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THE SYNTHESIS AND SPECTRAL CHARACTERIZATION
OF ESTERS OF 4, 4' - SULFONYLDIPHENOL

THESIS

BY

FATEMEH BIDABADI

1997

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**THE SYNTHESIS AND
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OF 4, 4' - SULFONYLDIPHENOL**

THESIS

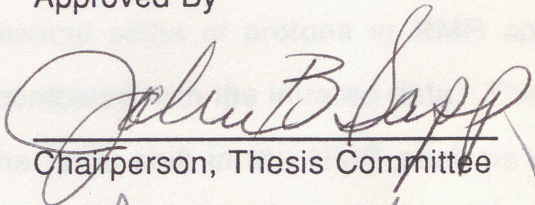
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of Texas Southern University

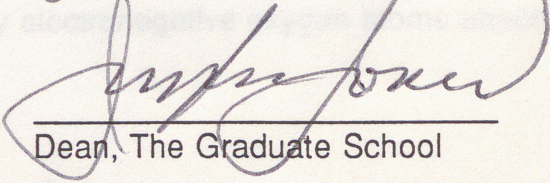
By

Fatemeh Bidabadi, B.S.

1997

Approved By


Chairperson, Thesis Committee


Dean, The Graduate School

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THE SYNTHESIS AND
SPECTRAL CHARACTERIZATION OF ESTERS
OF 4'-SULFONYLBIPHENOL

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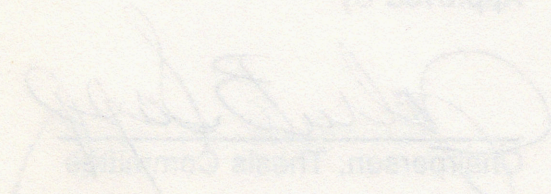

Presented in Partial Fulfillment of the Requirements for
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of Texas Southern University

BY

Patricia B. Bishop, B.S.

1987

Approved By


Patricia B. Bishop, B.S.
Chairman, Thesis Committee

Dean, The Graduate School

showed the presence of the resulting functional groups and the nuclear magnetic resonance data helped identify the location of all of the protons. The Raman spectra were not directly involved in the identification of the resulting esters, which offered an unequivocal proof of structure.

THE SYNTHESIS AND SPECTRAL CHARACTERIZATION OF ESTERS OF 4,4' - SULFONYLDIPHENOL

BY

Fatemeh Bidabadi, M.S.

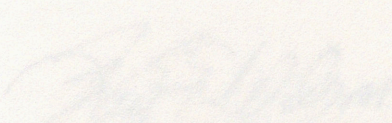
Texas Southern University, 1997

Professor John B. Sapp, Jr., Advisor


The acetyl and phenylacetyl esters were prepared of 4, 4' - sulfonyldiphenol and 4, 4' - thiodiphenol. As part of the characterization, elemental analyses were performed on the products to confirm the proposed molecular formulas. Additional mass data was obtained through Gas Chromatography - Mass Spectrometry, GC-MS, analysis.

Spectral data was obtained by subjecting all of the products to Infrared, Nuclear Magnetic Resonance, NMR, spectra and Raman Spectroscopy. The presence or absence of functional groups was confirmed by vibrational frequencies in the infrared and chemical shifts of protons in NMR spectra. Raman spectra were obtained and compared with the infrared data. The most dramatic evidence appears to be the large shift in the NMR analysis of the aromatic protons closest to the highly electronegative oxygen atoms attached to the sulfur of the sulfone group.

showed the presence of the resulting functional groups and the nuclear magnetic resonance data helped identify the location of all of the protons. The Raman spectra were produced but, in this research, were not directly involved in the identification process. Comparison of spectral data of the resulting esters, which differed only at the site of the sulfur atom gives unequivocal proof of structure.


Professor



Date


Committee Member


Date


Committee Member


Date


Committee Member


Date

Approved By

John B. Sapp
Chairperson, Thesis Committee

8/12/97
Date

Jeff Wilson
Representative, Graduate School

8/13/97
Date

Conita Mc Donald
Committee Member

8/13/97
Date

MA Saha
Committee Member

8/27/97
Date

Deborah Hiler
Committee Member

8/28/97
Date

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VITA

March 21, 1958.....	Born - Bourjerd, Iran
1993	B.S., Texas Southern University Houston, Texas
1994-1997	Teaching Assistant Department of Chemistry Texas Southern University
Major Field	Chemistry

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CHAPTER 2
CHAPTER 1
REVIEW OF RELATED LITERATURE
INTRODUCTION
Phenol

The organic chemist is usually involved in three basic activities in the laboratory. In most cases, all of these activities may be necessary to come to a conclusion about the final product. These three activities are: (1) synthesis, (2) dynamics of the reaction, (3) structure analysis.

In the synthesis, the chemist attempts to create molecules by converting substances of known structure in to compounds of a desired molecular structure. This conversion takes place through a sequence of controlled chemical reactions. Throughout this sequence, the dynamics of the reactions are carefully monitored and recorded.

Once formed and isolated, the next task is to establish the identity of the product through structure analysis. Over the past forty years, structure analysis has been made some what easier by instrumentation that allows for examination of certain physical properties of a newly synthesized compound. The basic instruments used for the purpose today are Gas Chromatography-Mass Spectroscopy, Infrared Spectroscopy, Raman Spectroscopy and Nuclear Magnetic Resonance.

In this research, all of these instruments were used, in conjunction with the elemental analysis, to correctly identify the synthesized products. The GC-Mass Spectroscopy data gave the molecular weight, the infrared spectra

CHAPTER 2
REVIEW OF RELATED LITERATURE

Phenol

The basic definition of the class of organic compounds called phenols is an aromatic ring to which a hydroxyl group is directly attached. The simplest of these, phenol, is shown in Figure 1. The phenols of lower molecular weight are liquids or low-melting solids and are only slightly soluble in water, with the exception of phenol itself. Because of hydrogen bonding, phenols have high boiling points when compared to non-hydroxyl containing compounds of similar molecular weight. Table 1 lists some of the most common phenols.

Because of its great utility in commercial use, phenol itself is produced in large quantities. Among the most important products of phenol is a polymeric substance resulting from the hydroxymethylation of phenols with formaldehyde called the Lederer-Manasse reaction [4]. Most of this substance is a resin with a structure similar to that in Figure 2. Some phenols and the cresols are obtained from coal tar, the volatile substance produced when coal is heated in the absence of air. However, the largest amount of phenol is synthesized. One of the methods used is that of the fusion of sodium benzenesulfonate with alkali.

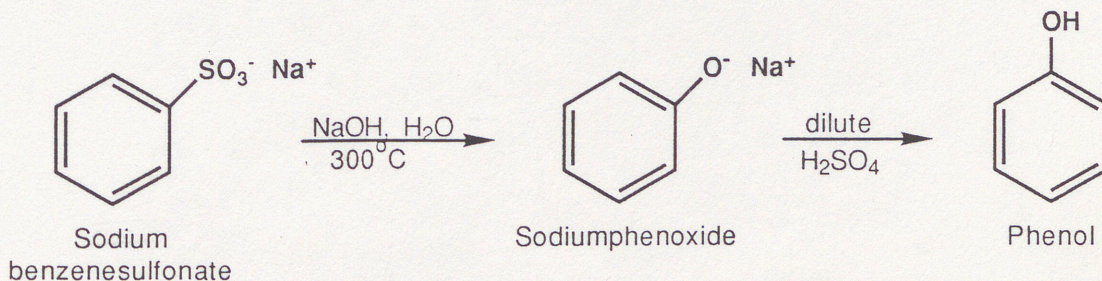


Figure 1

Phenol

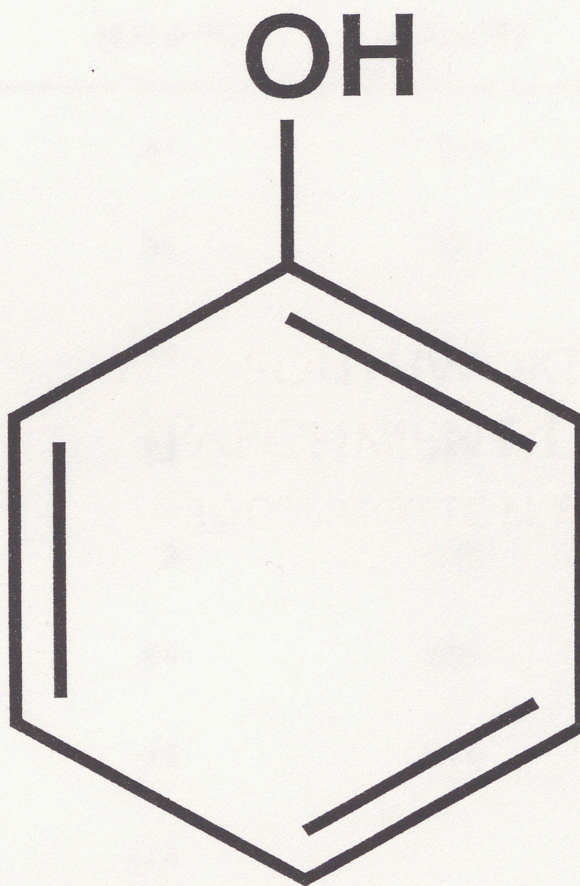


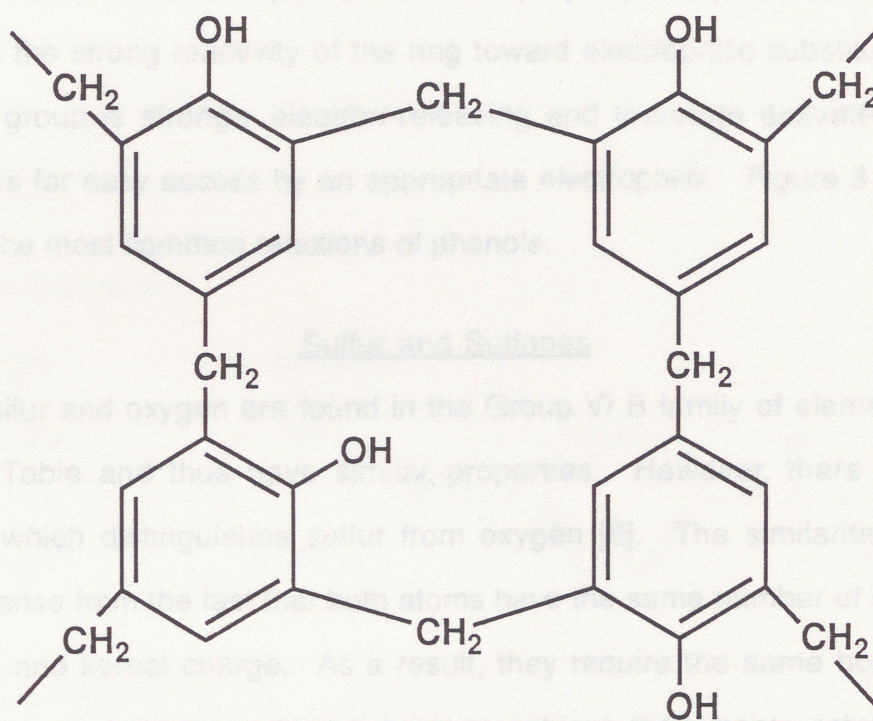
Table 1
Some of the Most Common Phenols

Name	M.P. in °C	B.P. in °C	Solubility g/100 mL of H ₂ O at 25°C
Phenol	41	182	9.3
o-Cresol	31	191	2.5
m-Cresol	11	201	2.6
p-Cresol	35	202	2.3
o-Chlorophenol	9	173	2.8
p-Bromophenol	64	236	1.4
o-Nitrophenol	45	217	0.2
p-Nitrophenol	114		1.7
2, 4-Dinitrophenol	113		0.6

Reactivity

Figure 2

Polymeric Structure



Reactivity

The presence of the hydroxyl group attached to the ring affords phenols a vast array of reactions. To begin with, phenols are fairly acidic. Thus they are able to form salts. Their salts are water soluble while the phenols are not. This characteristic is quite useful in the separation and purification of phenols.

Probably the most important chemical property of a phenol, other than its acidity, is the strong reactivity of the ring toward electrophilic substitution. The hydroxyl group is strongly electron-releasing and therefore activates the ring and allows for easy access by an appropriate electrophile. Figure 3 is a list of some of the most common reactions of phenols.

Sulfur and Sulfones

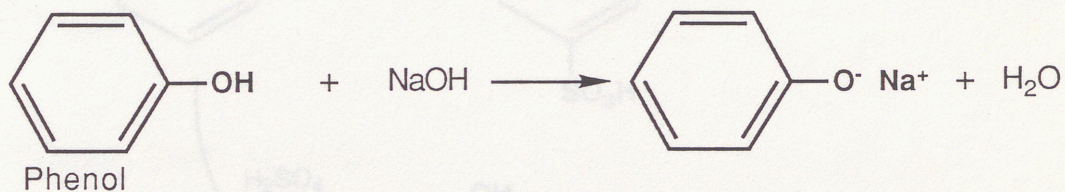
Sulfur and oxygen are found in the Group VI B family of elements in the Periodic Table and thus have similar properties. However, there are some features which distinguish sulfur from oxygen [8]. The similarities in their property arise from the fact that both atoms have the same number of outer shell electrons and kernel charge. As a result, they require the same bonding and form the same s- and p- orbital hybrids to achieve their stable octet of outer-shell electrons.

The differences emerge from the fact that sulfur has an extra inner electron shell beneath the outer, bonding shell. Sulfur, being a larger atom than oxygen, has outer electrons further from the nucleus and more shielded from its attractive force. In addition to the s- and p- orbitals, sulfur has empty d- orbitals which may be used for covalent bonding. These orbitals are not much higher in energy and can be filled on demand. The oxygen atom does not have this option.

