Synthesis And Properties Of Thieno And Thianaphthenothiapyrylium Perchlorates.

Citation

HAMEL, COLEMAN RODNEY. *Synthesis And Properties Of Thieno And Thianaphthenothiapyrylium Perchlorates.* 1969, https://preserve.lehigh.edu/lehigh-scholarship/graduate-publications-theses-dissertations/theses-dissertations/synthesis-30.

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HAMEL, Coleman Rodney, 1937-
SYNTHESIS AND PROPERTIES OF THIENO
AND THIANAPHTHENOTHIAPYRYLIUM
PERCHLORATES.

Lehigh University, Ph.D., 1969
Chemistry, organic

University Microfilms, Inc., Ann Arbor, Michigan

SYNTHESIS AND PROPERTIES OF
THIENO AND THIANAPHTHENOTHIAPYRYLIUM PERCHLORATES

by

Coleman R.odney Hamel

A DISSERTATION

Presented to the Graduate Faculty

of Lehigh University

in Candidacy for the Degree of

Doctor of Philosophy

Lehigh University

1969

CERTIFICATE OF PRESENTATION

This dissertation is respectfully submitted to the Graduate Faculty of Lehigh University, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

Coleman R. Hamel

Coleman R. Hamel

CERTIFICATE OF APPROVAL

Approved and recommended for acceptance as a dissertation in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

May 15, 1969
Date

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Professor in Charge

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ACKNOWLEDGEMENTS

The author wishes to thank Dr. Thomas E. Young for suggesting the problem and for his concern and advice during the course of this research.

In addition, the author wishes to express his appreciation to the late Dr. Velmer B. Fish for performing the elemental analyses, to Dr. James Sturm for the mass spectrum, and to Mr. James Stuart for assistance with the polarography experiments.

The author is indebted to the National Science Foundation for the financial support of this research in the form of a Traineeship. Lehigh University is to be thanked for previous financial aid in the form of a Teaching Assistantship and the Wm. S. Merrill Fellowship.

This thesis is dedicated to the author's wife.

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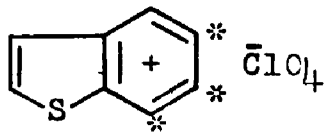
ABSTRACT

The synthesis of the isomeric thieno and thianaphthenothiapyrylium perchlorate salts, (1) and (2), with the sulfur atom at each of the starred positions, respectively, has been accomplished. To aid in the interpretation of the nmr spectra, three methyl substituted salts were also synthesized. The nmr spectra indicate that the compounds exist in the form as in (3) with the positive charge mainly on the thiapyrylium sulfur. However, canonical form (3a) does make some contribution to the overall structure since H-6 and H-7 are shifted downfield in the nmr spectrum from the corresponding protons in thiophene itself. A correlation of the observed ^1L_b (π-π^*) transitions in the electronic spectra with the transition energies calculated from Hückel Molecular Orbital theory using previously established coulombic and resonance integral parameters for thionium sulfur was not found as it was in the polynuclear hydrocarbon thiapyrylium series. Similarly, the



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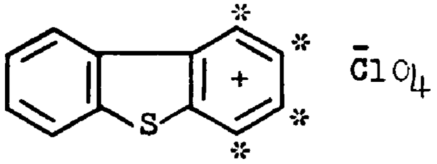

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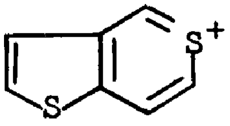

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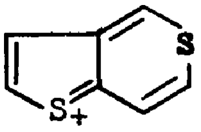
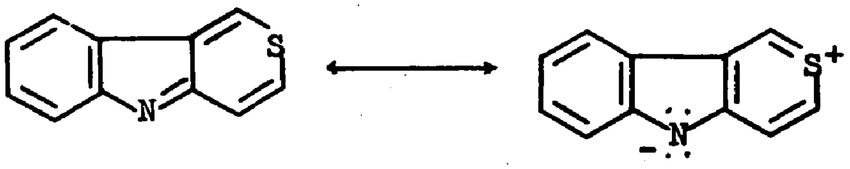


3a

polarographic half-wave potentials for these compounds did not correlate with the energies of the lowest vacant molecular orbitals. The half-wave potentials for six known polynuclear hydrocarbon thiapyrylium salts were also determined and did show a correlation with the calculated energies of the lowest vacant molecular orbitals. Comparison of the calculated electron densities and the nmr spectra yielded no quantitative correlation, although in each case the most deshielded proton is associated with the lowest electron density.

Reactions of thiapyrylium salts with phenyllithium have been reported to yield products different from those obtained in reactions with Grignard reagents. Attempted reactions with thieno[3,2-c]thiapyrylium perchlorate yielded only gums and tars.

Four substituted thiapyrano[4,3-b]indoles (4) were synthesized. Their nmr spectra add support to the thiapyrylium character of the sulfur containing ring as in the canonical form (4a).



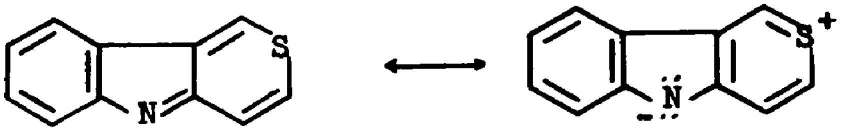
4 4a

INTRODUCTION

Several benzologs of thiapyrylium perchlorate have been synthesized[1]. Excellent correlations of their visible and ultraviolet spectra with the lowest Hückel Molecular Orbital Theory (HMO) transition energies have been obtained. Similar results have been shown for azines[2], some substituted pyrylium salts[3], and other heterocyclic compounds[4]. Although empirical linear correlations of π-electron densities with proton chemical shifts of mononuclear nitrogen heterocycles have been reported[5], and reliable methods for prediction of ring-current effects in polynuclear aromatic hydrocarbons have also appeared[6], additional contributions to resonance shifts owing to anisotropic effects of heteroatoms in polycondensed systems are not easily evaluated[7]. No quantitative correlations of the nmr shifts of the thiapyrylium perchlorate benzologs with the calculated electron densities could be made[8]. In each case, however, the proton adjacent to the thionium sulfur exhibited an unusually large downfield shift attributed to the high electronegativity of the thionium sulfur.

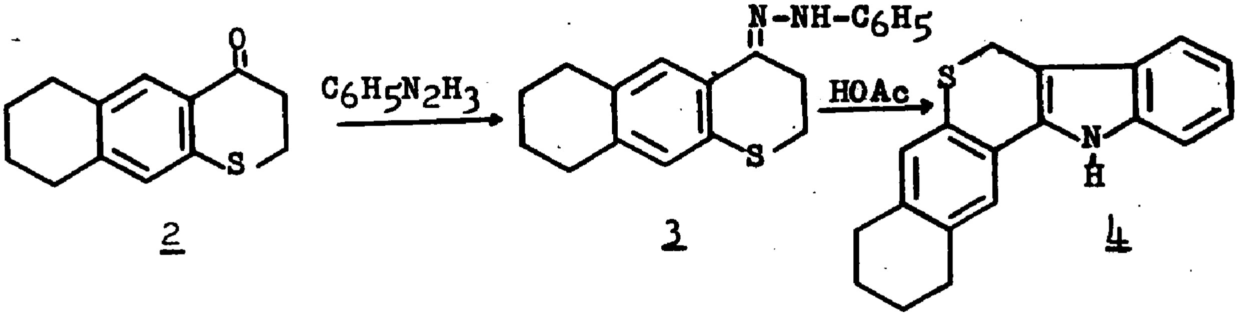
Other types of correlations, _e.g._ polarographic half-wave reduction potentials with the energy of the lowest vacant molecular orbitals or conversely, polarographic half wave oxidation potentials with the energy of the highest occupied molecular orbitals, have been found for aromatic hydrocarbons[9].

Heterocyclic systems derived from benzologs of the thiapyrylium salts by replacing two vinyl carbons with a nitrogen atom as in thiapyrano[4,3-b]indole (1) also show an unusually large downfield shift for the proton adjacent to the thionium center[10]. The interpretation of this phenomenon is that the dipolar canonical form (1a), where each ring tends toward the aromatic sextet condition enhancing the stability of the resulting π-system, contributes greatly to the ground state structure.



1 1a

The first of these systems reported was the 1,2,3,4-tetrahydronaphth[2,3-b]indolo[2,3-d]thiapyran (6)[10]. It was synthesized from the ketone (2) by forming the phenylhydrazone (3) which was cyclized to the indole (4) in boiling glacial acetic acid. Abstraction of a hydride ion by trityl perchlorate yielded the perchlorate salt (5) which upon treatment with ammonia gave (6). Buu-Hoi and co-workers have synthesized the unsubstituted tetranuclear system and two higher benzologs[11,12].



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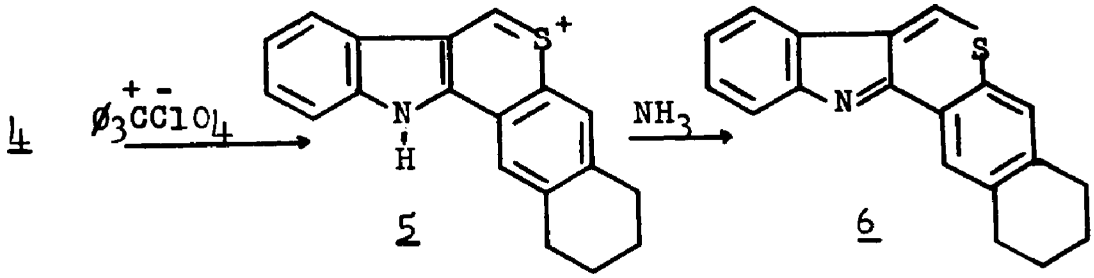
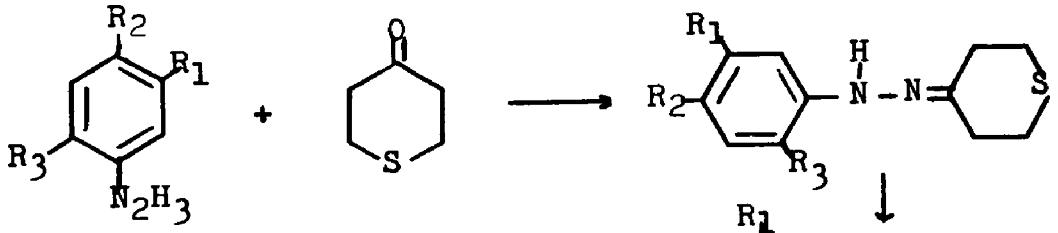
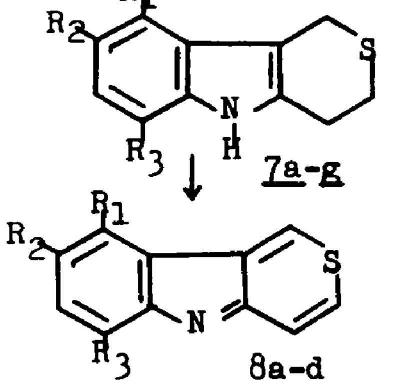


Some of the 1,3,4,5-tetrahydrothiapyrano[4,3-b]indoles (7a-g) have been synthesized by Fischer ring closure of the appropriate phenylhydrazone of thiacyclohexan-4-one[13].





