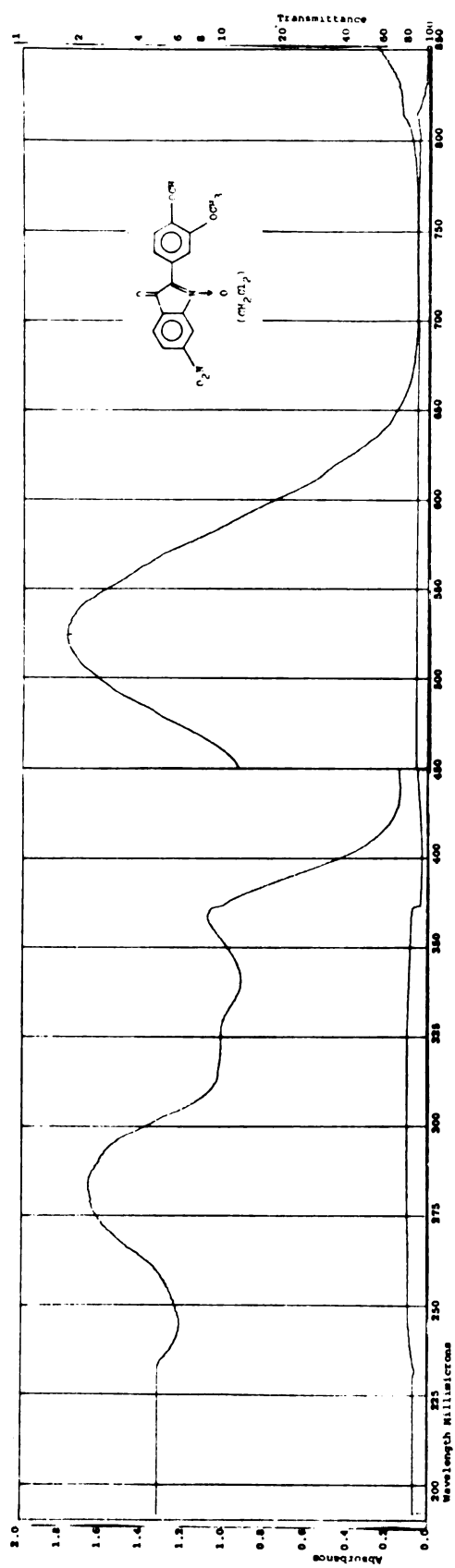


Figure 22. Ultra-violet and visible spectra of 2-(3,4-dimethoxyphenyl) 6-nitro-3H-indol-3-one-N-oxide (14).

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