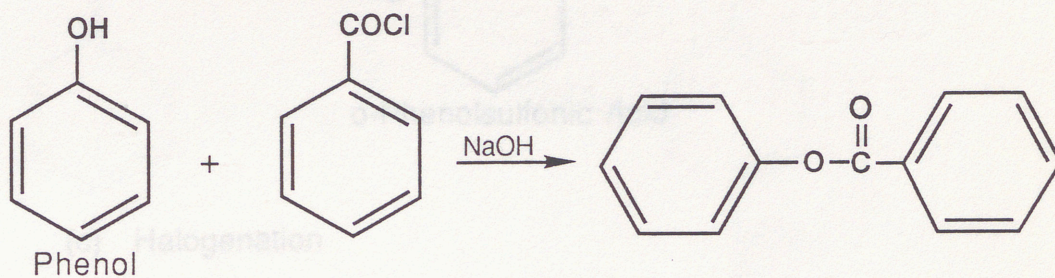
Figure 3

Some of the Most Common Reactions of Phenols

1. Salt Formation

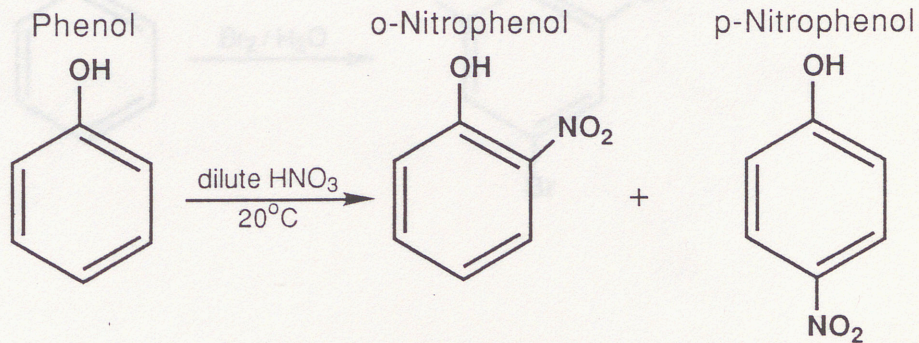


2. Ester Formation



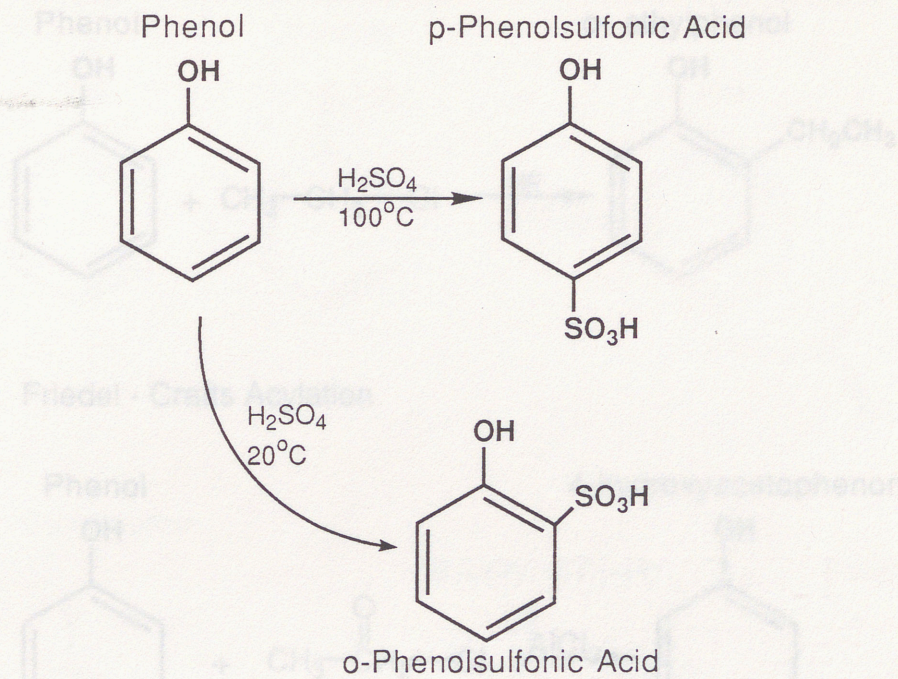
3. Ring Substitution

(a) Nitration

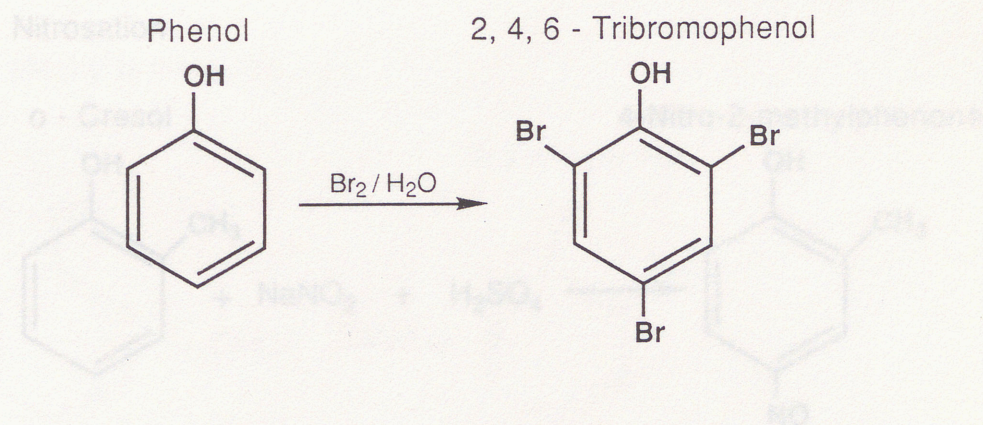


(Figure continues)

(b) Sulfonation

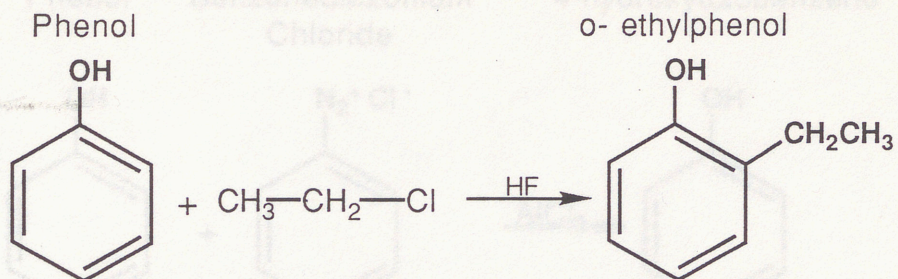


(c) Halogenation

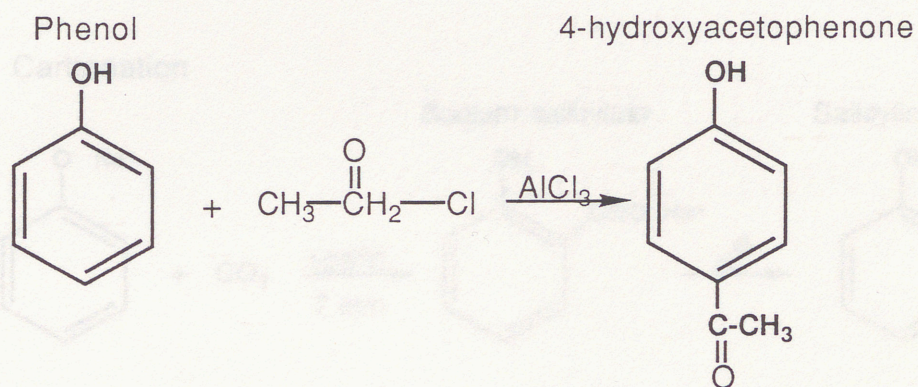


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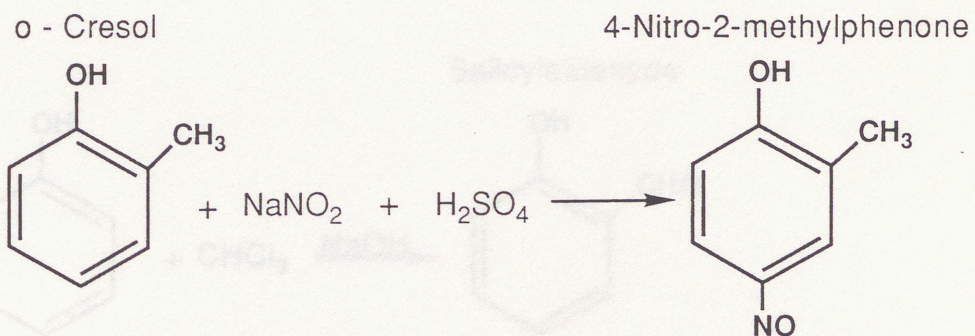
(d) Friedel - Crafts Alkylation



(e) Friedel - Crafts Acylation

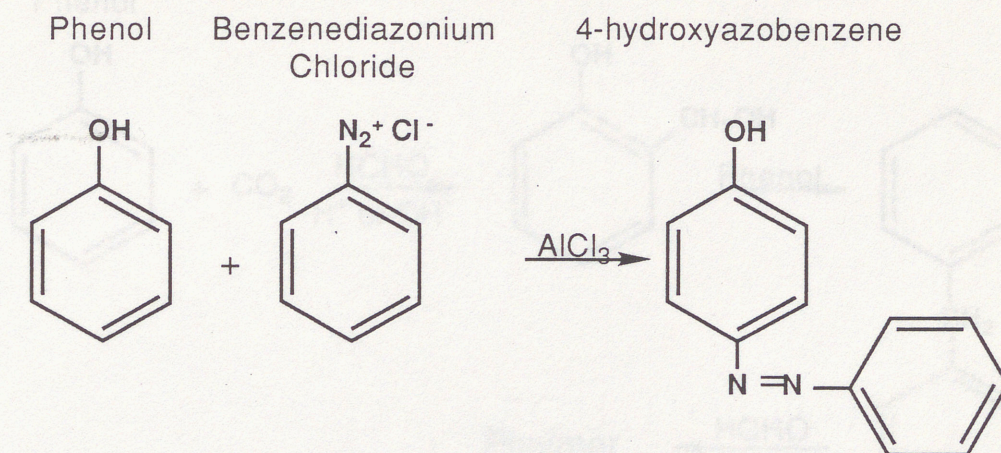


(f) Nitrosation

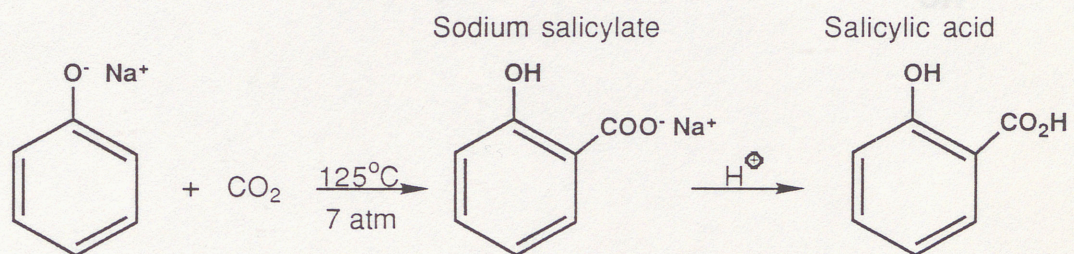


(Figure continues)

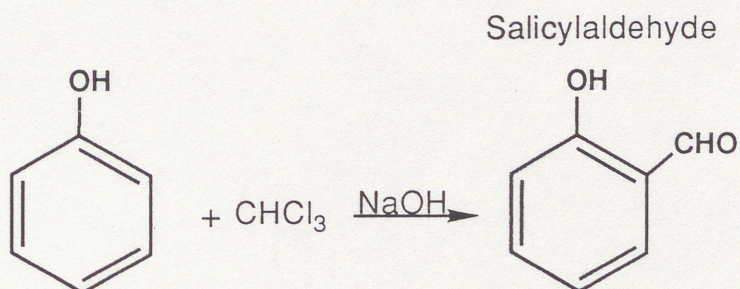
(g) Coupling with diazonium salts



(h) Carbonation

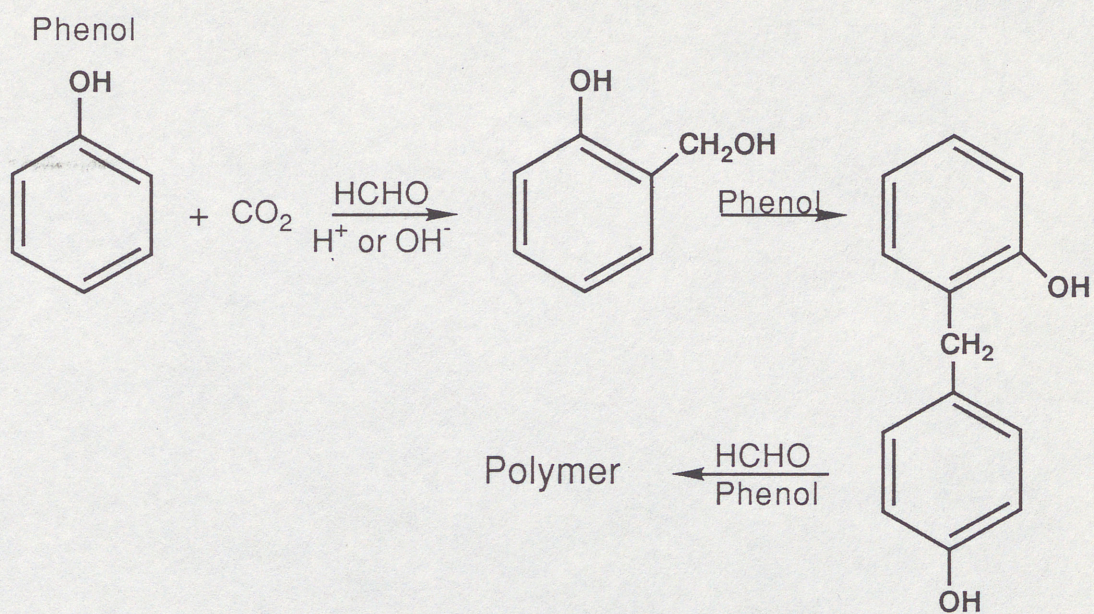


(i) Aldehyde formation



(Figure continues)

(j) Reaction with formaldehyde

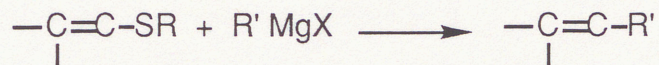


The differences in sulfur creates three major effects in the chemistry of its compounds. First, sulfur is less electronegative, and its unshared electron pairs are better nucleophiles through weaker bases (to H^+). Second, normal p-orbital double bonds are unstable and very rarely occur with sulfur. And third, sulfur can form more than four covalent bonds.

Among the many compounds containing multiple bonded sulfur is the sulfones shown in Figure 4. The R-groups attached to the sulfur atom may be alkyl, aryl or a mixture of the two. The tetravalent sulfur is tetrahedrally bonded to two oxygen atoms and two other groups. Evidence shows that, even though two of the four groups to sulfur are oxygen, sulfones that are optically active may be prepared [14].

Reactions of Sulfones

(a) Organometallic Reagent Coupling with Sulfur. Grignard reagents have been shown to undergo coupling, in the presence of nickel complexes, with a variety of compounds [10]. Among those are aryl sulfides and aryl sulfones. The product of the coupling is an alkene.



(b) Halogenation. Sulfones have been chlorinated by treatment of their conjugate bases with a variety of reagents [13], two of which are SO_2Cl_2 and CCl_4 .

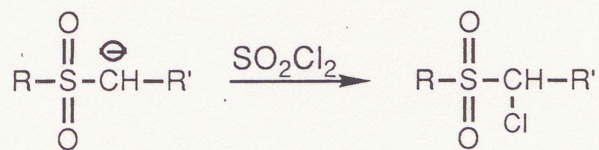
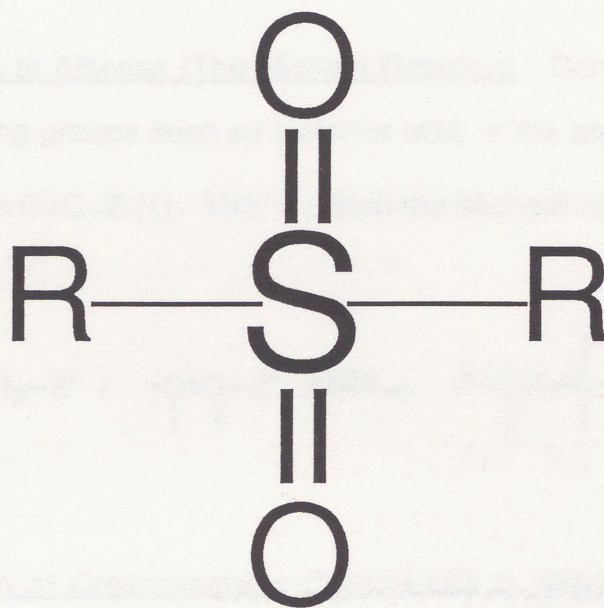


Figure 4

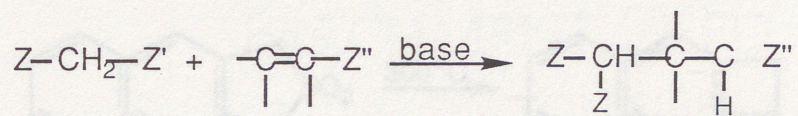
A Sulfone



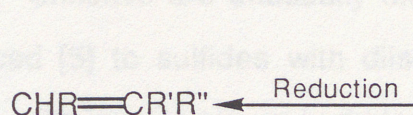
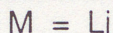
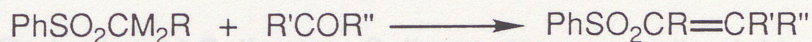
(c) Nitration. Positions activated by the electron-withdrawing sulfone have been shown to be nitrated with alkyl nitrates if a very strong base, such as tBuOK or NaNH₂, is present to convert the substrate to the carbanionic form [6].