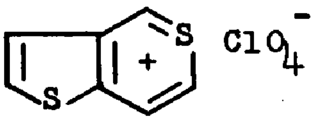
7a-g

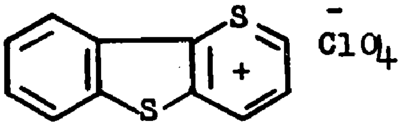
8a-d

7	R_1	R_2	R_3	Ref.
a	H	H	H	14
b	H	Br	H	14
c	H	Cl	H	15
d	H	CH_3	H	16
e	CH_3	H	CH_3	15
f	H	CH_3O	H	15
g	H	NO_2	H	15

Dehydrogenation of 7a,b and d by chloranil in refluxing xylene gave the corresponding thiapyrano[4,3-b]indoles (8a, b and d)[16], while 8c[16] was obtained using dicyanodichloroquinone as the dehydrogenating agent. In this work four new thiapyrano[4,3-b]indoles have been synthesized whose nmr spectra add support to the thiapyrylium character of the sulfur containing ring as in 1a.

Similarly, synthesis of the corresponding compounds with a sulfur atom replacing the nitrogen should result in a series of thienothiapyrylium and thianaphthenothiapyrylium salts, both of which were new classes of compounds when this work was begun. Since, in these compounds, differing locations of the sulfur atom in the thiapyran ring would still yield thiapyrylium salts, all of the isomeric compounds with the sulfur atom at the various positions could be synthesized and their properties compared. An isomer of each series is illustrated below.



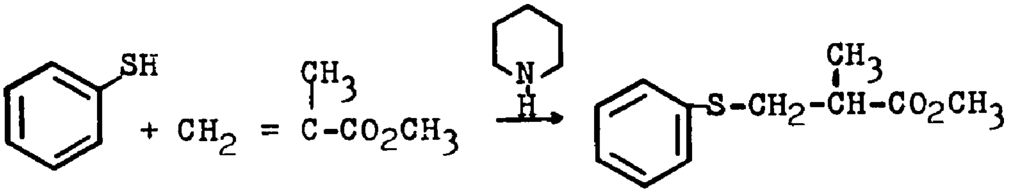


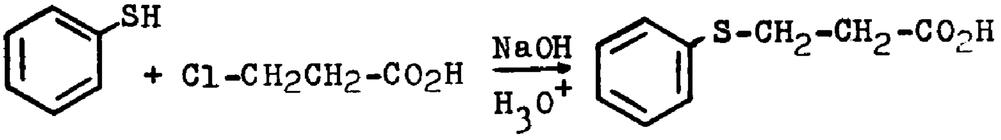
In these series of compounds, the polarographic, nmr, visible and ultraviolet spectral correlations with HMO theory could be tested. In the HMO calculations for these systems, the same parameters would be used for both sulfur atoms and the success or failure of these correlations would provide an excellent test of the previously developed parameters for thiapyrylium sulfur. Therefore the synthesis of these compounds was undertaken.

The problem of synthesizing the various thieno- and thianaphthenothiapyrylium salts initially involves substituting a sulfur for a carbon atom in the required position in a 4-Ar-butyric acid. After these compounds were obtained, cyclization to the intermediate ketone, followed by reduction to the alcohol and aromatization with trityl perchlorate, provided the salts.

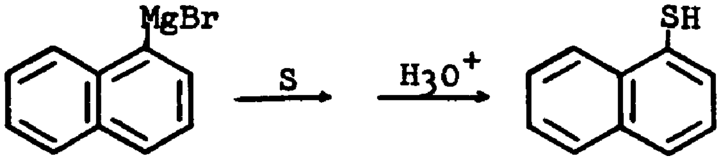
Two general pathways involving halogen displacement are available. The first involves placing the sulfur atom on the appropriately substituted aromatic compound as Ar-SH or Ar-CH$_2$-SH and then using the sulfur atom as an anion to displace halogen or add to a double bond in the acid or ester with the prerequisite number of carbon atoms needed to form a six-membered ring upon cyclization. Conversely, a mercapto acid as the dianion could be used to displace a halogen from ArCH$_2$X, again yielding the required acid. Examples of all of these types of reactions are known with the corresponding benzene or naphthalene compounds.

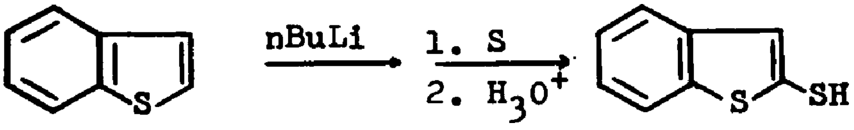
3-Arylthio-propionic acids have been prepared from the reaction of an appropriate arylthiolate ion with 3-chloropropionic acid[17], β-propiolactone[18], methyl acrylate[19] (after ester hydrolysis) and crotonic acid[20] as illustrated below:



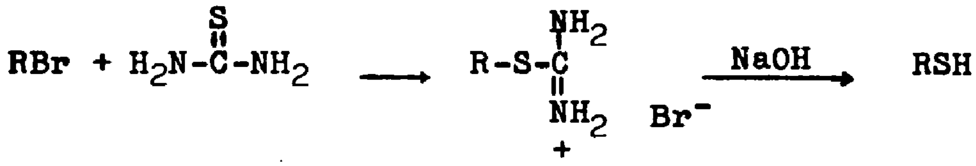


Aromatic thiols (ArSH) can be synthesized by treatment of the Grignard reagent with elemental sulfur and subsequent hydrolysis[21]. Another preparation involves reaction of aromatic compounds with n-butyl lithium to give the litho derivative and the use of sulfur as with the Grignard Reagent[22].



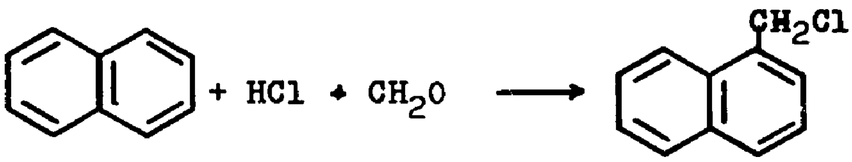


The formation of $R-CH_2-SH$ compounds from the corresponding $R-CH_2X$ compound through the hydrolysis of the intermediate isothiuronium halide is well known[23]. Although both of the 2- and 3-thenylthiols are known[24,25], they were not used in this study, as the reaction of the precursor halides with the thiolate anion of mercaptoacetic acid provided the required sulfur moiety.

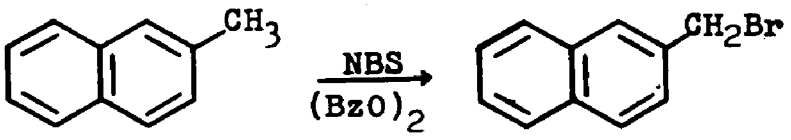


$$RBr + H_2N-\overset{\overset{S}{\|}}{C}-NH_2 \longrightarrow R-S-\underset{\underset{+}{NH_2}}{\overset{NH_2}{\underset{\|}{C}}}\quad Br^- \xrightarrow{NaOH} RSH$$

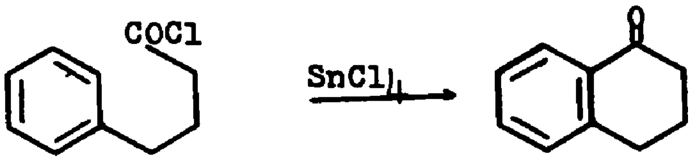
The preparation of the required halogen compounds, $Ar-CH_2X$, was accomplished using methods analogous to those in the non-heterocyclic series. Those compounds which readily undergo electrophilic substitution in the required position were chloromethylated using formaldehyde and hydrochloric acid[26].



The use of N-bromosuccinimide (NBS) to introduce a bromine atom into an aromatic methyl group provided a route to those compounds $ArCH_2Br$[27].

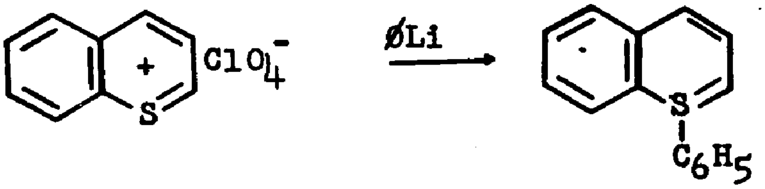


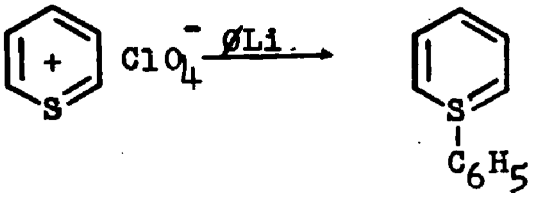
Ring closure of 3-aryl thiopropionic acids have been carried out using P_2O_5[19], cold concentrated sulfuric acid[28], polyphosphoric acid[29], and the action of stannic chloride on the acid chlorides[30].



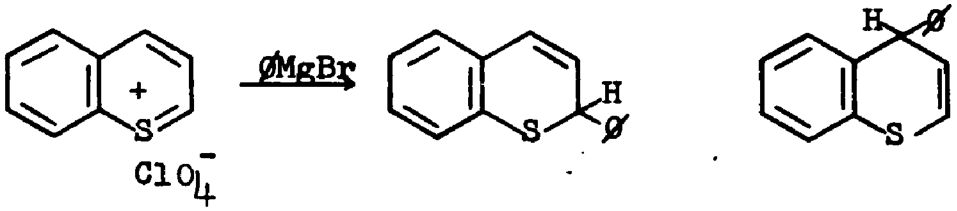
Adaptations of the foregoing methods were used to produce the precursors to the thiapyrylium salts in this study.

Thiapyrylium salts have been reported to react with phenyl lithium to yield aromatic tetravalent sulfur[31,32],

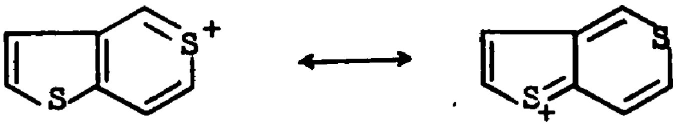




In contrast, Grignard reagents react with thiapyrylium salts at positions ortho or para to the sulfur atom[33].



Reaction of thieno[3,2-c]thiapyrylium perchlorate (9) and its 3-methyl analog (10) would provide an excellent test of these reactions since each proton is distinguishable in the nmr spectra. The changes in the chemical shift and the number of protons in the nmr spectra would enable the modes of addition to be distinguished. Since both sulfur atoms are equivalent, *viz.*



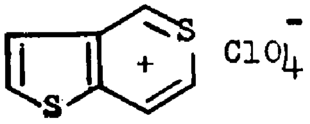
it could possibly distinguish which sulfur atom was being attacked by the phenyl lithium as well as which ring was being attacked by the Grignard Reagent.