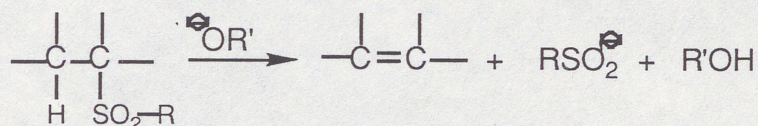
(d) Addition to Alkenes (The Michael Reaction). Compounds containing electron-withdrawing groups such as sulfones add, in the presence of bases, to alkenes of the form C=C-Z [1]. This is called the Michael reaction and involves conjugate addition.



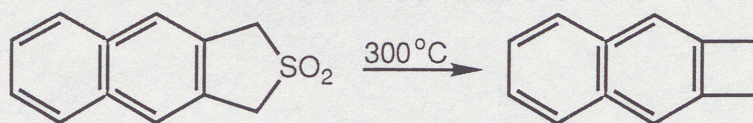
(e) Addition of Organometallic Compounds to Aldehydes and Ketone. α, α-dilithium derivatives of phenyl sulfones react with aldehydes or ketones to give good yields of α,β-unsaturated sulfones [11].



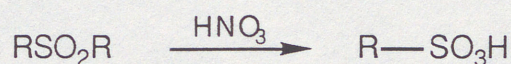
(f) Cleavage of Sulfones. Sulfones with a β -hydrogen undergo elimination on treatment with alkoxide or hydroxide [16]. The reaction is referred to as hydro-alkylsulfonyl-elimination. Although the leaving groups are uncharged, the orientation follows Hofmann's rule.



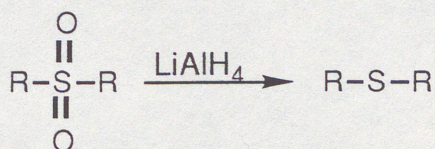
(g) Extrusion of SO₂. Certain cyclic sulfones extrude SO₂ on heating or photolysis to form ring-contracted products [15].



(h) Oxidation of Sulfones to Sulfonic Acids. Sulfones are among a number of sulfur compounds that may be oxidized to sulfonic acids with many oxidizing agents [7].



(i) Reduction of Sulfones. Sulfones are unusually stable to reducing agents. Some have been reduced [5] to sulfides with diisobutylaluminum hydride. A less general reagent is lithium aluminum hydride, which reduces some sulfones to sulfides, but not other [2].

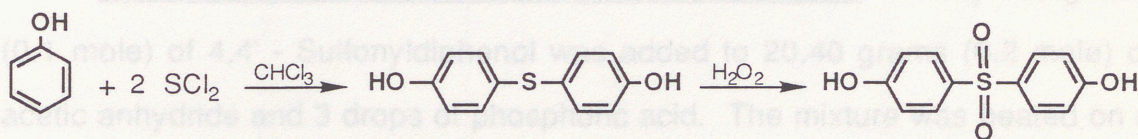


CHAPTER 3

DESIGN OF THE EXPERIMENT

Synthesis of the Compounds

The starting materials, 4, 4'-Thiodiphenol and 4, 4'-Sulfonyldiphenol, are easily made by the following equation:



However, due to the severe toxicity associated with sulfur dichloride, as well as the cost involved with its storage and disposal, both starting materials were purchased, at 99.9% purity, from Aldrich Chemicals.

Synthesis (A-3) 4, 4' - Thiodiphenoldiphenylacetate. Four grams (0.1 mole) of NaOH was added to 100 mL of water. The solution was stirred until dissolved. To the cooled solution of NaOH was added, with stirring, 11.0 grams (0.05 moles) of 4, 4' - Thiodiphenol. The solution was allowed to cool to room temperature. To the solution of NaOH and 4,4' - Thiodiphenol was added 15.40 grams of Phenylacetyl chloride slowly, with stirring. A white precipitate formed immediately. The mixture was stirred for one hour with cooling. The white precipitate was filtered and allowed to air dry. A portion of the crude product was recrystallized from boiling methanol.

Synthesis (A-5) 4,4' - Thiodiphenoldiacetate. Eleven grams (0.05 mole) of 4,4' - Thiodiphenol was added to 10.20 grams of acetic anhydride and 3 drops of phosphoric acid, used as a catalyst. The mixture was heated on a water bath at 100°C until dissolved, ~ 1 hour. The mixture was then cooled in an ice bath. A white precipitate was formed. The mixture was filtered, washed with cold water and allowed to air dry. Recrystallization from boiling methanol gave a pure sample.

Synthesis (A-7). 4,4' - Sulfonyldiphenoldiacetate. Twenty-five grams (0.1 mole) of 4,4' - Sulfonyldiphenol was added to 20.40 grams (0.2 mole) of acetic anhydride and 3 drops of phosphoric acid. The mixture was heated on a water bath at 100°C until dissolved. Cooling the mixture in an ice bath produced a light yellow precipitate. The mixture was filtered, washed with cold water and allowed to air dry. Recrystallization from boiling methanol gave a pure sample.

Synthesis (A-9). 4,4' - Sulfonyldiphenoldiphenylacetate. Eight grams (0.2 moles) of a cooled NaOH solution was dissolved in 200 mL of water, with stirring, to 25.0 grams (0.1 mole) of 4,4' - Sulfonyldiphenol. To this solution was then added, slowly and with stirring, 31.0 grams (0.2 moles) of phenyl acetyl chloride. After three minutes, a precipitate began to form. The mixture was stirred for more than one hour and then placed in an ice bath. The solid was filtered, washed with cold water and allowed to air dry. Recrystallization from boiling methanol gave a white solid.

Analytical Determinations. Elemental analyses were performed by Texas Analytical Laboratories, Inc., Houston, Texas. The resulting data is shown as Table 2.

TABLE 2

Experimental Data for Compounds
A-3, A-5, A-7 and A-9

Number	Compound	C°	M.P.	% Yield	Empirical Formula	Calculated			Found		
						C	H	S	C	H	S
A - 3	4,4' - Thiodiphenol diphenylacetate	105 - 109		98	C ₂₈ H ₂₂ O ₄ S	74.01	4.85	7.04	72.38	4.58	7.16
A - 5	4,4' - Thiodiphenol diacetate	90 - 92		96	C ₁₆ H ₁₄ O ₄ S	63.57	4.63	10.59	63.07	4.68	10.48
A - 7	4,4' - Sulfonyldiphenol diacetate	159 - 163		82	C ₁₆ H ₁₄ O ₆ S	57.48	4.19	9.58	57.32	4.25	9.39
A - 9	4,4' - Sulfonyldiphenol diphenylacetate	90 - 97		96	C ₂₈ H ₂₂ O ₆ S	69.13	4.52	6.58	69.03	4.48	6.54

Infrared Spectra. The infrared spectra were obtained on a Perkin Elmer 2000 FTIR instrument.

Mass Spectra. The mass spectral data was obtained on a 5890 Plus Hewlett Packard GC attached to a 5972 Mass Selective Detector System.

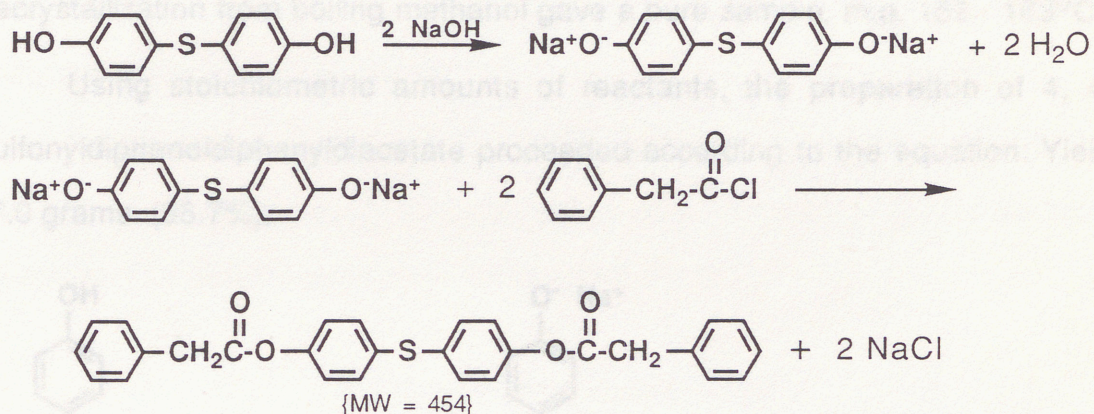
Raman Spectra. The Raman spectra were produced using a Perkin Elmer 2000 FTIR-Raman instrument.

Proton Nuclear Magnetic Resonance (NMR) Spectra. NMR spectra were obtained using a GE Model QE 300 NMR spectrometer operated at 300 MHz, in deuterated chloroform. The mass spectra, proton NMR spectra, infrared spectra, and Raman spectra are shown in Chapter 4.

CHAPTER 4

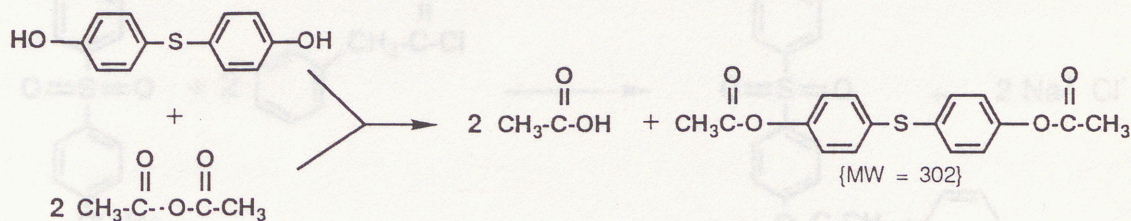
RESULTS AND DISCUSSION

Using stoichiometric amounts of reactants, the preparation of 4, 4'-Thiodiphenoldiacetate proceeded according to the equation: Yield: 23.24 grams (98%).



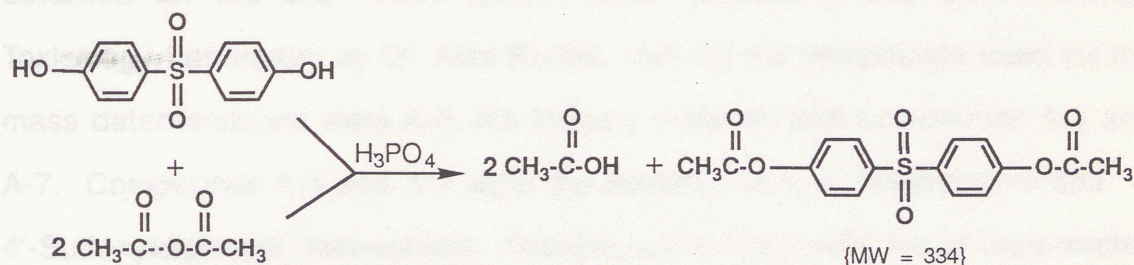
A portion of the crude product was recrystallized from boiling methanol, m.p. 105 - 109 °C.

Using stoichiometric amounts of reactants, the preparation of 4, 4'-Thiodiphenoldiacetate proceeded according to the equation: Yield: 14.5 grams (96%)



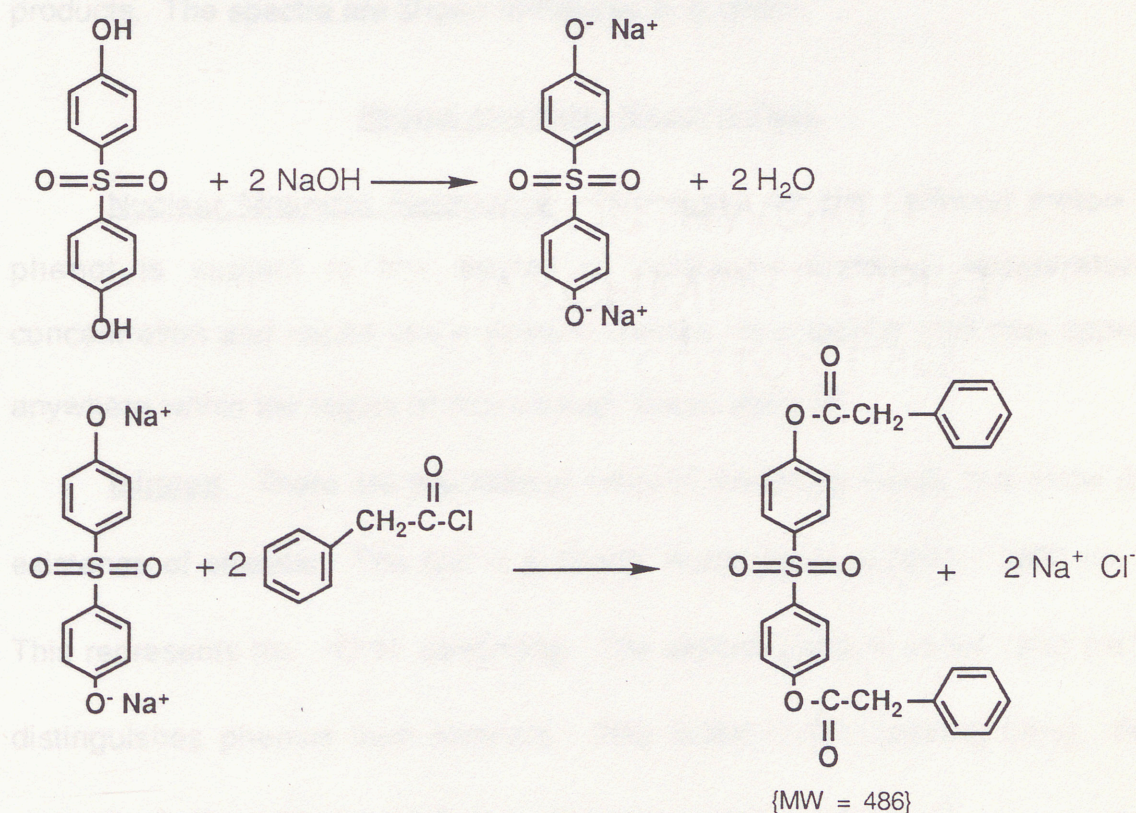
Recrystallization from boiling methanol gave a pure sample, m.p. 90 - 92 °C.

Using stoichiometric amounts of reactants, the preparation of 4, 4'-Sulfonyl-diphenoldiacetate proceeded according to the equation: Yield: 27.5 grams (82%)



Recrystallization from boiling methanol gave a pure sample, m.p. 159 - 163°C.

Using stoichiometric amounts of reactants, the preparation of 4, 4'-Sulfonyldiphenoldiphenyldiacetate proceeded according to the equation: Yield: 47.0 grams (96.7%).



Recrystallization from boiling methanol gave a pure sample, m.p. 90 - 92°C.

Mass Spectrum

Data regarding the molecular weights of the compounds prepared was obtained on the GC- Mass spectrometer located in the Environmental Toxicology Laboratory by Dr. Alaa Kamel. Among the compounds used for the mass determinations were A-0, the starting material, and compounds A-5 and A-7. Compounds A-5 and A-7 were the acetates of 4, 4'-Thiodiphenol and 4, 4'-Sulfonyldiphenol, respectively. Compounds A-3 and A-9, the phenylacetates of 4, 4'-Thiophenol and 4, 4'-Sulfonyldiphenol, were not volatile enough to be analyzed under these conditions.

Compounds A-0, A-5 and A-7 show molecular ions at masses 250, 302 and 334, respectively, which corresponds to the calculated masses for the same products. The spectra are shown in Figures 5, 6, and 7.