RESULTS AND DISCUSSION

In this dissertation, the synthesis of nine new thiapyrylium perchlorates (9-17) is reported. A tenth salt (18) appeared in the literature as it was simultaneously synthesized in the laboratory[34]. The remaining thienothiapyrylium perchlorate isomer (19) was not prepared, since it was reported before the proposed synthetic pathway was undertaken[34]. Hückel molecular orbital calculations were made for the eight basic isomeric systems.

Four new thiapyrano[4,3-b]indoles (20-23) and a tetrahydrothiapyrano[4,3-b]indole (24) were synthesized to complement the previously synthesized thiapyrano[4,3-b]indoles.

Thienothiapyrylium perchlorates



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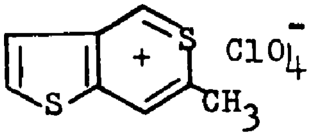

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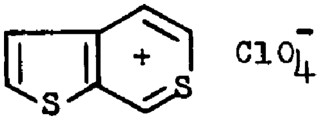

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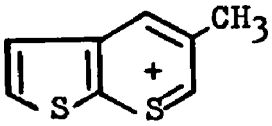

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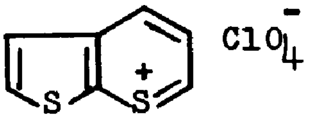

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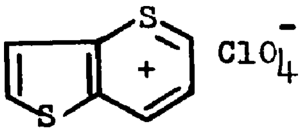

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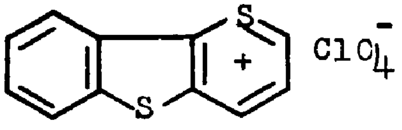
Thianaphthenothiapyrylium Perchlorates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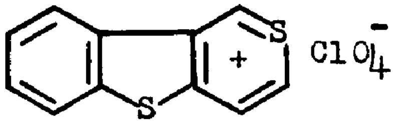
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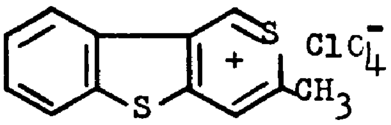
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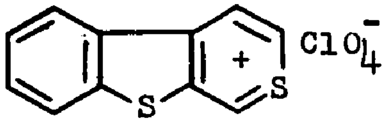
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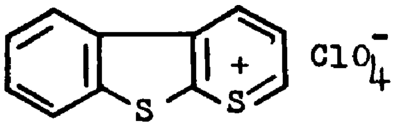
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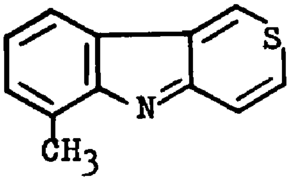
Thiapyrano[4,3-b]indoles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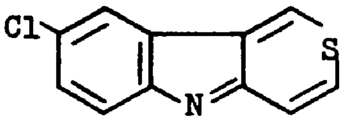
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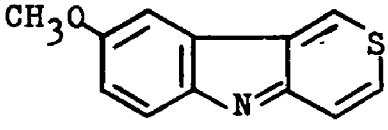
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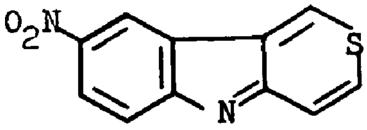
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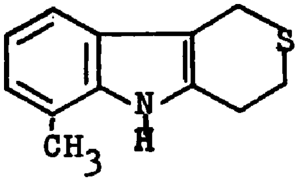
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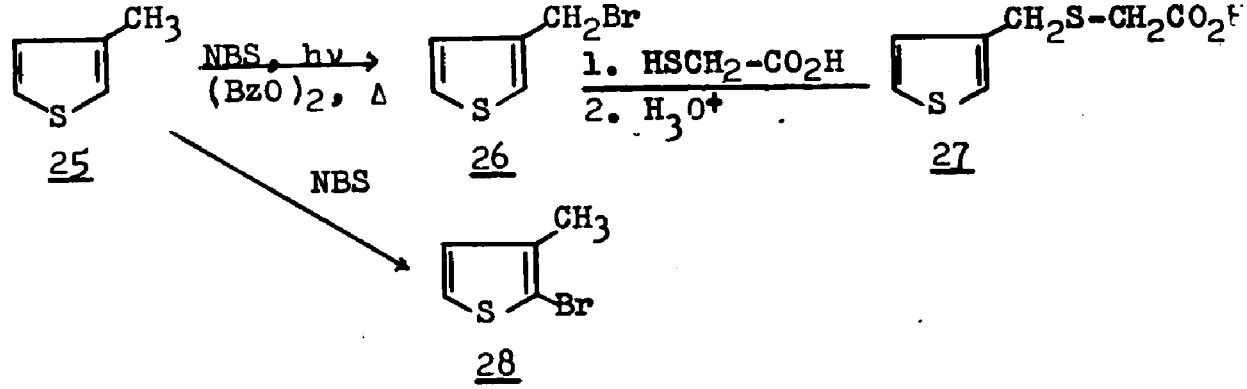
I. Syntheses

A. Synthesis of the Thienothiapyrylium Perchlorates

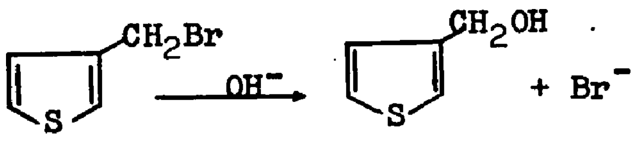
Thieno[3,2-c]thiapyrylium perchlorate (9) was the first of the new salts to be synthesized. The sequence undertaken involved initial bromination of 3-methylthiophene (25) on the methyl group with N-bromosuccinimide[35] (NBS) followed by displacement of the halogen with the thiolate anion from mercaptoacetic acid.



The preparation of 3-bromomethylthiophene (26) was fraught with difficulty. In the initial experiment, the mixing together of 3-methylthiophene and the NBS before the solvent and benzoyl peroxide were added resulted in a reaction yielding 43% of 2-bromo-3-methylthiophene (28) as shown from nmr studies[35]. The nmr spectrum of 2-bromo-3-methylthiophene in carbon tetrachloride consisted of δ 7.02 (d, 1, J = 5.5 Hz, H-4), 6.65 (d, 1, J = 5.5 Hz, H-3) and 2.13 (s, 3, $C\underline{H}_3$) ppm in contrast to that of the 2- and 3-methylthiophenes where the resonances of the aromatic protons occur as multiplets at about 7 ppm. The introduction of a bromine atom in an aromatic methyl group also shifts the methylene resonance downfield; *cf.* $C_6H_5C\underline{H}_2Br$ = 4.41 ppm *vs.* 4.33 ppm for $C\underline{H}_2Br$ in 3-bromomethylthiophene as compared to 2.55 ppm for $C\underline{H}_3$ in toluene *vs.* 2.20 ppm in 3-methylthiophene[36].

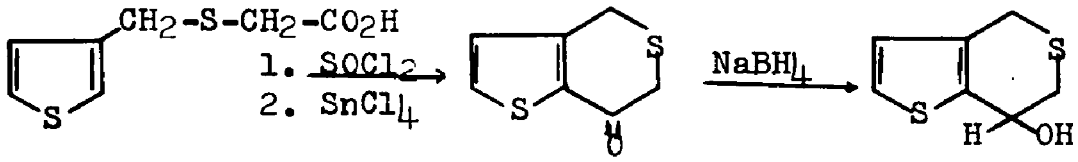
After several experiments, the final procedure which produced pure 3-bromomethylthiophene involved: (1) use of freshly recrystallized NBS dried over P_2O_5 at 0.05 mm for four hours;[37] (2) ultraviolet irradiation of the reaction mixture during the addition of the NBS admixed with the benzoyl peroxide and for the five minute reflux afterward. The product was pure by nmr spectroscopy. Other similar procedures yielded products contaminated with ten percent of 2-bromo-3-methylthiophene[38,39,40]. The lachrymatory powers of 3-bromomethylthiophene have not been exaggerated.

The S-(3-thenyl)-mercaptoacetic acid[25] (27) was prepared by reacting the 3-bromomethylthiophene with mercaptoacetic acid in the presence of two equivalents of potassium hydroxide and stirring the two-phase mixture overnight at 74°. Since the organic layer remaining after this treatment possessed a hydrogen bonded hydroxyl group absorption in the infrared spectrum, further reactions of this type were usually run in dry glyme to eliminate the possibility of hydroxyl attack yielding 3-hydroxymethylthiophene. The necessary mercaptoacetic anion was generated with two equivalents of sodium methoxide.



Cyclization of the acid (27) to the ketone (29) also proved to be a problem. Experiments using polyphosphoric acid yielded a gum. The use of phosphorous pentoxide on

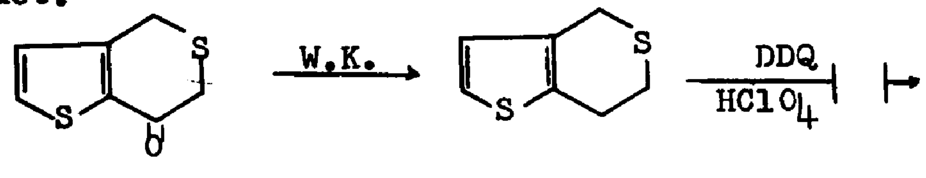
Celite in refluxing benzene, a procedure which worked well in the naphthalene series[41], resulted in no isolable product. It was found that the ketone could be prepared in reasonable yield and quality by the action of anhydrous stannic chloride on the acid chloride. Since this reaction was always accompanied by considerable tar formation, it was thought that isolation of the acid chloride might improve the reaction. However, no improvement of yield or quality was noted upon distillation of the acid chloride and then further reaction with stannic chloride.



27 29 30

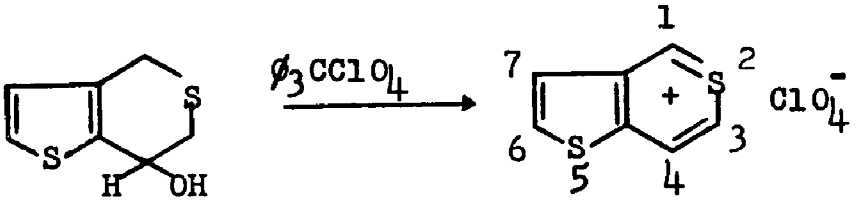
The ketone (29) was reduced to the alcohol (30) with sodium borohydride in refluxing isopropanol. Previous experiments with methanol as a solvent did not yield the alcohol. No reduction took place and the ketone decomposed under the reaction conditions. Presumably the sodium borohydride decomposed in the solvent before effecting reduction of the ketone[42]. In this work, the reductions were run on 1-2 g quantities of the ketone. Increasing the amount of ketone resulted in a lower yield (90% → 65-70%) even though the amount of solvent was proportionately increased. The use of lithium aluminum hydride in ether also resulted in lower yield (77%).