Phenol and Ester Spectral Data

Nuclear Magnetic Resonance. The signal for the hydroxyl proton in phenol is subject to the degree of hydrogen bonding, temperature, concentration and nature of the solvent. Hence, its chemical shift may appear anywhere within the region of four through seven delta (δ).

Infrared. There are two distinct infrared stretching bands that show the existence of phenols. The first is a strong, broad band at $3200 - 3600 \text{ cm}^{-1}$. This represents the -O-H stretching. The second band at about 1230 cm^{-1} , distinguishes phenols from alcohols. This is the C-O stretching band. For alcoholic C-O stretching, this band is located at $1050 - 1200 \text{ cm}^{-1}$.

Figure 5
MS Spectra for Compound A 0

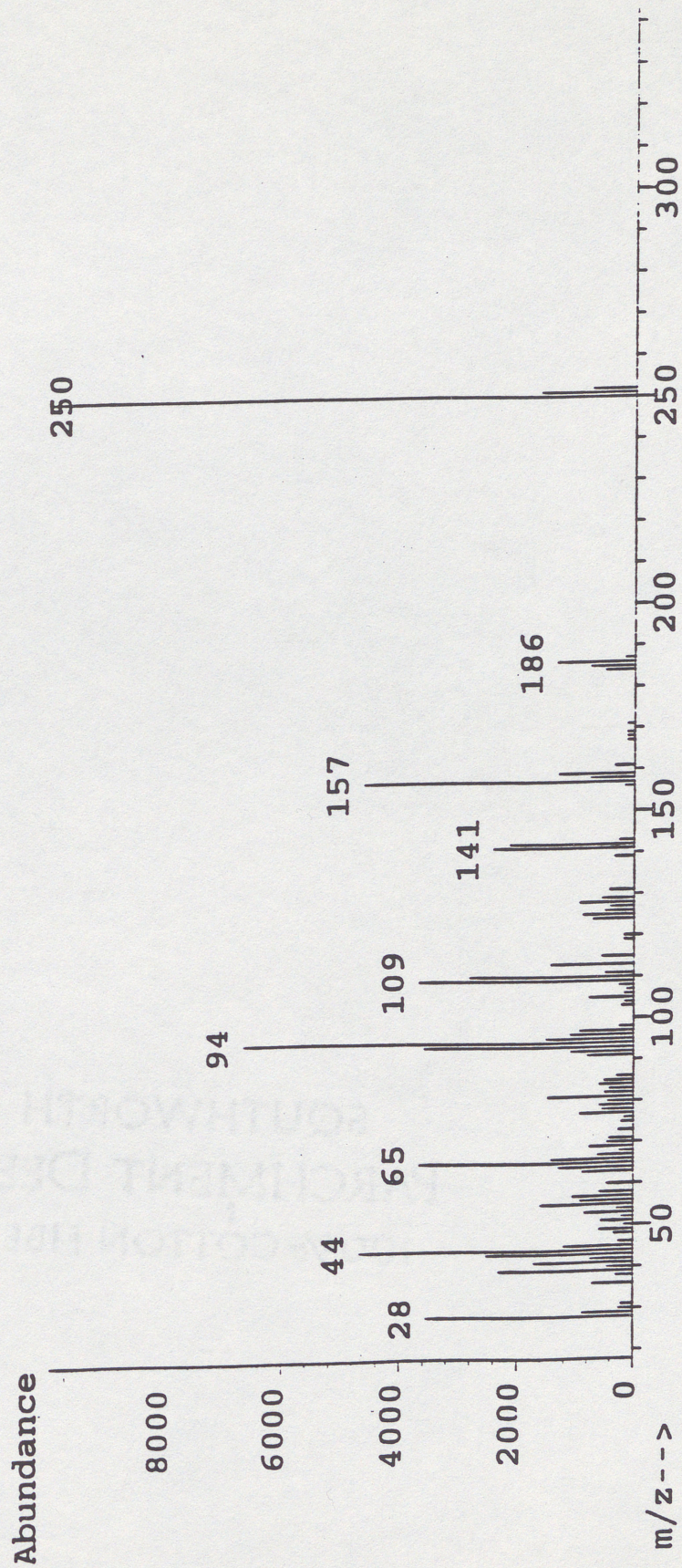


Figure 6
MS Spectra for Compound A 5

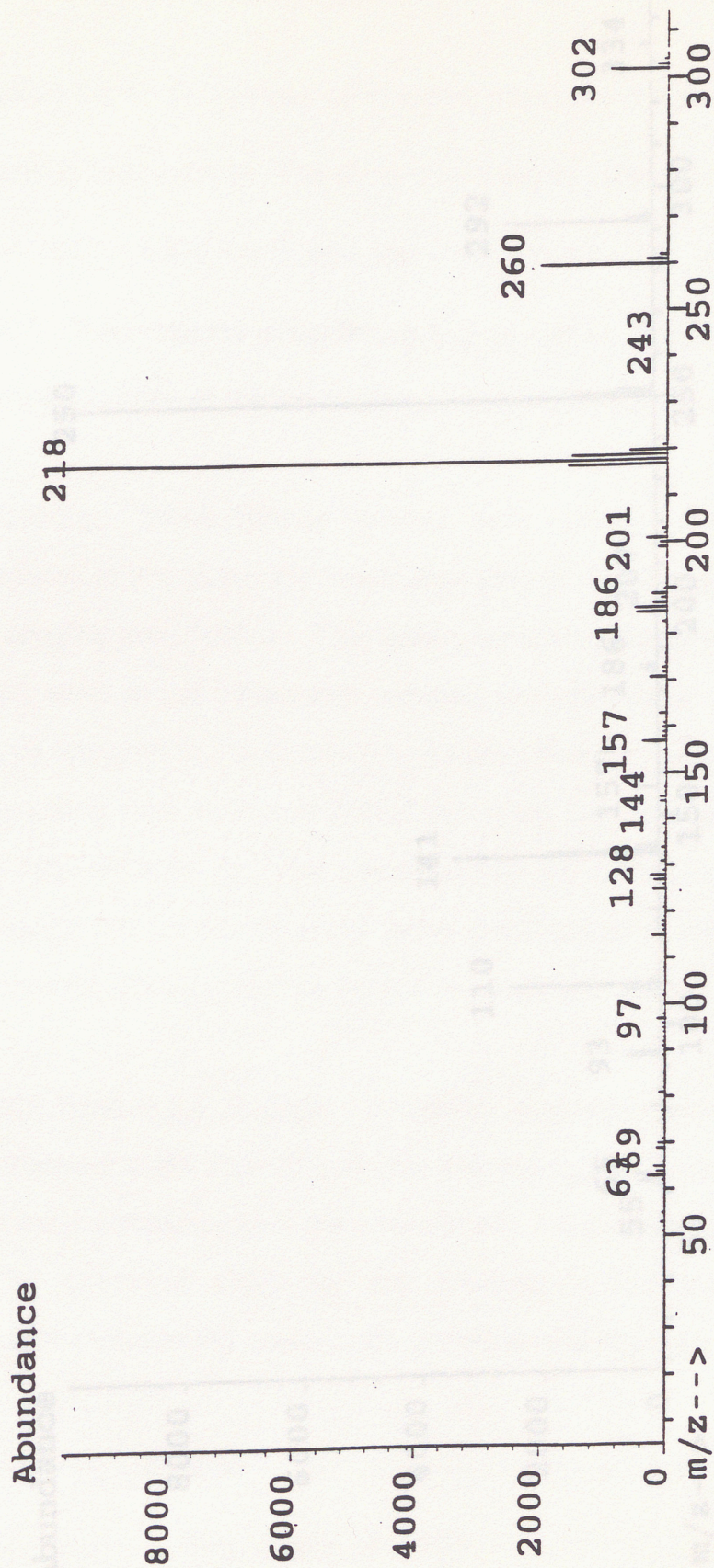
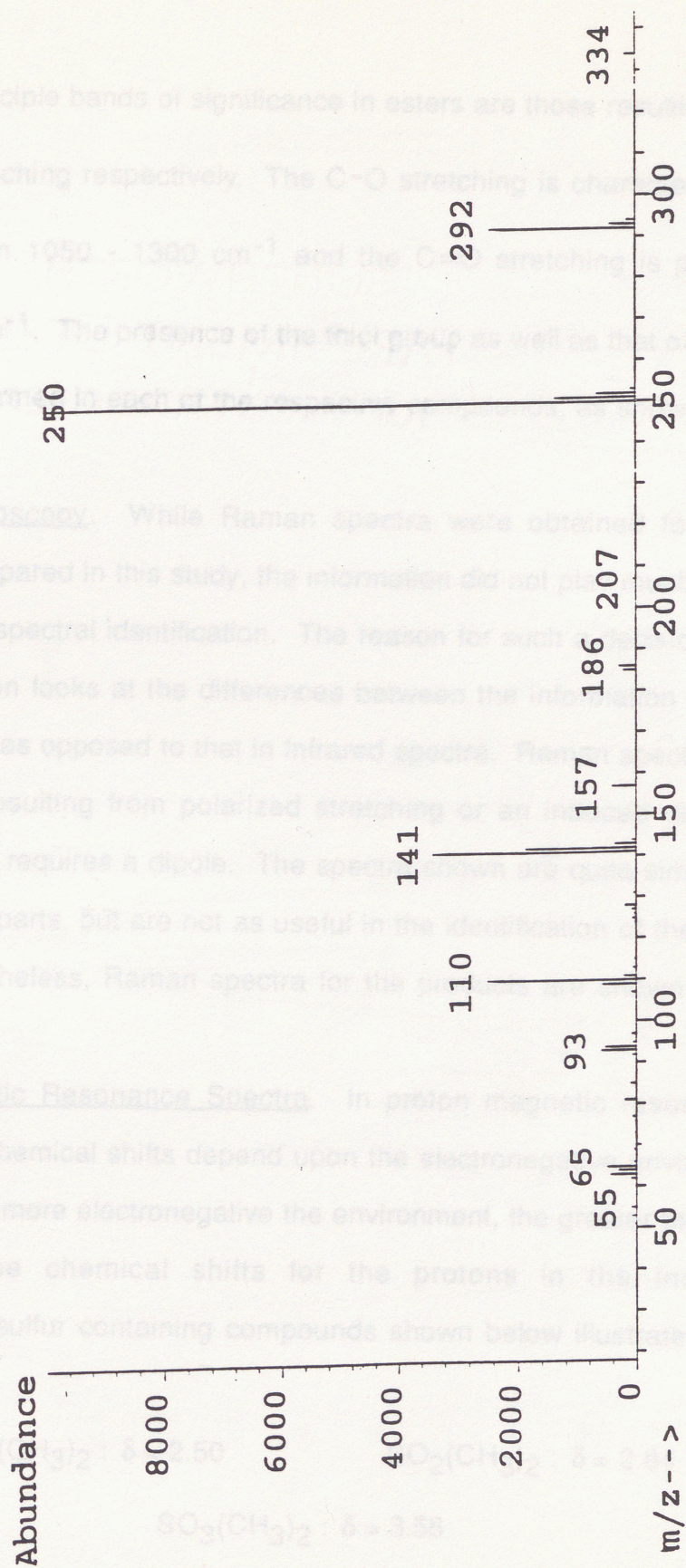


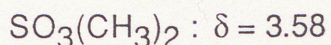
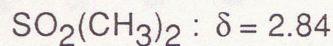
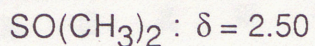
Figure 7
MS Spectra for Compound A 7



The principle bands of significance in esters are those resulting from C-O and C=O stretching respectively. The C-O stretching is characterized by two bands between $1050 - 1300 \text{ cm}^{-1}$ and the C=O stretching is prominent at $1715 - 1740 \text{ cm}^{-1}$. The presence of the thiol group as well as that of the sulfonyl group are confirmed in each of the respective compounds, as shown in Figures 8 - 12.

Raman Spectroscopy. While Raman spectra were obtained for all of the compounds prepared in this study, the information did not play much of a role in the systematic spectral identification. The reason for such a decision becomes obvious when one looks at the differences between the information provided in Raman spectra as opposed to that in Infrared spectra. Raman spectra is based on scattering resulting from polarized stretching or an induced dipole, while infrared spectra requires a dipole. The spectra shown are quite similar to their infrared counterparts, but are not as useful in the identification of the functional groups. Nevertheless, Raman spectra for the products are shown in Figures 13 - 17.

Nuclear Magnetic Resonance Spectra. In proton magnetic resonance, the location of the chemical shifts depend upon the electronegative environment of the proton. The more electronegative the environment, the greater the affect on the proton. The chemical shifts for the protons in the increasingly electronegative sulfur containing compounds shown below illustrate this point [12].



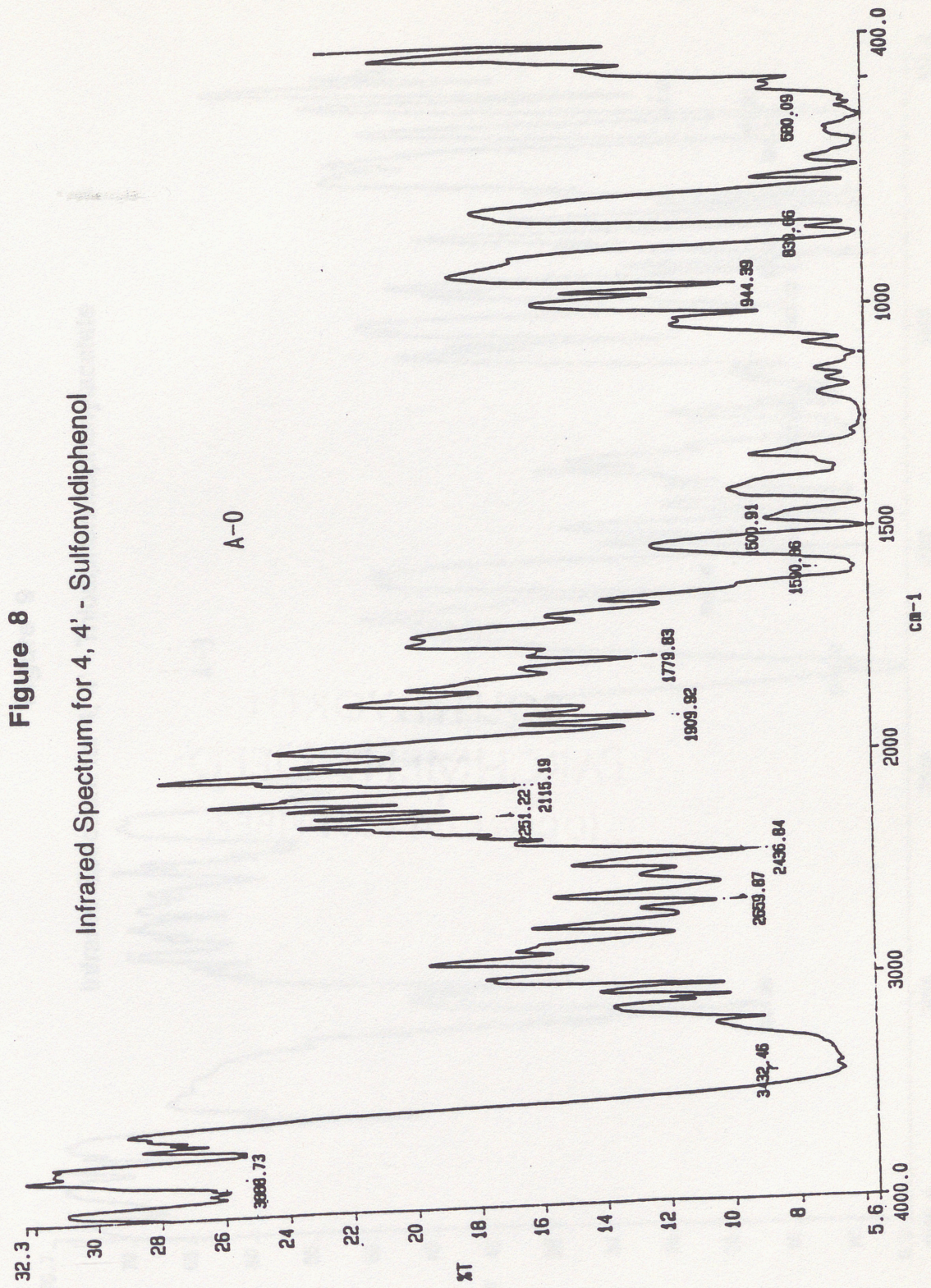


Figure 9

Infrared Spectrum for 4, 4' - Thiodiphenoldiphenylacetate

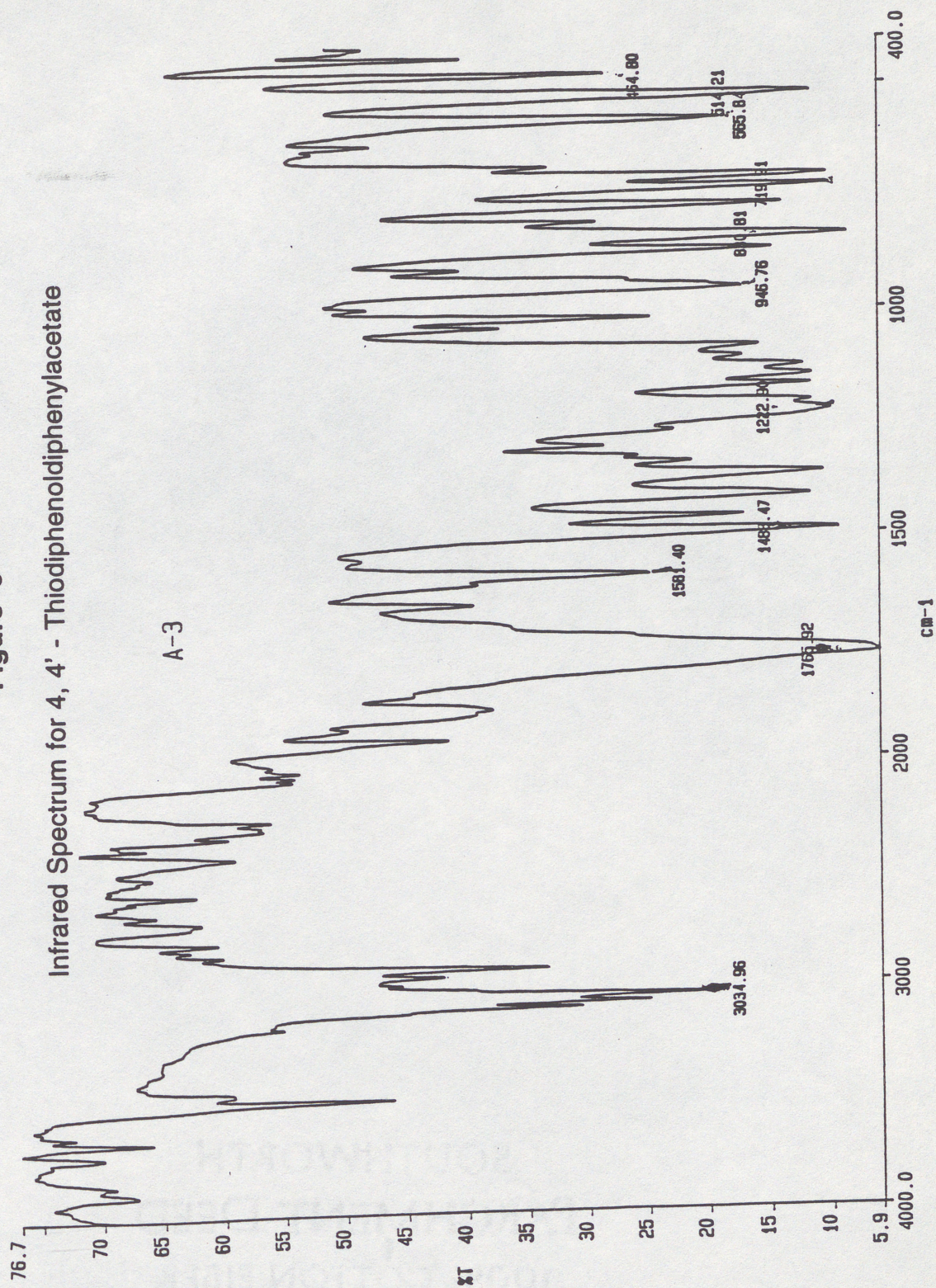


Figure 10

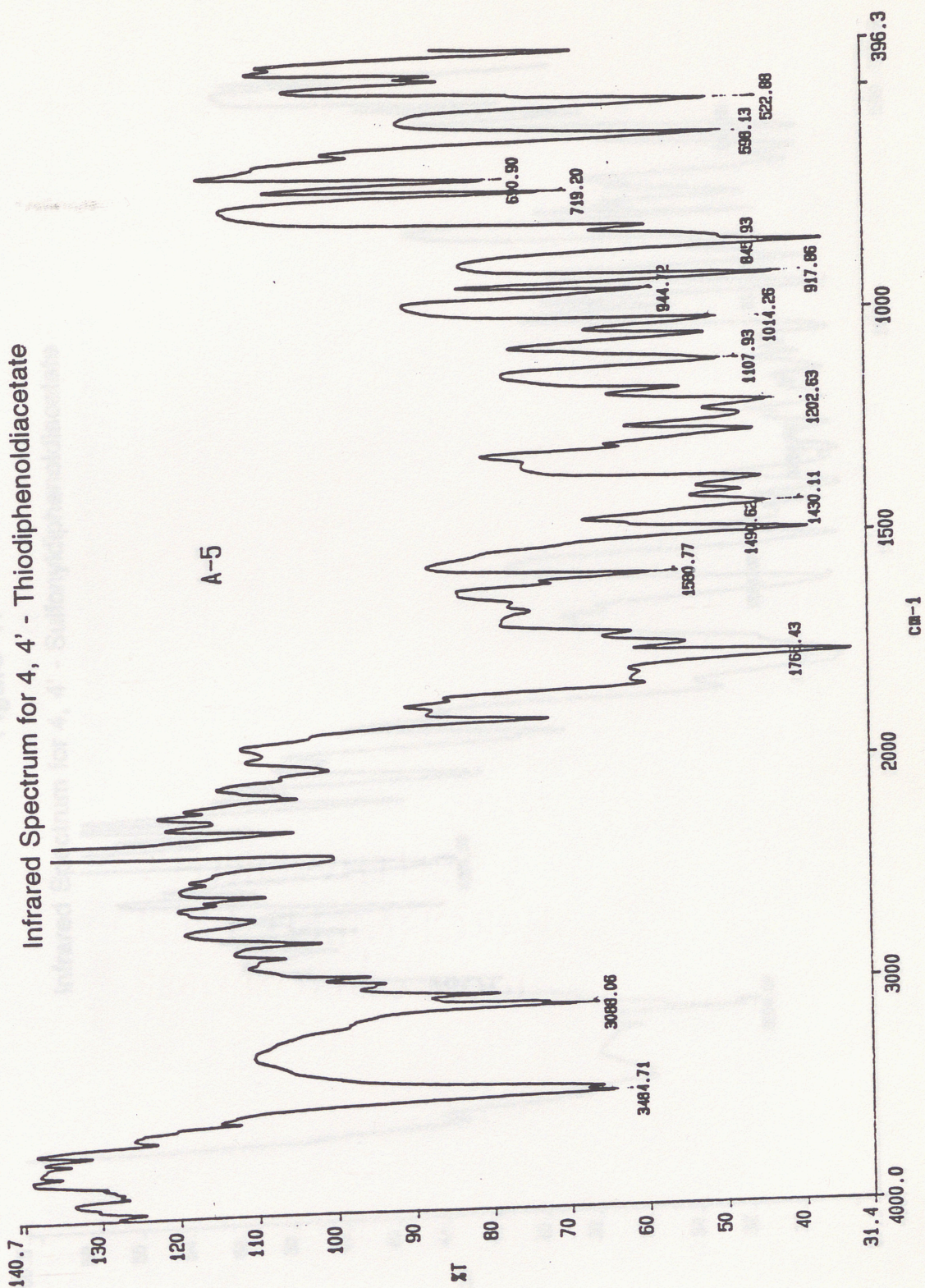


Figure 11

Infrared Spectrum for 4, 4' - Sulfonoldiphenoldiacetate

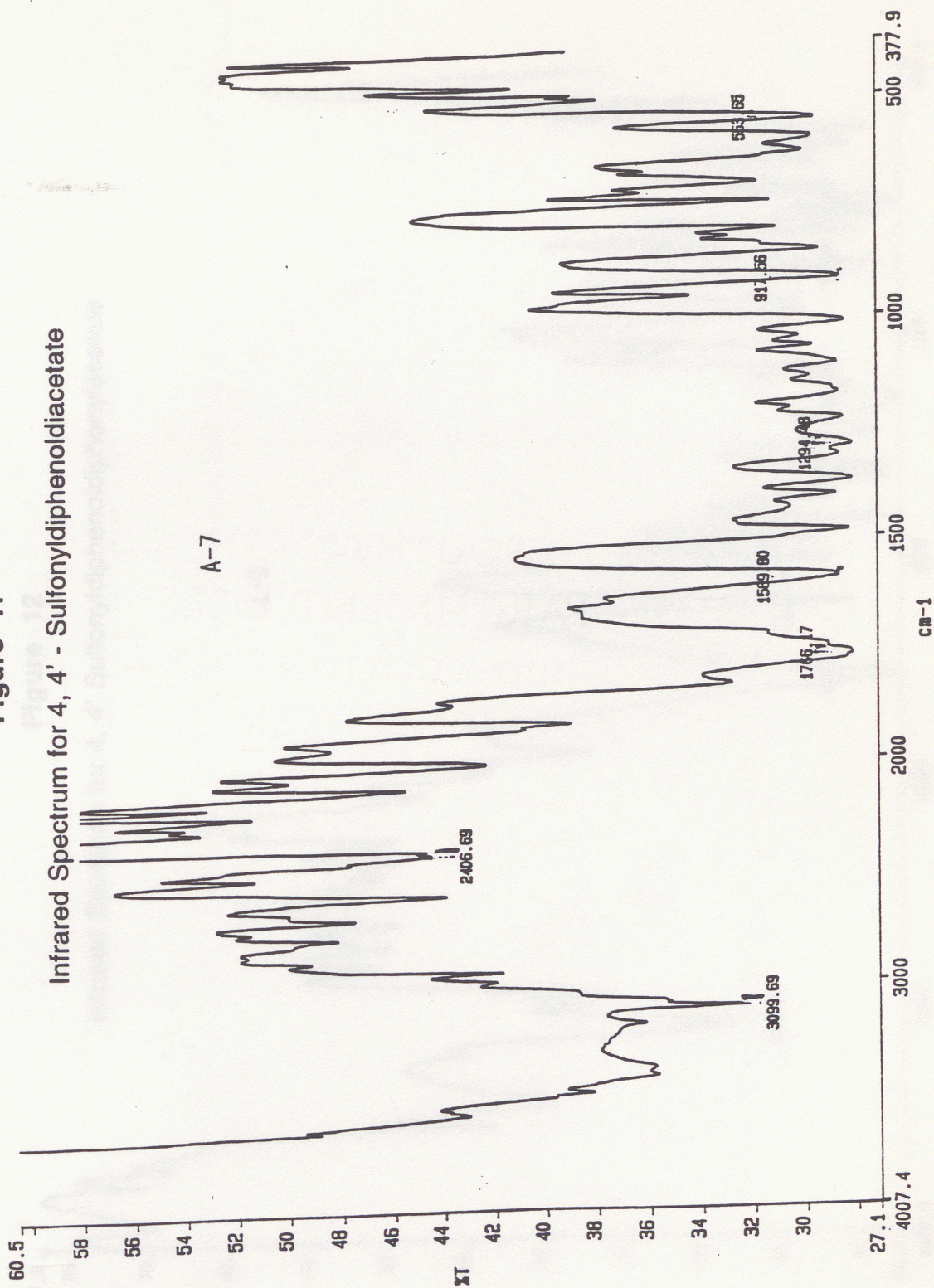


Figure 12
Infrared Spectrum for 4, 4' Sulfonoldiphenylacetate

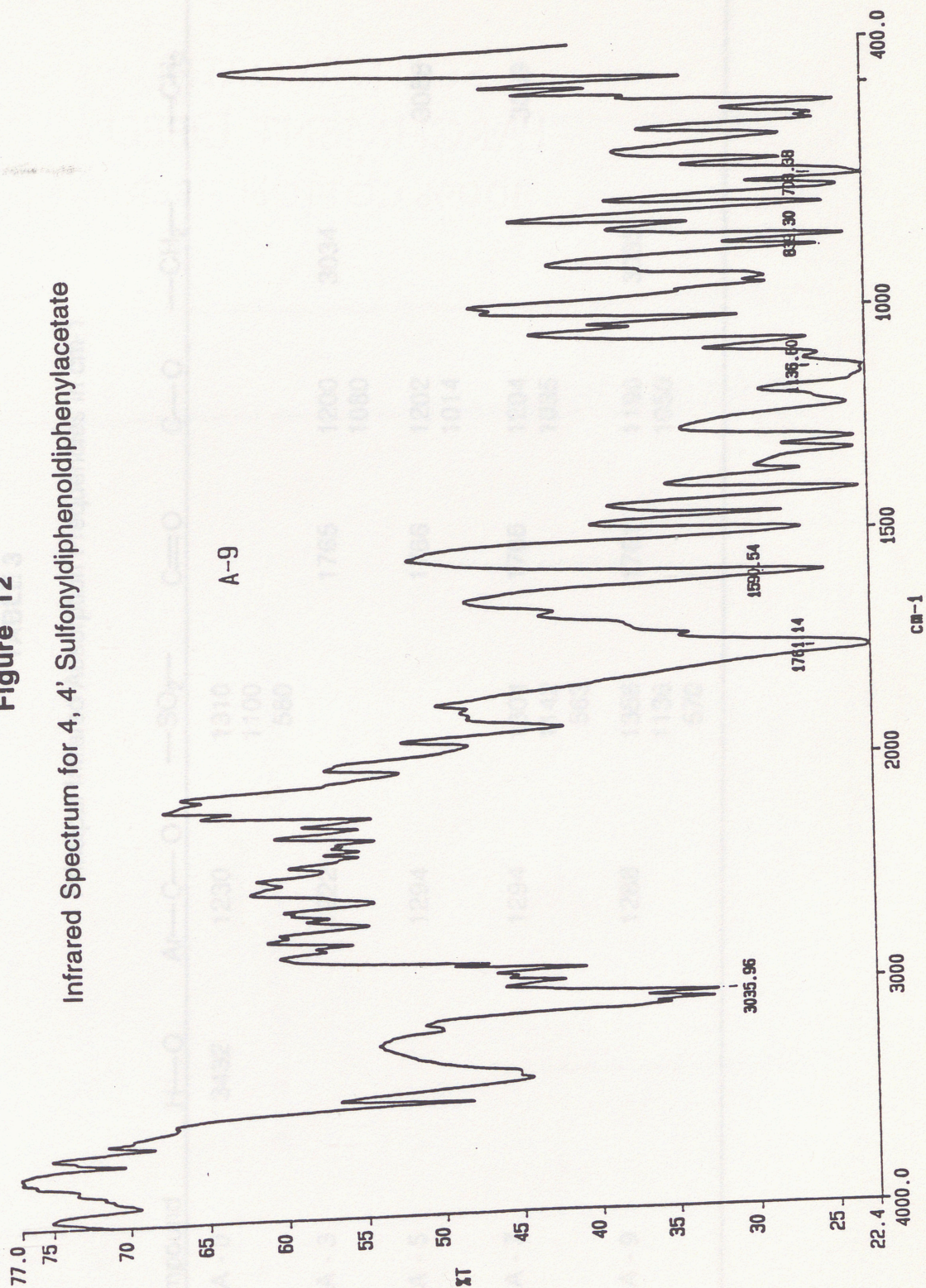
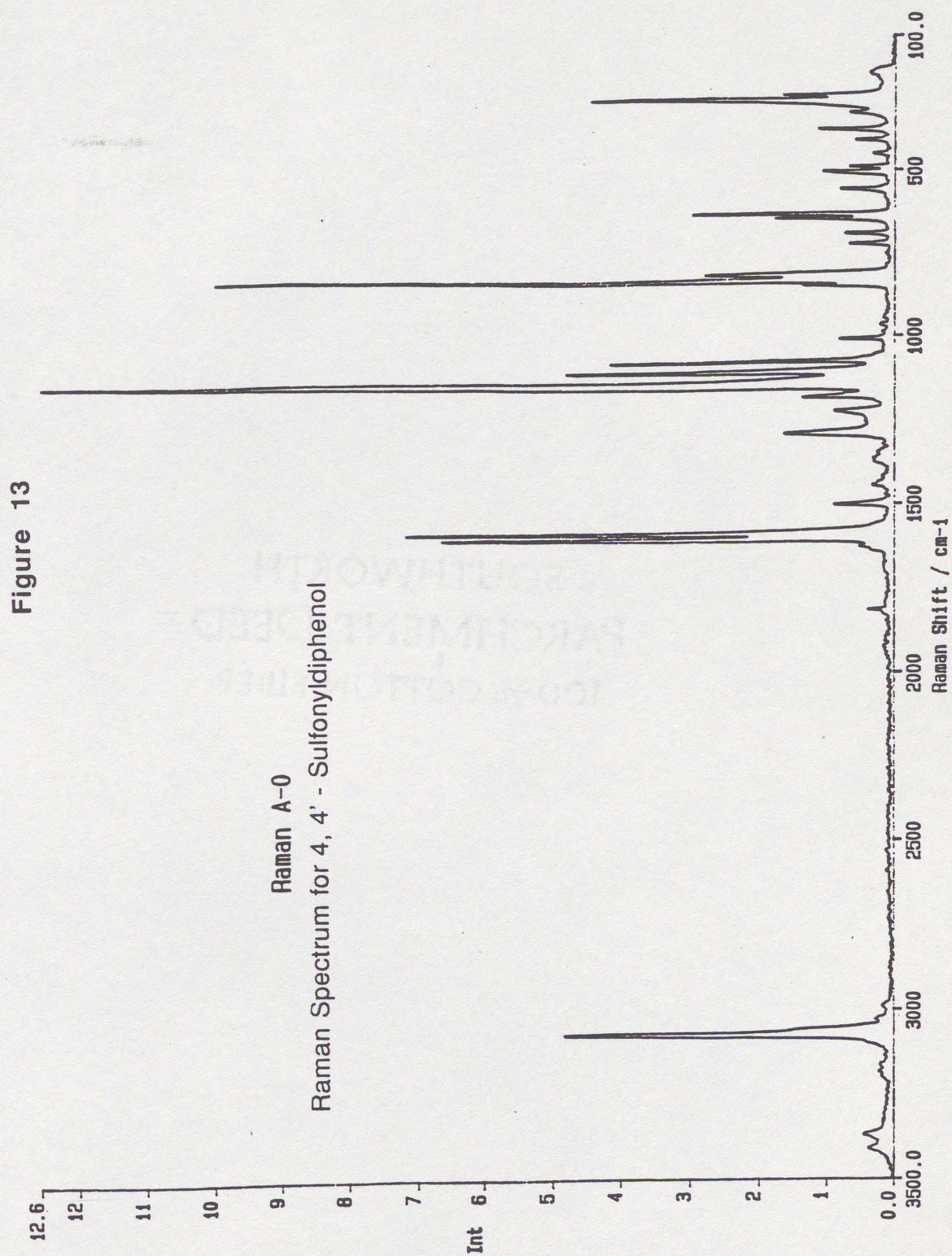


Figure 13

TABLE 3