Wolff-Kishner reduction of the ketone gave a product (31) with no carbonyl absorption in the infrared spectrum. Its infrared spectrum was identical with that in the literature[25]. Attempted dehydrogenation with dichlorodicyanoquinone (DDQ) and perchloric acid did not produce an isolable product.



29 31

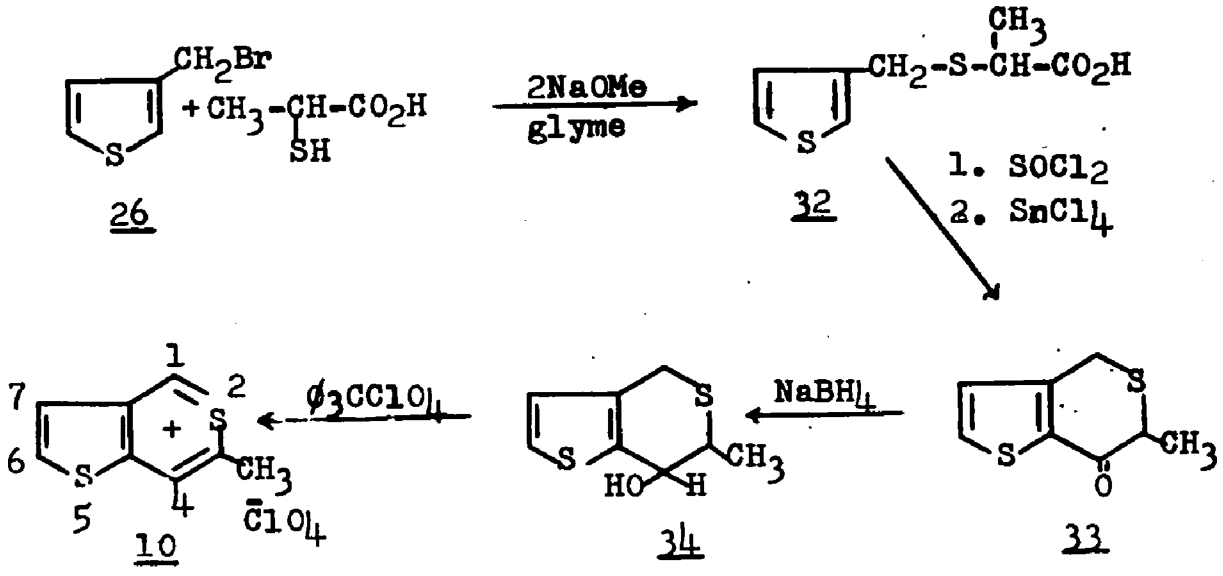
Reaction of the alcohol (30) with trityl perchlorate produced thieno[3,2-c]thiapyrylium perchlorate (9), a beige salt, in 20% overall yield after several recrystallizations from glacial acetic acid and an initial carbon treatment. Later on, the same salt was prepared with difficulty from the alcohol (30) using DDQ as the dehydrogenating agent and perchloric acid to produce the salt. Thereafter the salts were prepared using trityl perchlorate as the aromatizing agent.



30 9

The nmr spectrum of (9) showed a multiplet at δ 10.60, integrating for one hydrogen and another multiplet at δ 9.43, integrating for two hydrogens. To clarify the situation as to which two hydrogens were superimposed, the corresponding salts with a methyl group in the 3-position and a benz-ring in the 6-7 position were synthesized. The nmr data throughout these sequences also allowed unambiguous assignments of the spectra in the non-methyl series.

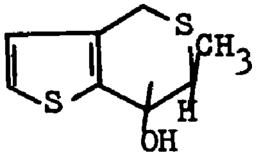
To obtain the 3-methyl salt, thiolactic acid was stirred with two equivalents of sodium methoxide in dry glyme until the thick, white precipitate was broken up. 3-Bromomethylthiophene was added to the mixture, which was stirred at reflux overnight. Upon workup, 74% of S-(3-thenyl)-thiolactic acid (32) was obtained. Cyclization to the ketone (33) was accomplished using the acid chloride-stannic chloride technique. The ketone was reduced by sodium borohydride to the alcohol (34) which was aromatized using trityl perchlorate to produce 3-methylthieno[3,2-c]thiapyrylium perchlorate (10), a beige salt which turned faintly blue on standing. Comparison of the nmr spectra of the salts, (9) and (10), and the corresponding benz-ring salts, (14) and (15), showed that the overlapping proton resonances in (9) are an H-3, H-4 combination. (See discussion of nmr spectra of salts.)



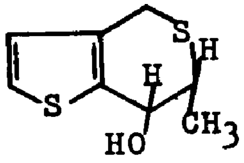
The nmr spectrum of S-(3-thenyl)-mercaptoacetic acid (27) showed two singlets each integrating for two protons, at δ 3.83 and 3.00 ppm. Comparison with the spectrum of the S-(3-thenyl)-thiolactic acid (32), which showed a quartet at 3.15 ppm, integrating for one proton, indicated that the upfield resonance at 3.00 ppm belonged to the $SC\underline{H}_2CO_2H$ methylene group. In the same spectrum (for 32), the remaining methylene protons are no longer equivalent and exhibit geminal coupling of 14 Hz because of the asymmetry of the $-CH(CH_3)CO_2H$ moiety.

Analogously, the assignments were made for the ketones (29) and (33). For (29), the lower field doublet at 3.85 ppm was assigned to the $-C\underline{H}_2S$ methylene group and the 3.48 ppm resonance was assigned to the $SC\underline{H}_2CO_2H$ moiety. In the spectrum of (33), the multiplet centered at 3.68 ppm is assigned to the $C\underline{H}_2SCH$ grouping. These spectra are in agreement with the literature spectra which appeared during the course of this work[25].

The interpretation of the spectrum of the alcohol (30) was quite straightforward (see Experimental). The reduction of the methylketone (33) apparently produced a mixture of *cis* and *trans* isomers as indicated by the nmr spectrum and wide melting range (64-75°) of the isolated waxy solid. The nmr spectrum consisted of a series of multiplets. The methyl group resonances appeared as a quartet or two doublets with $J = 7$ Hz indicating two environments for the methyl grouping as in (34a) and (34b).

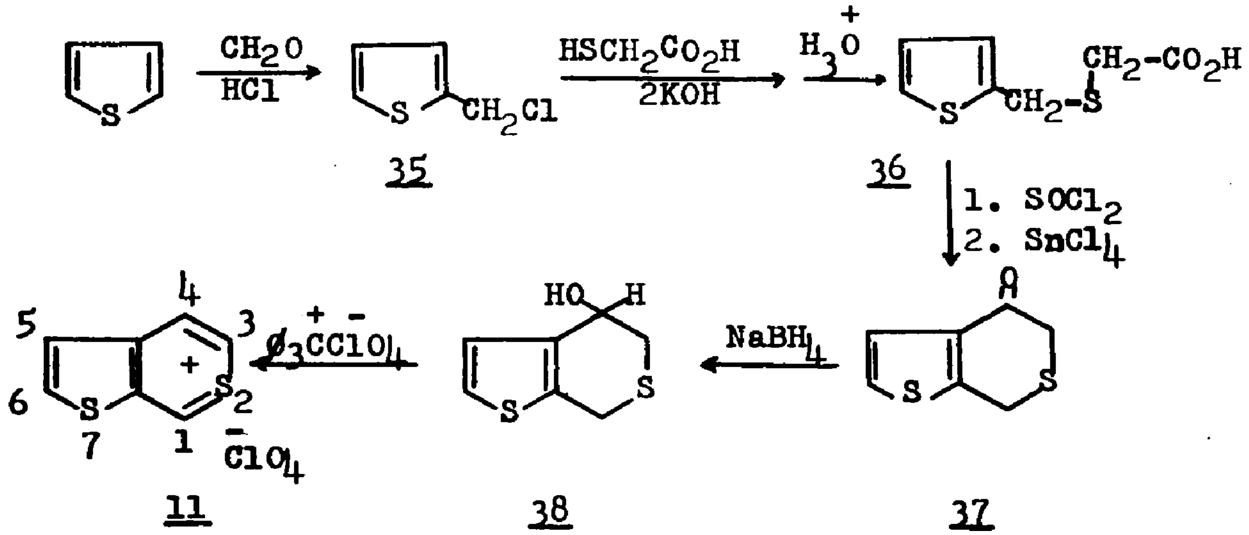


34a

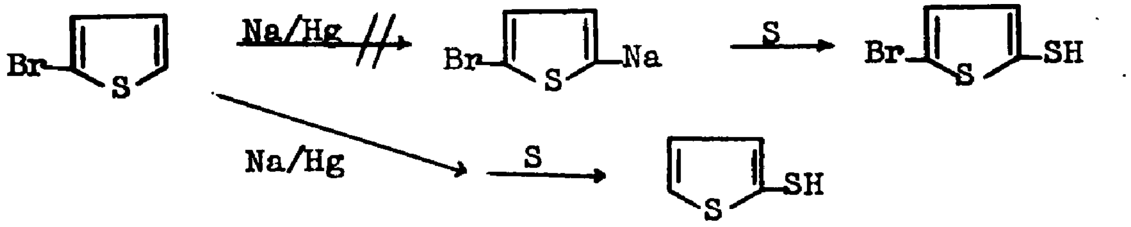


34b

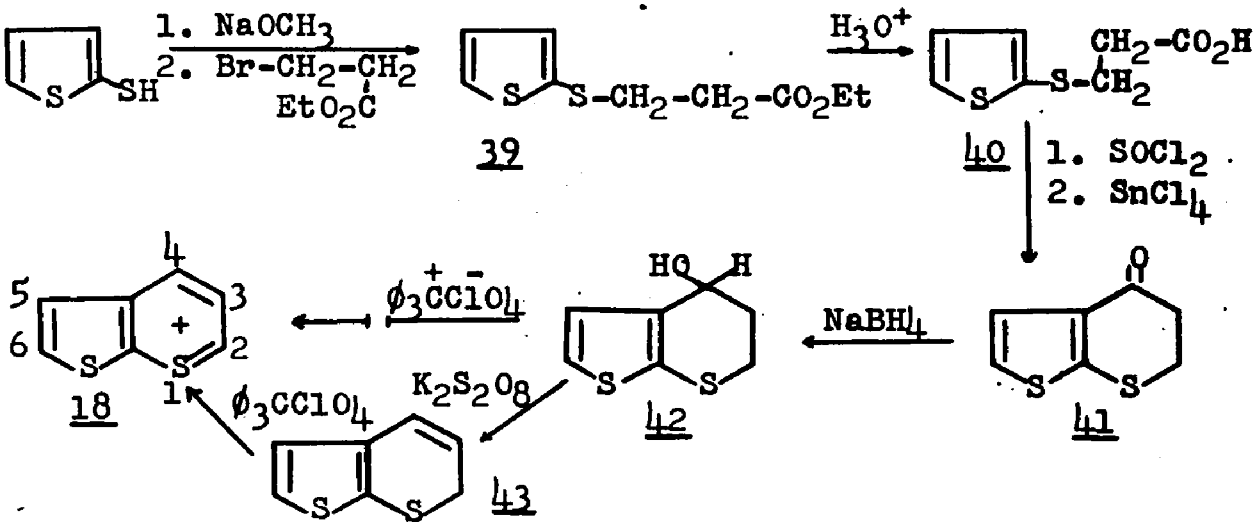
The corresponding isomer with the sulfur atom also at a position β to the thiophene ring was synthesized in the following manner. Thiophene reacted with formaldehyde in the presence of hydrogen chloride gas to give 2-chloromethylthiophene (35)[43]. Experiments using Hartough's alternate procedure with concentrated hydrochloric acid instead of gaseous hydrochloric acid produced little or no product[43]. Reaction of the 2-thenyl chloride with mercaptoacetic acid and two equivalents of potassium hydroxide in water produced S-(2-thenyl)-mercaptoacetic acid (36) in 46.5% yield. Cyclization to the ketone (37) via the acid chloride and stannic chloride was accomplished with difficulty. Since the β-positions in thiophene are much less reactive to electrophilic substitution[44], much tar formation occurred, presumably by the electrophilic attack at the other α (5) position in another molecule. Reduction with sodium borohydride produced the alcohol (38), which reacted with trityl perchlorate to produce the vivid yellow salt, thieno[2,3-c]thiapyrylium perchlorate (11). The nmr spectral assignments were made using the knowledge gained from the previous series.