Principal Infrared Absorption Frequencies in cm⁻¹

Compound	H—O	Ar—C—O	—SO ₂ —	C=O	C—O	—CH ₂ —	—CH ₃	—S—
A - 0	3432	1230	1310 1100 580					
A - 3		1222		1765	1200 1080	3034		719 830
A - 5		1294		1766	1202 1014		3088	719 845
A - 7		1294	1304 1142 563	1766	1204 1035		3099	
A - 9		1288	1356 1136 570	1761	1190 1050	3035		



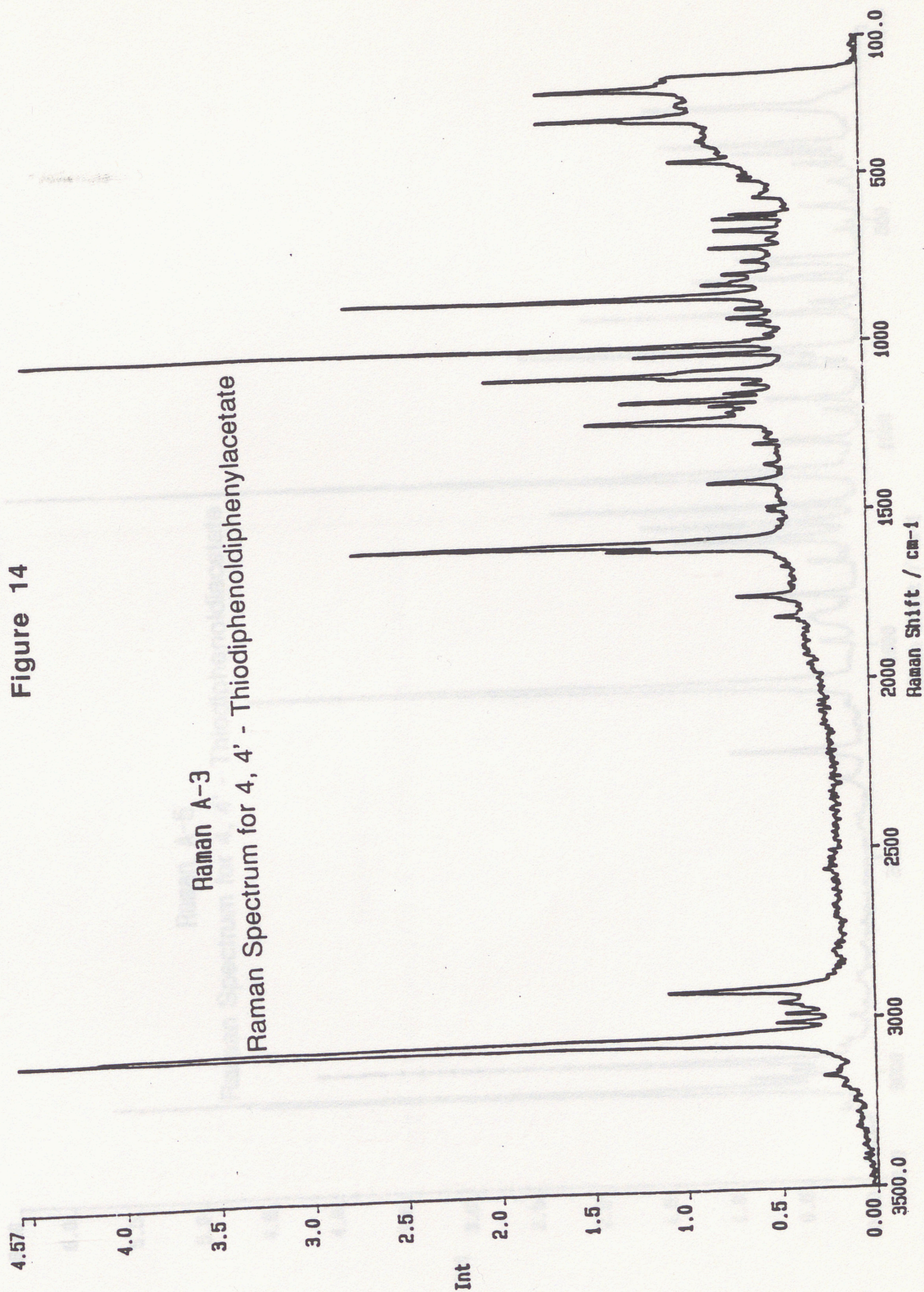
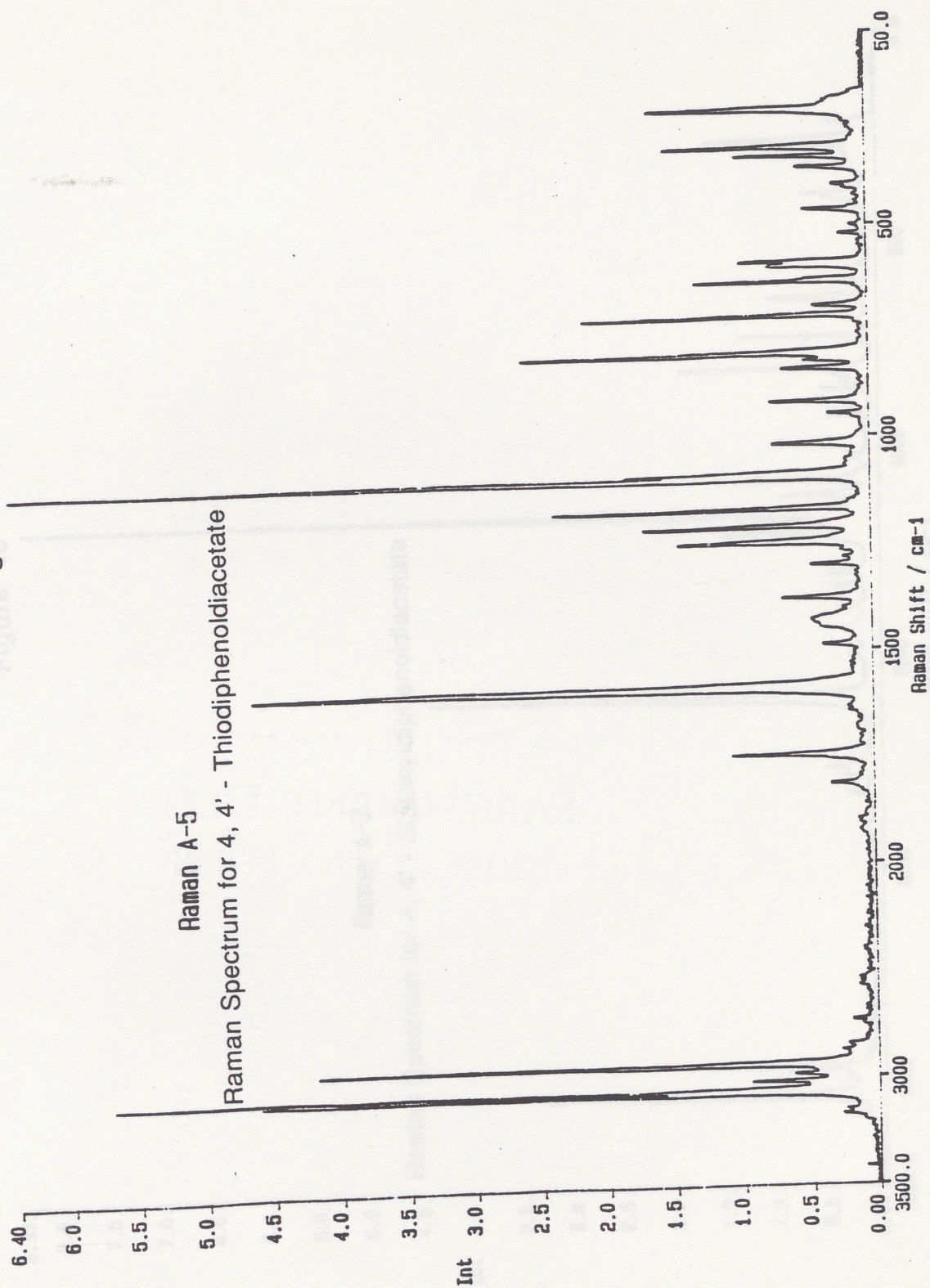
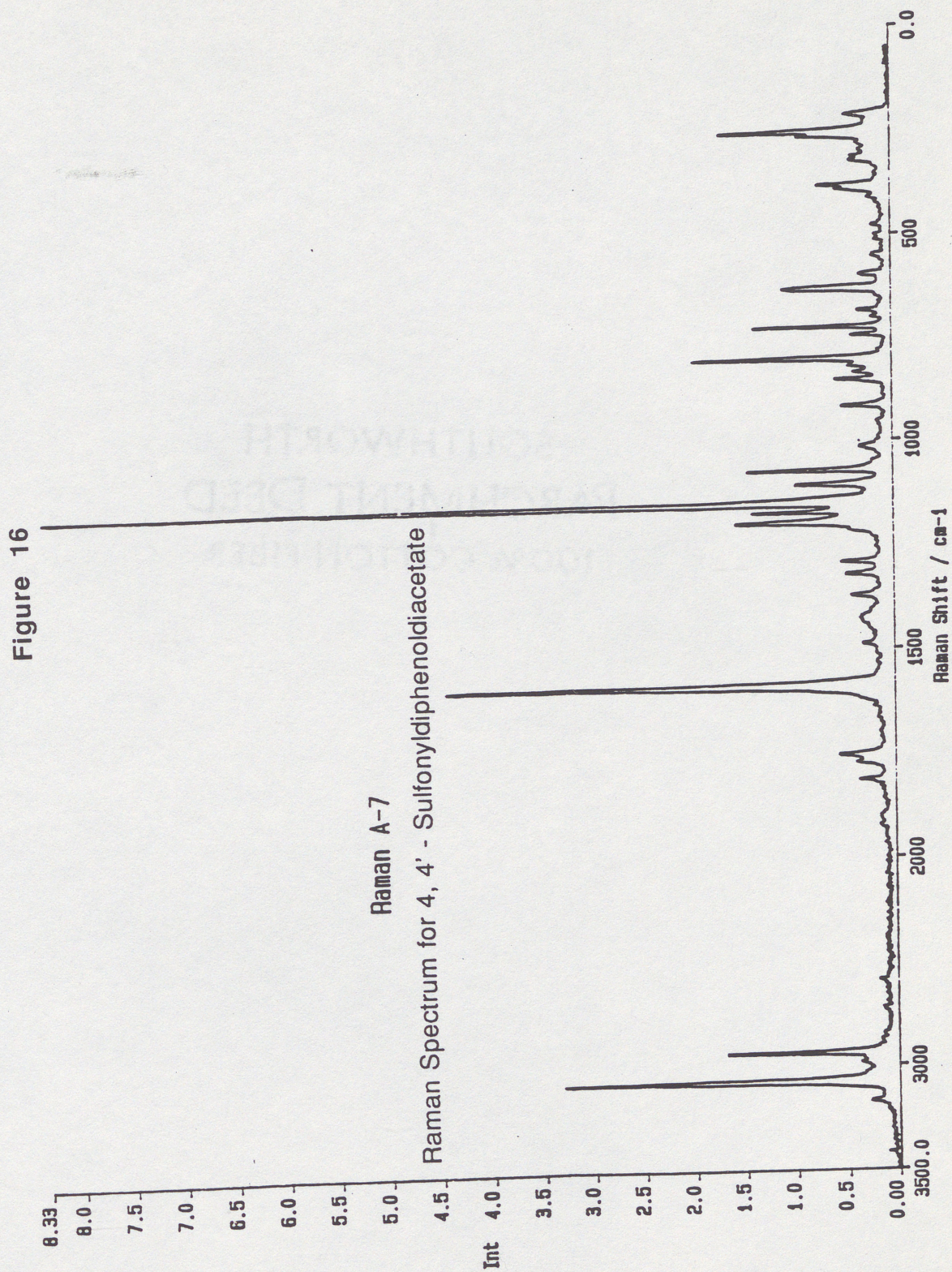
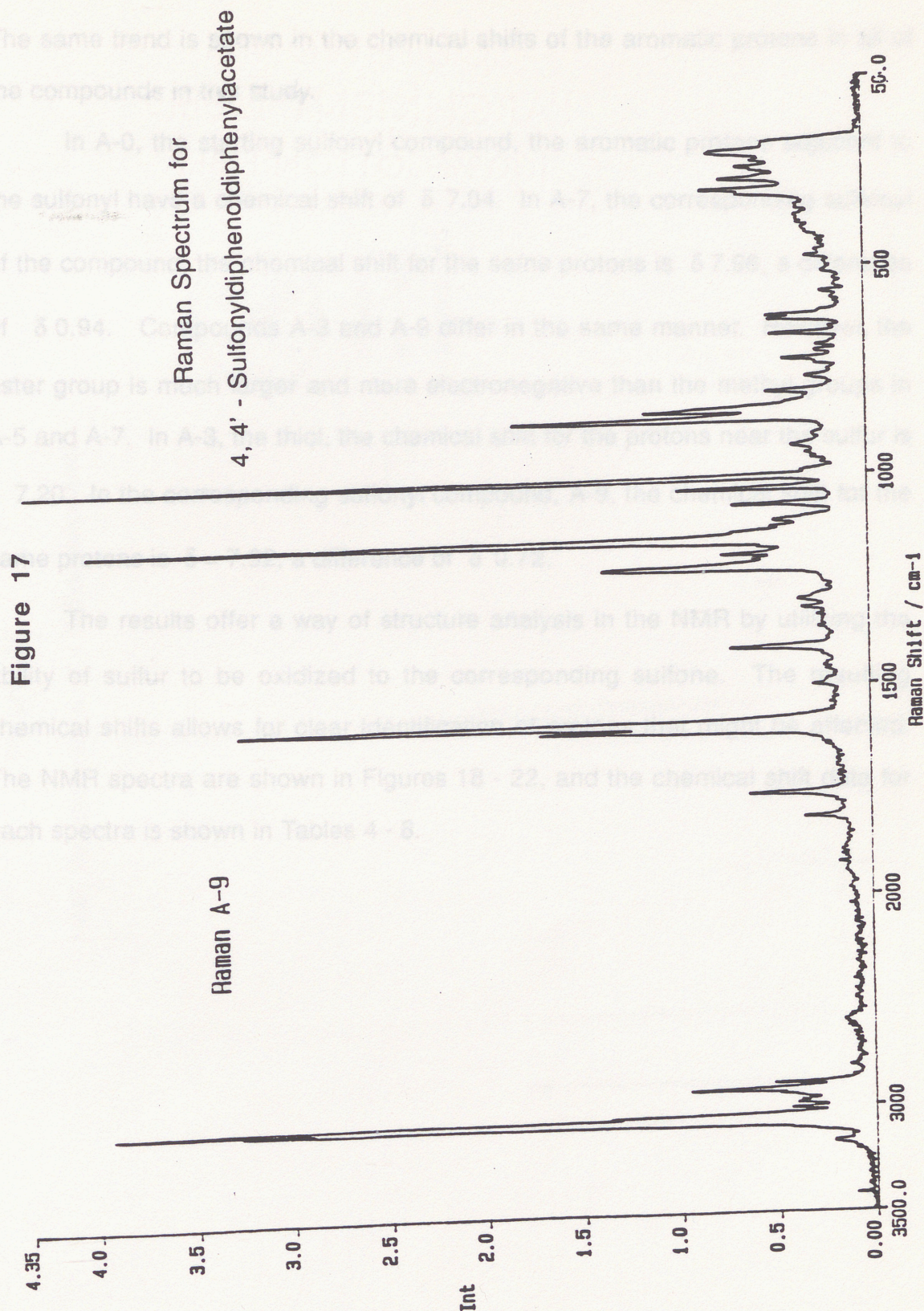