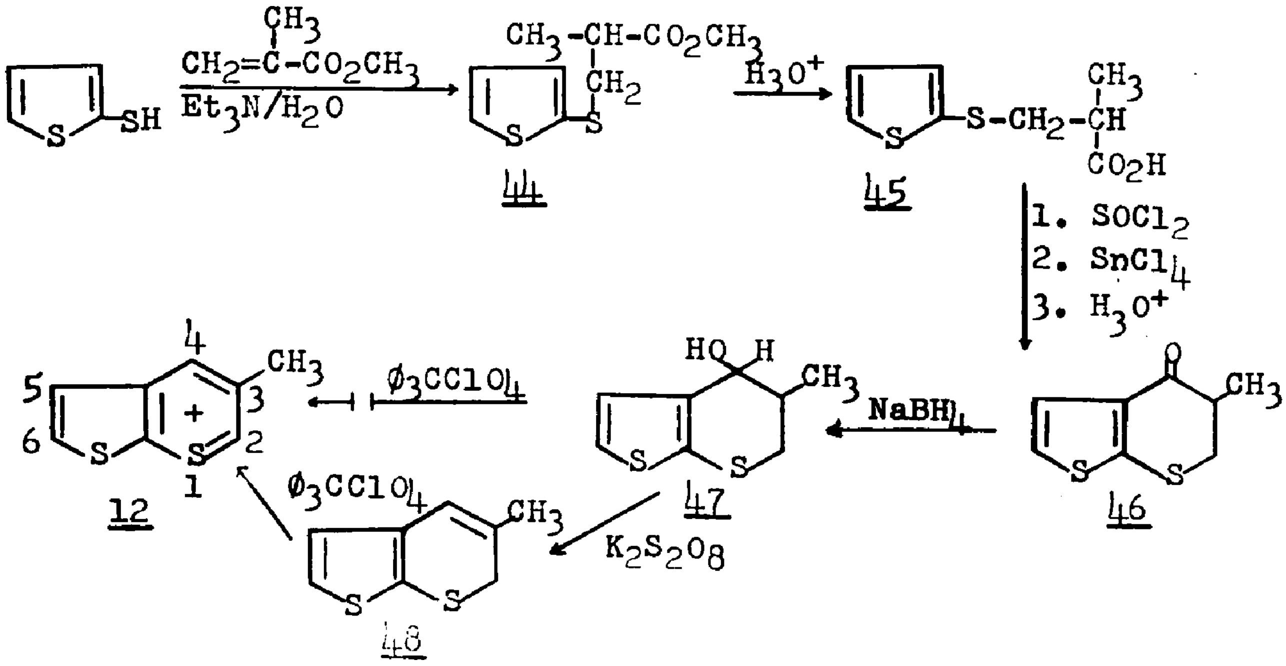
Since difficulty had been experienced in cyclizing the acids to the β-position in the thiophene nucleus, a blocking group for the other α (5) position was sought which could be removed after cyclization. An attempt was made to form the sodium salt of 2-bromothiophene using a sodium amalgam as had been done with 2-chlorothiophene and was also stated to occur with 2-bromothiophene[45]. Further reaction with sulfur would yield 5-bromo-2-thiophenethiol. However, reduction of the bromine occurred and the desired 5-substituted product was not obtained; only the unsubstituted thiol was found.



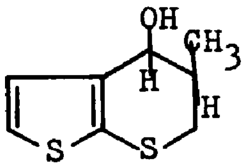
The synthesis of the isomer (18) with the sulfur in the position α to the ring proceeded as follows. Thiophene was lithiated using n-butyl lithium and sulfur was added to the reaction mixture to yield, after acidification, 2-thiophenethiol. The nmr spectrum showed an allylic coupling of the -S-H of 1 Hz. Reaction of the 2-thiophenethiol with ethyl 3-bromopropionate yielded ethyl S-(2-thienyl)-3-mercaptopropionate (39). Hydrolysis with refluxing 50% hydrochloric acid gave S-(2-thienyl)-3-mercaptopropionic acid (40). Cyclization of the acid chloride with anhydrous stannic chloride yielded the ketone (41). Reduction with sodium borohydride in isopropanol gave the alcohol (42). Reaction of the alcohol with trityl perchlorate yielded a maroon solid from which neither starting material nor a product could be isolated. The salt was prepared by first dehydrating the alcohol with potassium pyrosulfate. Reaction of the resulting 2H-thieno[2,3-b]thiapyran[34] (43) with trityl perchlorate in acetonitrile produced the yellow-green salt, thieno[2,3-b]thiapyrylium perchlorate (18).



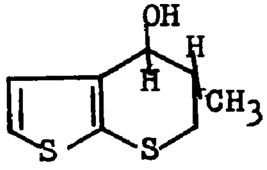
The 3-methyl derivative (12) was prepared simultaneously because of the common starting materials, so that an anticipated problem of distinguishing the protons in the nmr spectrum of (18) could be resolved. 2-Thiophenethiol reacted with methyl methacrylate in the presence of a triethylamine-water catalyst to yield methyl S-(2-thienyl)-3-mercapto-2-methylpropionate (44). Hydrolysis with refluxing 50% hydrochloric acid gave the acid (45). Cyclization of the acid chloride with stannic chloride gave the ketone (46). Reduction with sodium borohydride in isopropanol produced the alcohol (47). Reaction of the alcohol with trityl perchlorate in acetic acid-nitromethane produced a maroon solid from which neither starting material nor a product could be isolated. Dehydration with potassium pyrosulfate produced 3-methyl-2H-thieno[2,3-b]thiapyran (48), which, due to its instability in air, was immediately converted to the yellow salt, 3-methylthieno[2,3-b]thiapyrylium perchlorate (12) with trityl perchlorate in acetonitrile.



Comparison of the nmr spectra of the corresponding compounds for the two previous sequences resulted in the following assignments. The lower field methylene group resonance (where distinguishable) in the acids, ketones and alcohols was that of the Ar-C$\underline{H}_2$S moiety. The higher field methylene resonance disappeared as in the thieno[3,2-c]thiapyrylium perchlorate series and was replaced with a quartet or multiplet when the substitution of a methyl group was made. The alcohol (47) was again a mixture of *cis* and *trans* isomers as evidenced by a 47-75° melting range and the methyl group resonance appeared as two doublets with J = 7 Hz as derived from the two isomers (47a) and (47b).



47a



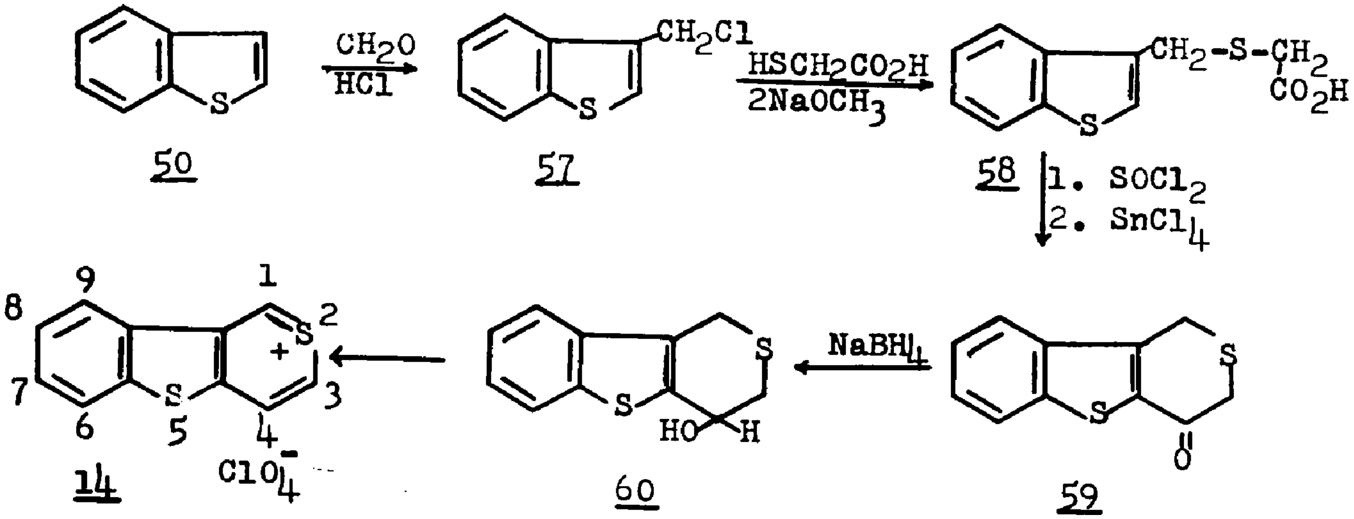
47b

The remaining isomer thieno[3,2-b]thiapyrylium perchlorate (19) with the thiapyrylium sulfur adjacent to carbon-3 in the thiophene molecule was not prepared for two reasons: The first was that it appeared in the literature as preparation was being attempted[34]; the second was that the initial reaction to produce 3-thiophenethiol produced 3-thenyl n-butyl sulfide (49) instead[46]. (See Experimental.) Therefore the literature nmr and ultraviolet-visible data were used as presented[34].