Figure 15







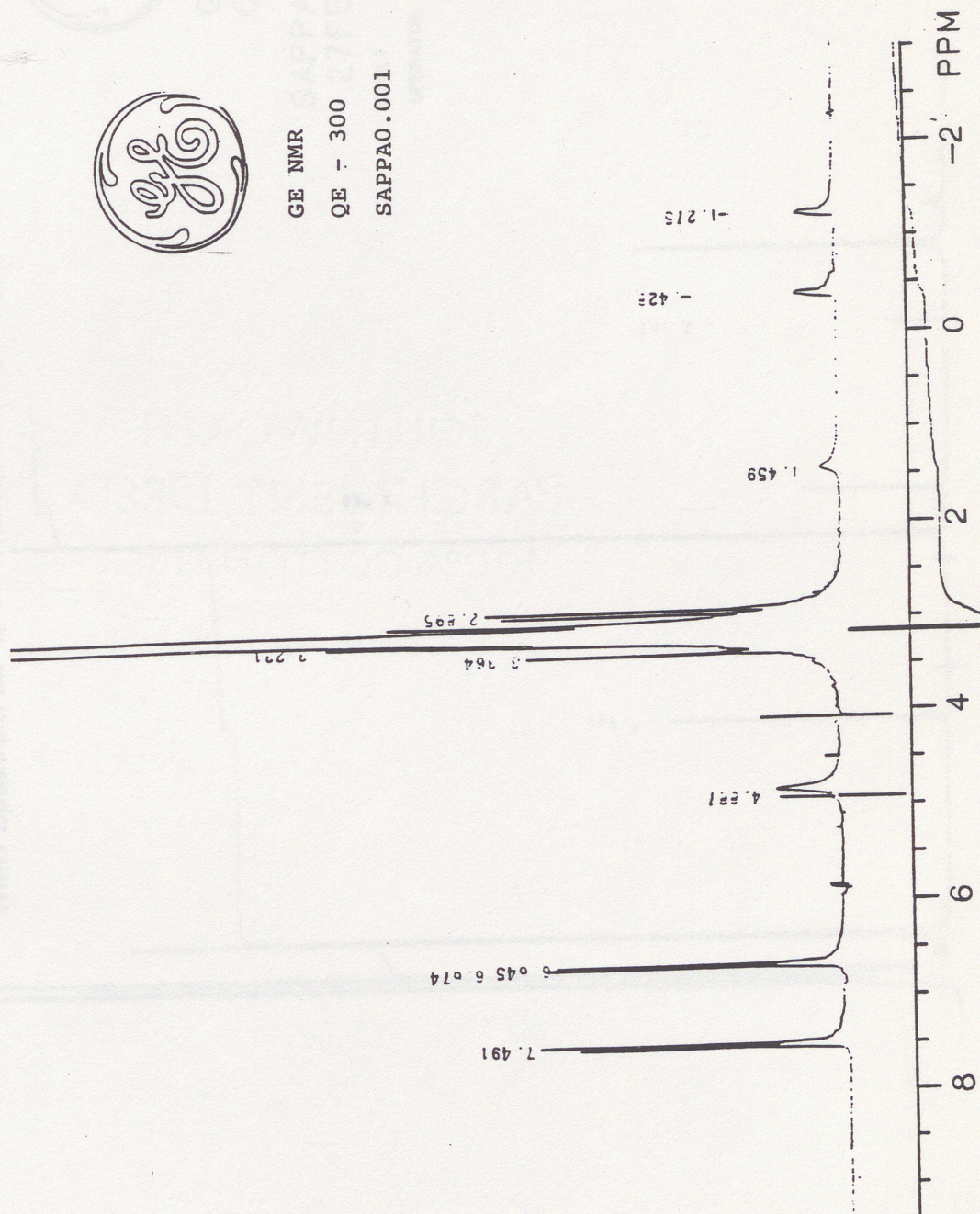
The same trend is shown in the chemical shifts of the aromatic protons in all of the compounds in this study.

In A-0, the starting sulfonyl compound, the aromatic protons adjacent to the sulfonyl have a chemical shift of δ 7.04. In A-7, the corresponding sulfonyl of the compound, the chemical shift for the same protons is δ 7.96, a difference of δ 0.94. Compounds A-3 and A-9 differ in the same manner. However, the ester group is much larger and more electronegative than the methyl groups in A-5 and A-7. In A-3, the thiol, the chemical shift for the protons near the sulfur is δ 7.20. In the corresponding sulfonyl compound, A-9, the chemical shift for the same protons is δ = 7.92, a difference of δ 0.72.

The results offer a way of structure analysis in the NMR by utilizing the ability of sulfur to be oxidized to the corresponding sulfone. The resulting chemical shifts allows for clear identification of protons that might be affected. The NMR spectra are shown in Figures 18 - 22, and the chemical shift data for each spectra is shown in Tables 4 - 8.