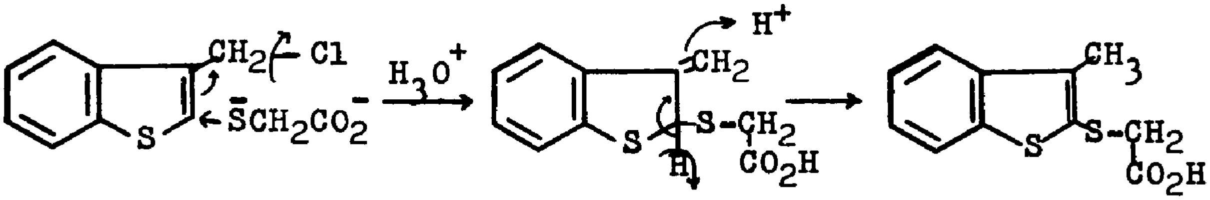
Thianaphthene (50) was brominated in chloroform to produce 3-bromothianaphthene[48] (51), which reacted with magnesium in ether in the presence of ethyl bromide. After some difficulty, the reaction proceeded and elemental sulfur was added slowly. Upon isolation, the product was a semi-solid, which possessed no infrared absorption at 2535 cm^{-1} (-SH). Since coupling products are often the result of side reactions of Grignard reagents[49], the material was treated with lithium aluminum hydride to reduce any disulfide present to the thiol. Distillation gave 27% of 3-mercaptothianapthene (52), whose nmr and infrared spectra were the same as the literature values[50]. The nmr spectrum showed an allylic coupling of 1 Hz in -S-H resonance.

The remainder of the sequence was accomplished without difficulty. Reaction of the 3-mercaptothianaphthene with 3-bromopropionic acid in absolute ethanol in the presence of sodium bicarbonate[34] yielded the acid (54). Cyclization to the ketone (55) was accomplished by the action of stannic chloride on the acid chloride. The alcohol (56) was prepared by sodium borohydride reduction. Reaction of the alcohol with trityl perchlorate in acetic acid-nitromethane yielded the green-yellow salt, thianaphtheno[3,2-b]thiapyrylium perchlorate (13).

Isomer (14) with the sulfur positioned β to the three carbon of thianaphthene was synthesized as follows:

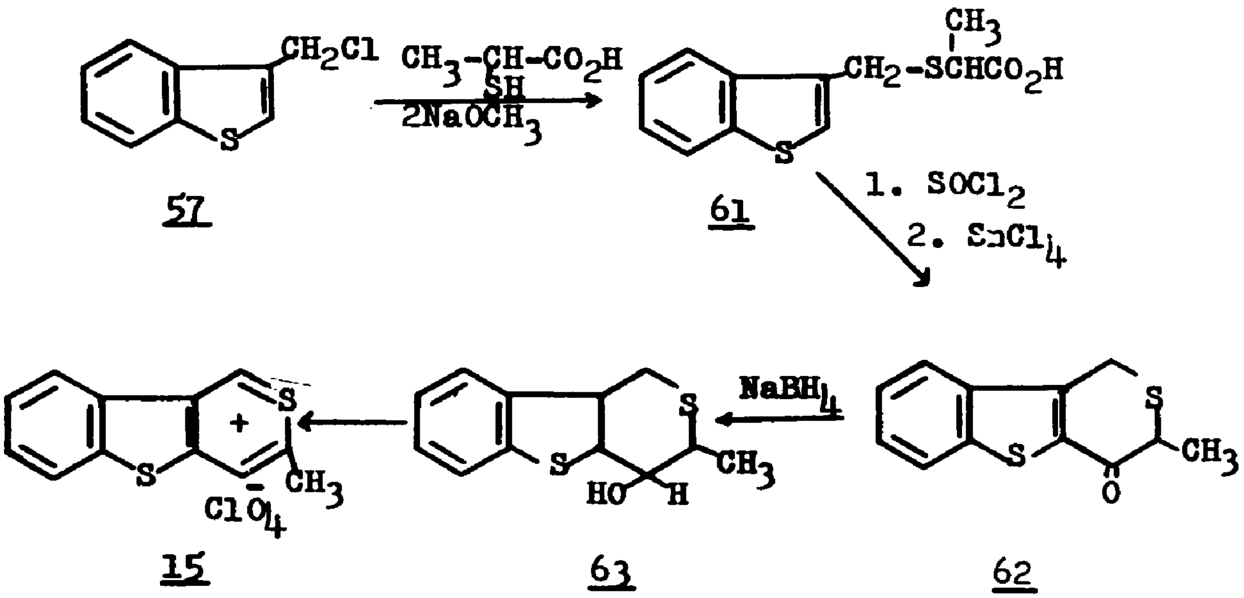


Thianaphthene was chloromethylated[51] and the 3-thianaphthenyl chloride (57) reacted with mercaptoacetic acid and two equivalents of sodium methoxide in dry glyme to produce the acid (58). Isolation of the acid initially produced a gummy solid. Extraction into boiling cyclohexane and subsequent purification yielded an analytical sample. The possibility that the reaction had proceeded by an SN2' mechanism[52] (see below) was dismissed when the nmr spectrum of the crude material was shown to be the same as that of the analytical sample.



Cyclization of the acid chloride with stannic chloride yielded the ketone (59) which was reduced to the alcohol (60). Reaction of the alcohol with trityl perchlorate yielded the ochre salt, thianaphtheno[3,2-c]thiapyrylium perchlorate (14).

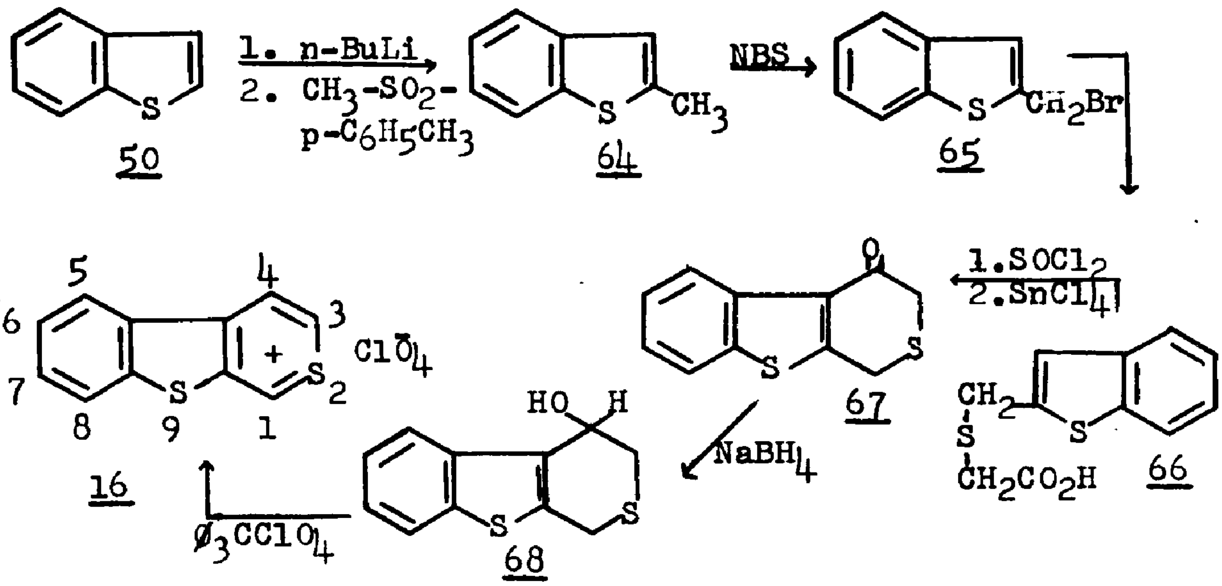
The green 3-methyl derivative, 3-methylthianaphtheno [3,2-c]thiapyrylium perchlorate, (15) was also prepared to aid in interpretation of the nmr spectra.



The 3-thianaphthenyl chloride (57) reacted with thiolactic acid in the presence of two equivalents of sodium methoxide to yield the acid (61). Cyclization of the acid chloride to the ketone (62) using stannic chloride proceeded without difficulty. Reduction with sodium borohydride gave the alcohol (63), which was aromatized with trityl perchlorate to the green salt, 3-methylthianaphtheno[3,2-c]thiapyrylium perchlorate, (15).

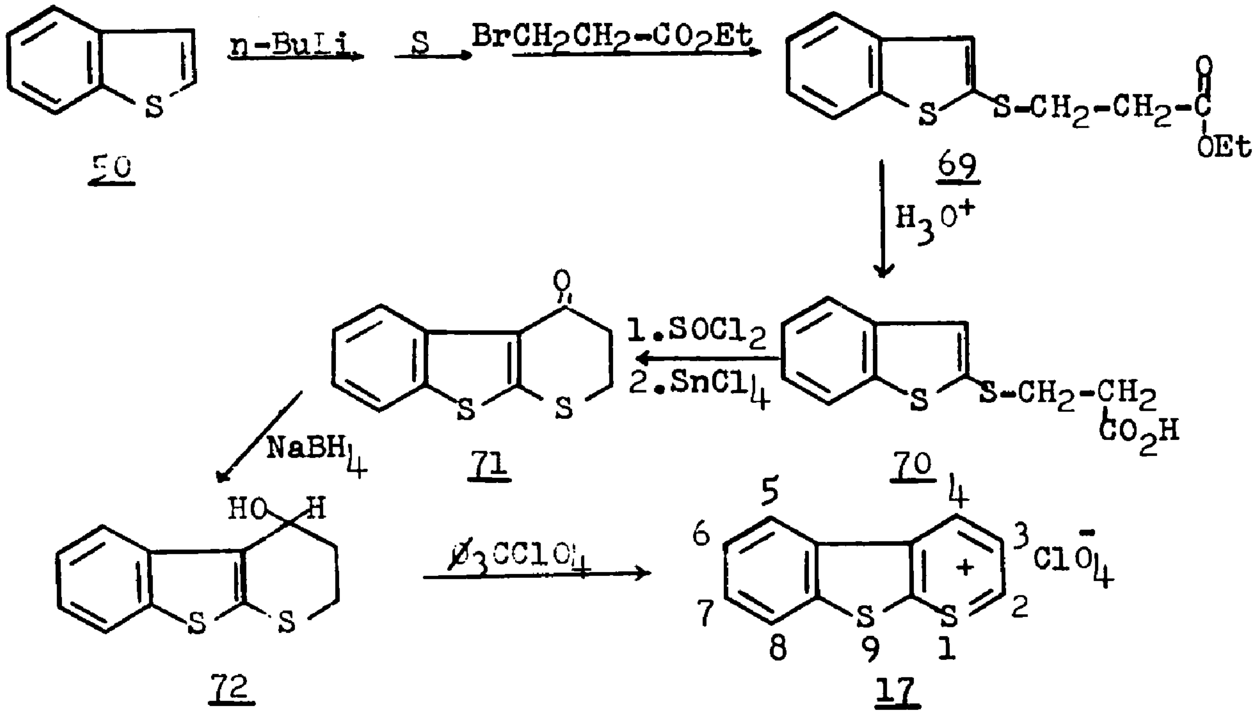
The nmr spectra of the acid (58), ketone (59) and alcohol (60) were compared to those of the corresponding methyl derivatives, (61), (62), and (63). In all cases the more downfield methylene resonance proved to be that of the Ar-C$\underline{H_2}$S moiety. The methyl-alcohol (63) was a mixture of isomers as evidenced by the melting range, 120-130°, and the nmr spectrum showed the methyl group as a multiplet.

Thianaphtheno[2,3-c]thiapyrylium perchlorate (16) was prepared from thianaphthene by reacting the 2-lithio salt with methyl p-toluenesulfonate to yield 2-methylthianaphthene (64)[22]. Bromination on the methyl group with NBS followed by displacement of the halogen with the thiolate anion of mercaptoacetic acid yielded the acid (66). The 2-bromomethylthianaphthene (65) was not pure even after two careful distillations as evidenced by the aromatic/aliphatic proton ratio of 3.65/1; calculated 2.5/1. The impurity was not starting material, since no methyl proton resonance showed in the nmr spectrum. The acid chloride was cyclized to the ketone (67) with stannic chloride and the ketone was reduced to the alcohol (68) with sodium borohydride. Aromatization with trityl perchlorate provided the bronze or copper colored salt (16).



The last isomer (17) was also prepared by lithiation of thianaphthene[22]. Sulfur was added to the reaction mixture, followed by ethyl 3-bromopropionate to yield the ester (69).

Hydrolysis of the ester with refluxing 50% hydrochloric acid gave the acid (70). Cyclization of the acid chloride with stannic chloride yielded the ketone (71), which was reduced to the alcohol (72) with sodium borohydride. The green salt, thianaphthieno[2,3-b]thiapyrylium perchlorate, (17) was prepared by reacting the alcohol with trityl perchlorate.

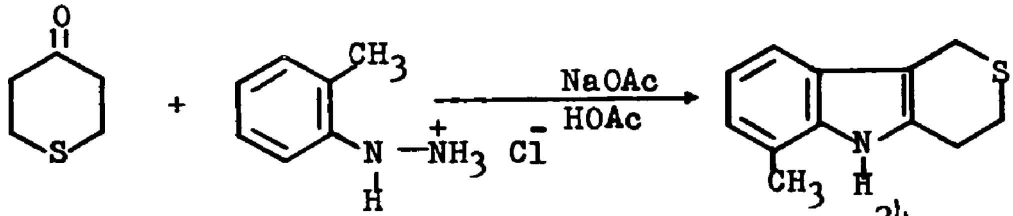


Grignard reagents are reported to react in a different manner with thiapyrylium salts than does phenyl lithium[31,32,33]. However, reaction of thieno[3,2-c]thiapyrylium perchlorate (9) with these reagents resulted in tars and oils from which no characterizable products could be isolated.

C. Synthesis of Thiapyrano[4,3-b]indoles

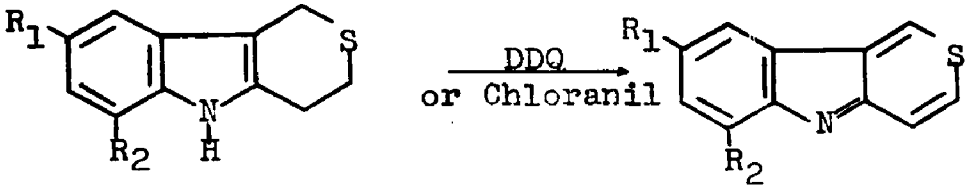
The thiapyrano[4,3-b]indoles were prepared by dehydrogenation of the 1,3,4,5-tetrahydrothiapyrano[4,3-b]indoles by reaction with DDQ in refluxing xylene followed by alkaline hydrolysis of the resulting complex. The 1,3,4,5-tetrahydrothiapyrano[4,3-b]indoles were obtained by condensation of the appropriately substituted phenylhydrazine and tetrahydro-1,4-thiapyrone in the presence of anhydrous sodium acetate in refluxing glacial acetic acid. The exception was the nitro compound, 7g. The condensation reaction yielded the tetrahydro-1,4-thiapyrone p-nitrophenylhydrazone, which underwent Fischer indolization when heated with concentrated hydrochloric acid[16].

In this work, 24 was synthesized by reacting o-tolylhydrazine hydrochloride and tetrahydro-1,4-thiapyrone.



24

The three 1,3,4,5-tetrahydrothiapyrano[4,3-b]indoles, 7c, 7f and 7g, were prepared by Ohnmacht[15]. Dehydrogenation with DDQ of 7f and 7g gave the thiapyrano[4,3-b]indoles, 22 and 23, in 2 and 15% yield, respectively. Treatment of 24 and 7c with chloranil gave the products 20 and 21 in 27 and 3% yields. Attempts to dehydrogenate 7f with 10% palladium on charcoal in refluxing decalin gave only recovered starting materials.



	R_1	R_2
24	H	CH_3
7c	Cl	H
7f	CH_3O	H
7g	NO_2	H

	R_1	R_2
20	H	CH_3
21	Cl	H
22	CH_3O	H
23	NO_2	H

The thiapyrano[4,3-b]indoles are stable, yellow-to-orange compounds. Their infrared spectra show no N-H stretching frequencies, and are otherwise not revealing except as fingerprints.

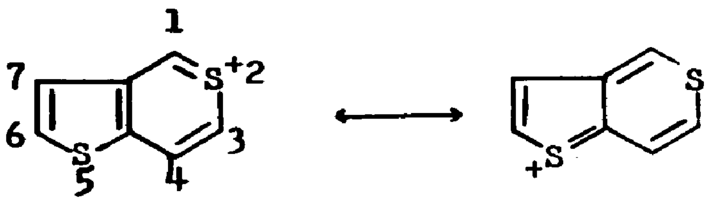
II. Discussion of Spectra

A. NMR Spectra

All spectra were obtained in deuteriotrifluoracetic acid, which gave clear, interpretable spectra. Previous investigators have shown that other solvents, particularly deuteriodimethylsulfoxide, gave complex, uninterpretable spectra for the polynuclear thiapyrylium series[53]. In all cases, the compounds were stable in the solvent, showing the same spectra even after a month of standing at room temperature. In the thienothiapyrylium series, all protons were distinguishable whereas, as expected, in the thianaphthenothiapyrylium series, the benz-ring protons showed as a broad multiplet. Therefore a group assignment rather than individual assignments were made where necessary.

NMR Spectrum of Thieno[3,2-c]thiapyrylium Perchlorate (Fig.1)

The nmr spectrum of 9 (Fig. 1) showed a multiplet at δ 10.60, integrating for one proton, a multiplet at δ 9.43, integrating for two protons and two doublets at δ 8.52 and 8.20, J = 6 Hz, each integrating for one proton. Since in this new system the positive charge could reside on either sulfur, as shown by the two canonical forms 9a and 9b, more



9a 9b

than one interpretation of this spectrum was possible. In one interpretation, as in 9a, the lowest field proton would be H-1 since it is adjacent to the positively charged sulfur atom. H-3 and H-4 might not differ enough from each other to cause a doublet and would be superimposed. H-6 and H-7 would split each other and be responsible for the two doublets; H-6 would be the further downfield of the two since it is closer to the sulfur atom as in thiophene itself. In another possible interpretation, as in 9b, the lowest field proton would be H-6; H-1 and H-7 could be superimposed while H-3 and H-4 would be responsible for the doublet.

The questions raised above were resolved by synthesizing the 3-methyl salt, 10 (Fig. 2) and the thianaphtheno salts 14 and 15 (Fig. 7 and 8, respectively). Comparing the spectra of these compounds (the individual spectra will be fully discussed later), the following is apparent:

1. Substitution of a benz-ring for protons H-6 and H-7 causes the two doublets to disappear, while leaving two downfield multiplets integrating for one and two hydrogens, respectively. Therefore, the doublets are due to H-6 and H-7.
2. Substitution of a methyl group for H-3 removes one of the superimposed pair of protons in Fig. 1 and one of the two superimposed multiplets in Fig. 8.

Previous work has shown that the proton adjacent to the thionium sulfur appears as the low field proton in thiapyrylium salts. Therefore the low field multiplet is assigned to H-1, the superimposed proton resonances are due to H-3 and H-4 and the doublets to H-6 and H-7 as in 9a. However since the thieno protons H-6 and H-7 are more deshielded than in thiophene, canonical form 9b does make a contribution to overall structure of 9, but the majority of the positive charge resides in the thiapyrylium ring.

NMR Spectrum of 3-Methylthieno[3,2-c]thiapyrylium Perchlorate (Fig. 2)

After consideration of the above-mentioned points, the following assignments were made for 10. The lowest field proton is H-1 at δ 10.33 and H-4 appears at δ 9.17. H-6 and H-7 are assigned to the doublets at δ 8.33 and 8.07, respectively. The methyl protons appear at δ 3.23.

NMR Spectrum of Thieno[2,3-c]thiapyrylium Perchlorate (Fig.3)

The spectrum of 11 shows a multiplet at δ 10.65, which is assigned to H-1. H-3 and H-4 are again superimposed at δ 9.28, while H-5 and H-6 appear as doublets, J = 5 Hz, at δ 8.20 and 9.12, respectively.

NMR Spectrum of 3-Methyl thieno[2,3-b]thiapyrylium Perchlorate (Fig. 4)

The nmr spectrum of 12 showed a proton at δ 9.72, assigned to H-2, and another at δ 9.25, assigned to H-4. The doublets at δ 8.44 and 8.07, J = 5.5 Hz, are assigned to H-6 and H-5, respectively. The methyl protons appear at δ 2.98.

NMR Spectrum of Thieno[2,3-b]thiapyrylium Perchlorate (Fig. 5)

The spectrum of 18 is assigned as follows: The lowest field doublet at δ 10.08, J - 8.5 Hz, is assigned to H-2. The doublet at δ 9.48, J = 8.5 Hz, is assigned to H-4. The triplet at δ 8.78, J = 8.5 Hz, is assigned to H-3. Protons H-2, H-3, and H-4 make up an AMX system where H-2 = X, H-3 = A, and H-4 = M. Here J_{AX} is the same as J_{AM} = 8 Hz, and J_{AX} = 0 Hz so that instead of the expected quartet, only a triplet appears. H-5 and H-6 are assigned to the doublets at δ 8.20 and 8.55, J = 5.5 Hz, respectively. Similar spectra have been observed in the corresponding benz-thiapyrylium series.

NMR Spectrum of Thianaphtheno[3,2-b]thiapyrylium Perchlorate (Fig. 6)

The spectrum of 13 is assigned as follows: The downfield doublet at δ 9.92, J = 8 Hz, is assigned to H-2 and the doublet at δ 9.52, J = 8 Hz, is assigned to H-4. Again this is an AMX situation and H-3 appears as a triplet at δ 8.75, J = 8 Hz. However, here J_{2-4} can be seen to be *ca.* 1 Hz. This is superimposed upon a multiplet, integrating for one proton which could be H-9. In phenanthrene, the angular H-4 and H-5 protons are the most deshielded and are separated from the others in the nmr spectrum[54]. Similarly in dibenzothiophene, the H-1 and H-9 protons appear as a downfield multiplet from the others in the nmr spectrum[55]. A like situation exists here. The remaining protons, H-6, H-7 and

H-8 comprise a broad multiplet, δ 8.40-7.70, and a group assignment is made.

NMR Spectrum of Thianaphtheno[3,2-c]thiapyrylium Perchlorate (Fig. 7)

The spectrum of 14 shows a multiplet at δ 10.57, which is assigned to H-1. A broad multiplet, δ 9.60-9.15, is assigned to H-3 and H-4. Another smaller multiplet, centered at δ 8.60, is probably H-9 and the remaining protons, H-6, H-7 and H-8 are grouped in a broad multiplet from δ 8.27-7.67.