Figure 18

NMR Spectrum for 4, 4' - Sulfonatediphenol



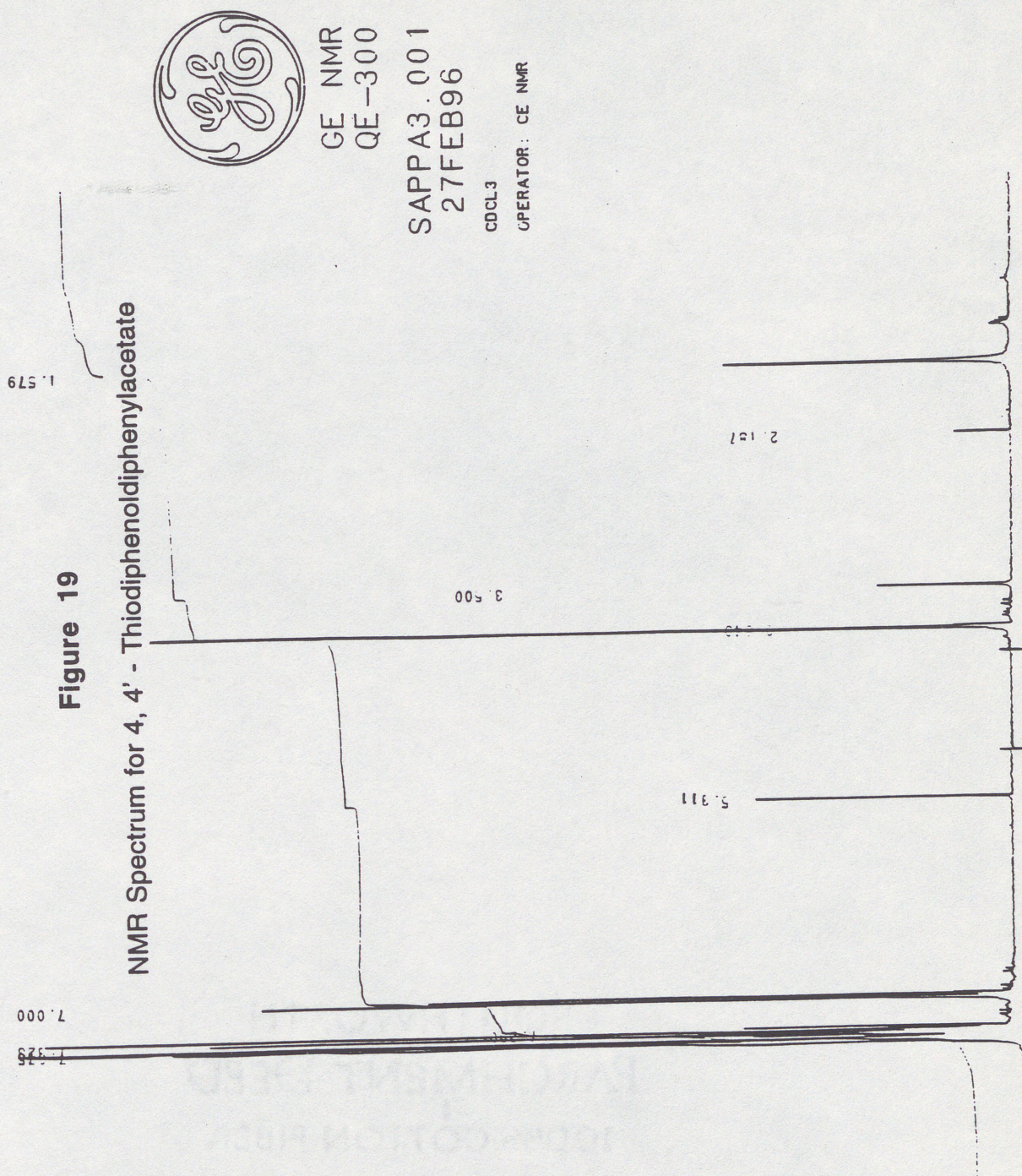


Figure 20

NMR Spectrum for 4, 4' - Thiodiphenoldiacetate

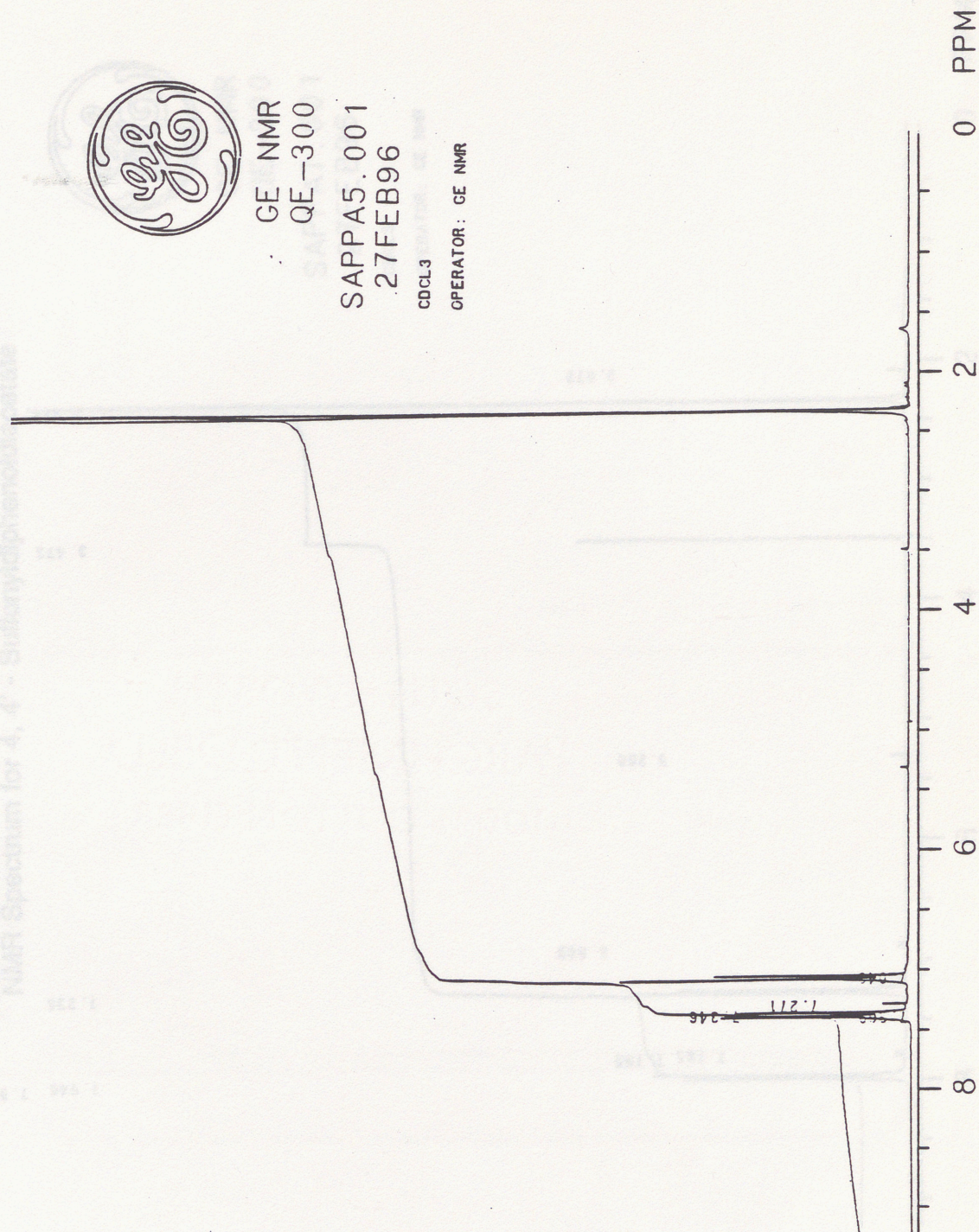


Figure 21

NMR Spectrum for 4, 4' - Sulfonoldiphenoldiacetate

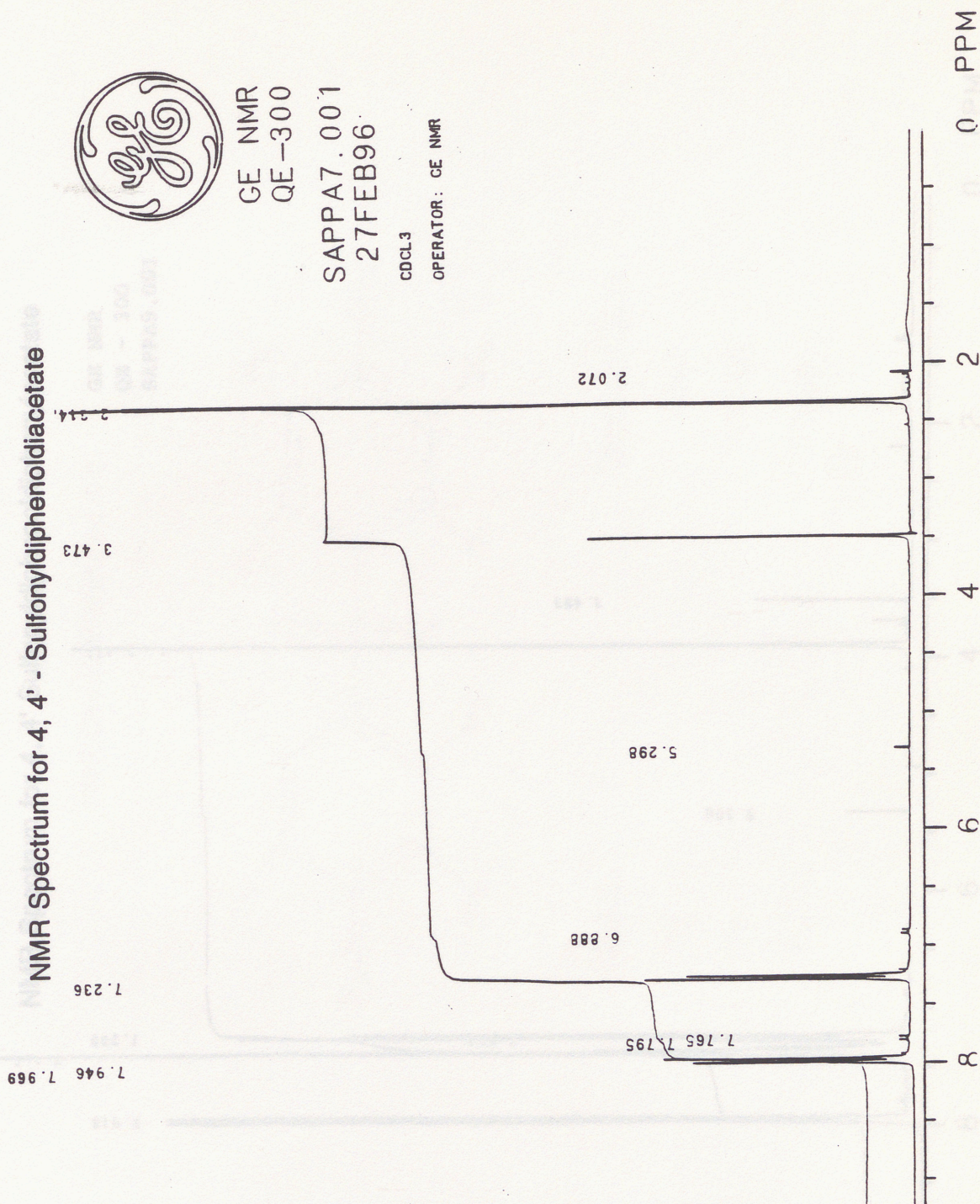


Figure 22

NMR Spectrum for 4, 4' Sulfonoldiphenylacetate

GE NMR
QE - 300
SAPPA9.001

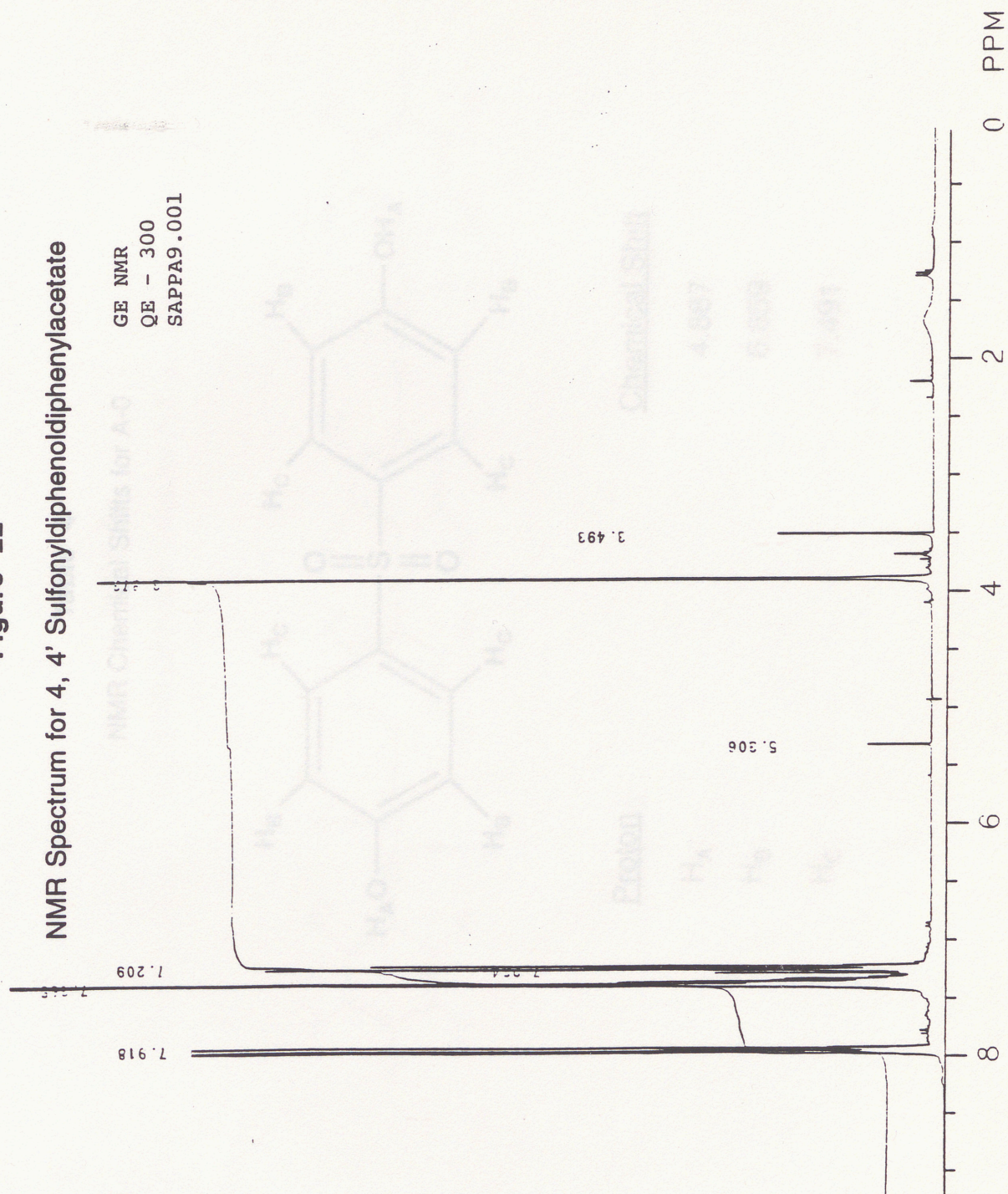
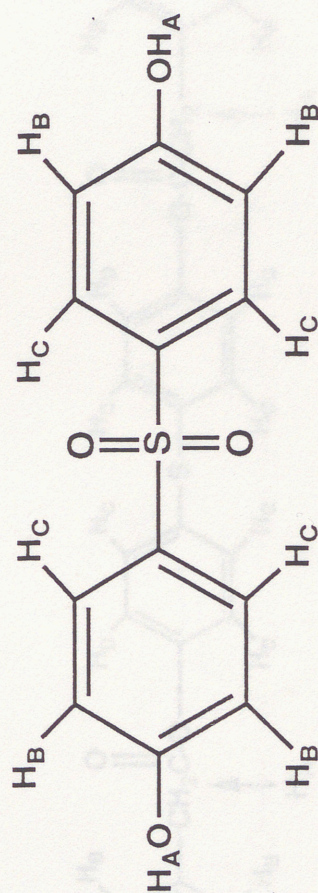


Table 4
NMR Chemical Shifts for A-0



Chemical Shift

4.887

6.659

7.491

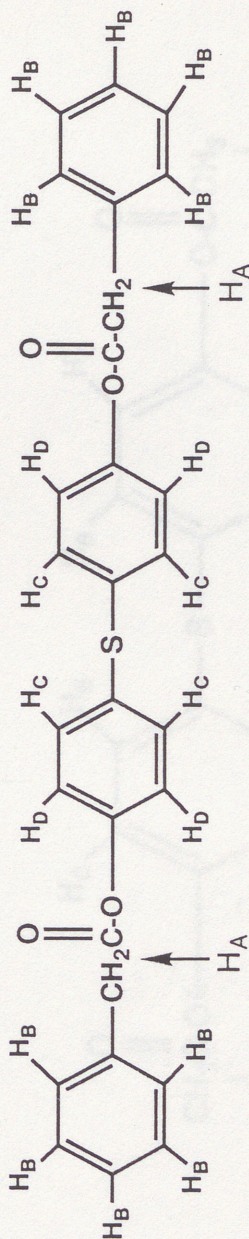
Proton

H_A

H_B

H_C

Table 5
NMR Chemical Shifts for A-3



Chemical Shift

1.579

7.000

7.200

7.349

Proton

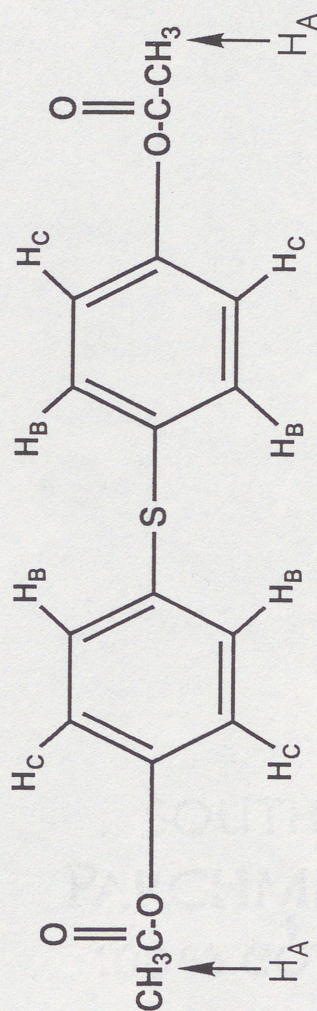
H_A

H_B

H_C

H_D

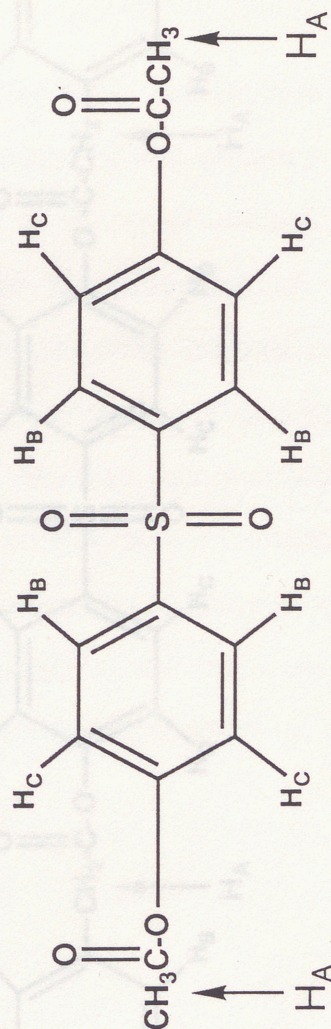
Table 6
NMR Chemical Shifts for A-5



<u>Proton</u>	<u>Chemical Shift</u>
H _A	2.295
H _B	7.043
H _C	7.357

Table 7

NMR Chemical Shifts for A-7

Proton H_A H_B H_C Chemical Shift

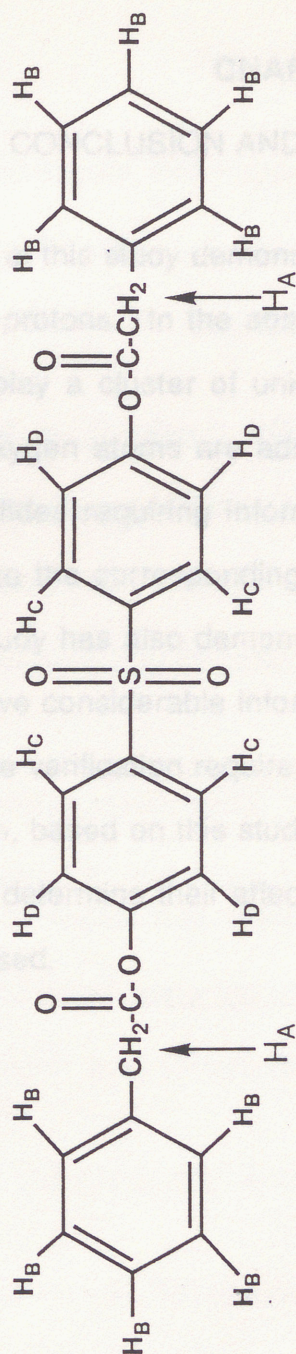
2.314

7.946

7.236

Table 8

NMR Chemical Shifts for A-9

ProtonH_A H_B H_C H_DChemical Shift1.680
7.234
7.918
7.365

CHAPTER 5

CONCLUSION AND RECOMMENDATION

2 The results of this study demonstrate the utility of 4, 4' - Sulfonyldiphenol in identifying ring protons. In the absence of the oxygens of the sulfonyl, the NMR spectra display a cluster of unidentifiable aromatic protons. Once the electronegative oxygen atoms are added, the protons are clearly discernible. Thus, organic sulfides requiring information on protons near the sulfur atom may be oxidized to the corresponding sulfonyl to gain a clear picture of their positions. This study has also demonstrated that while spectral data from one instrument may give considerable information about the structure of an organic molecule, complete verification requires a combination of analytical techniques. A recommendation, based on this study, would be to prepare a series of esters of the diphenol to determine their affect on the chemical shifts, as the length of ester chain increased.

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