NMR Spectrum of 3-Methylthianaphtheno[3,2-c]thiapyrylium Perchlorate (Fig. 8)

The spectrum of 15 is assigned as follows: The lowest field singlet at δ 10.33 is due to H-1; the singlet at δ 9.00 is due to H-4. A multiplet centered at 8.50 is probably H-9 and the remaining aromatic protons are grouped in a broad multiplet from δ 8.20-7.70. The methyl protons appear at δ 3.12.

NMR Spectrum of Thianaphtheno[2,3-c]thiapyrylium Perchlorate (Fig. 9)

The spectrum of 16 is assigned as follows: The triplet at δ 10.40, J = 2 Hz, is due to H-1 and the pair of singlets at δ 9.55 is due to H-3 and H-4. The multiplet centered at δ 8.77 is probably H-5 and the remaining protons form a broad multiplet from δ 8.32-7.68.

NMR Spectrum of Thianaphtheno[2,3-b]thiapyrylium Perchlorate (Fig. 10)

The spectrum of 17 is assigned as follows: The multiplet from δ 9.93-9.60 is due to H-2 and H-4. H-3 and probably H-5 show as a multiplet at δ 9.13-8.50 and the remaining protons as another multiplet from δ 8.33-7.75.

NMR Spectrum of 8-Methoxythiapyrano[4,3-b]indole (Fig. 11)

The nmr spectrum showed H-1 at δ 8.75 as a doublet, J = 3.0 Hz, and H-4 at δ 8.15 also as a doublet, J_{34} = 9.5 Hz. H-3, H-6, H-7 and H-9 showed as a multiplet from δ 7.96-7.16 and the methyl protons appeared as a singlet at δ 3.93.

NMR Spectrum of 8-Chlorothiapyrano[4,3-b]indole (Fig. 12)

The nmr spectrum showed H-1 at δ 8.80 as a doublet, J = 3.0 Hz, and H-4 at δ 8.18 as a doublet, J_{34} = 10 Hz. The remaining four protons showed as a multiplet from δ 8.00-7.50, H-3, H-6, H-7 and H-9.

NMR Spectrum of 6-Methylthiapyrano[4,3-b]indole (Fig. 13)

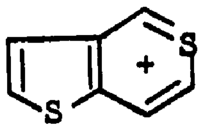
The nmr spectrum showed H-1 at δ 8.76 as a doublet, J_{13} = 3.0 Hz and H-4 at δ 8.27 also as a doublet, J_{34} = 9.5 Hz. H-3, H-7, H-8 and H-9 showed as a multiplet from δ 8.00-7.20 and the methyl protons appeared as a singlet at δ 2.82.

The 8-nitrothiapyran[4,3-b]indole was too insoluble in $CDCl_3$ for its spectrum to be obtained.

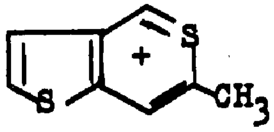
The data are summarized in Tables 1, 2 and 3.

TABLE 1

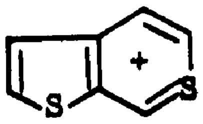
NMR SPECTRA OF THIENOTHIAPYRYLIUM PERCHLORATES



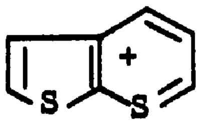
9



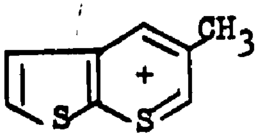
10



11



18

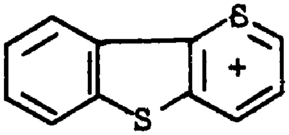


12

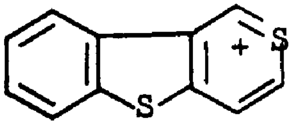
δ ppm (multiplicity)					Proton Assignments
----	3.23(s)	----	----	2.98(s)	CH_3
10.60(m)	10.33(s)	10.65(m)	----	----	H_1
----	----	----	10.00(d)	9.72(s)	H_2
9.43(m)	----	9.28(m)	8.78(t)	----	H_3
9.43(m)	9.17(s)	9.28(m)	9.48(d)	9.25(s)	H_4
8.52(d) and 8.20(d)	8.33(d) 8.78(d)	8.20(d) 9.12(d)	8.20(d) 8.55(d)	8.44(d) 8.07(d)	H_5,H_6(7)

TABLE 2

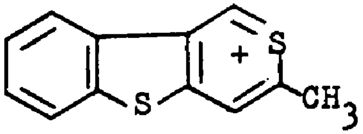
NMR SPECTRA OF THIANAPHTHENOTHIAPYRYLIUM PERCHLORATES



13



14

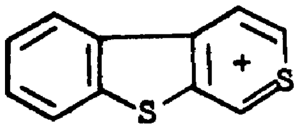


15

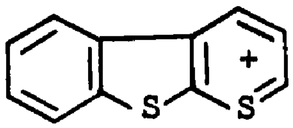
δ ppm (multiplicity)			Proton Assignments
----	----	3.12	CH_3
----	10.57(m)	10.33(s)	H_1
9.92(d)	----	----	H_2
8.75(t)	9.37(m)	----	H_3
9.52(d)	9.37(m)	9.00(s)	H_4
8.75(m)	8.60(m)	8.50(m)	H_9
8.05(m)	7.97(m)	7.95(m)	H_6, H_7, H_8

TABLE 2 (Continued)

NMR SPECTRA OF THIANAPHTHENOTHIAPYRYLIUM PERCHLORATES



16

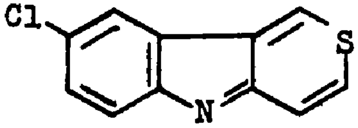
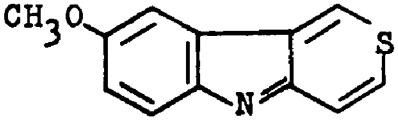
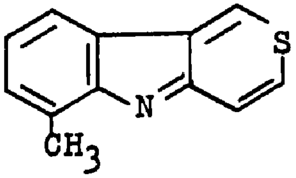


17

δ ppm (multiplicity)		Proton Assignments
----	----	CH_3
10.40(t)	----	H_1
----	9.76(m)	H_2
9.55(s)	8.82(m)	H_3
9.55(s)	9.76(m)	H_4
8.77(m)	8.82(m)	H_5
7.95(m)	8.01(m)	H_6, H_7, H_8

TABLE 3

NMR SPECTRA OF THIAPYRANO[4,3-b]INDOLES

			
δ ppm (multiplicity)			Proton Assignments
----	3.93(s)	2.82(s)	CH_3
8.80(d)	8.75(d)	8.76(d)	H_1
8.18(d)	8.15(d)	8.27(d)	H_4
7.75(m)	7.56(m)	7.60(m)	H_3, H_{6-9}

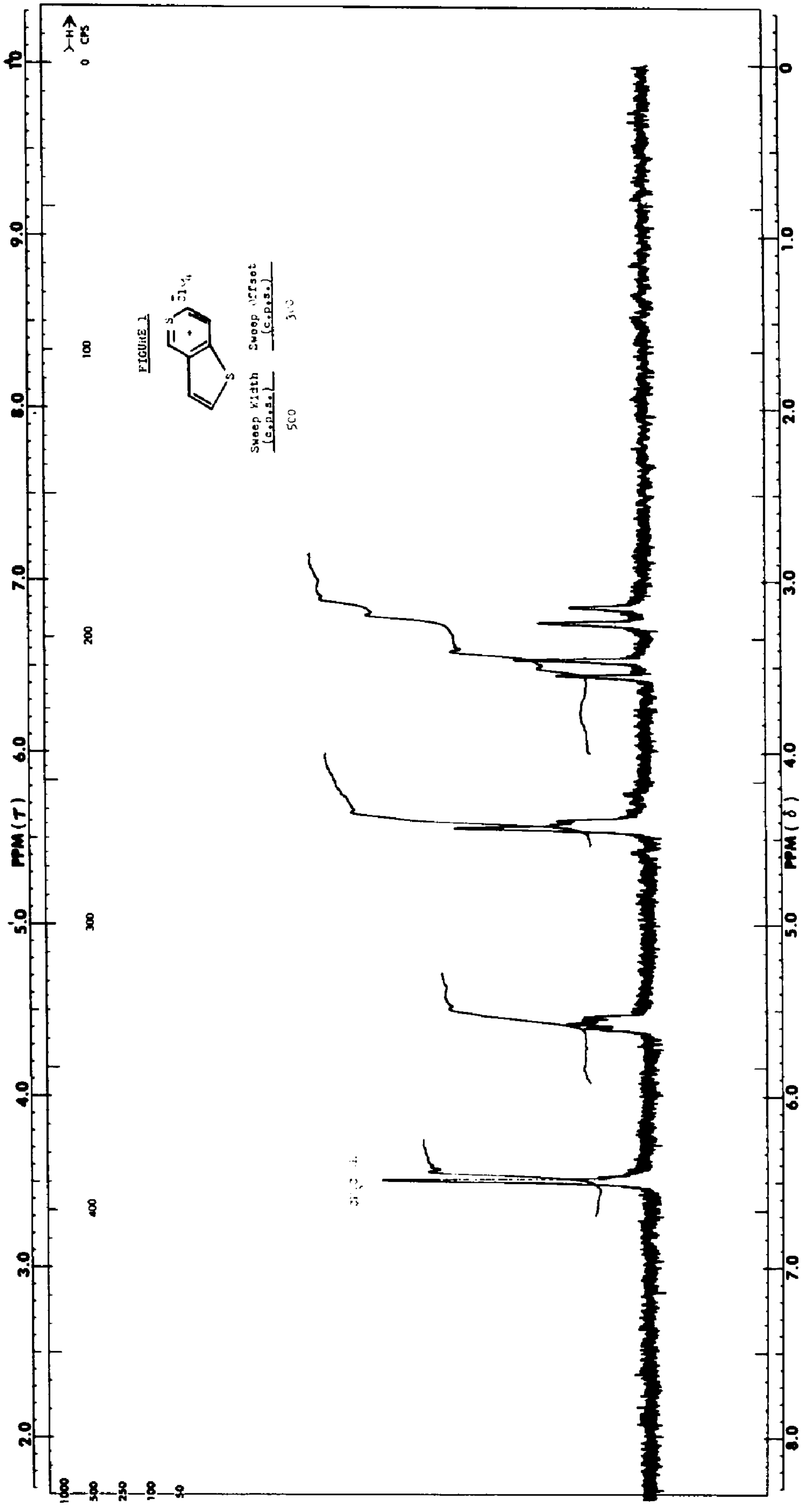


FIGURE 1

ClO4
S
S
Sweep Width (c.p.s.)
500
Sweep Offset (c.p.s.)
300
PPM (τ)
PPM (δ)
0 CPS
100
200
300
400
1000
500
250
100
50
10
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0

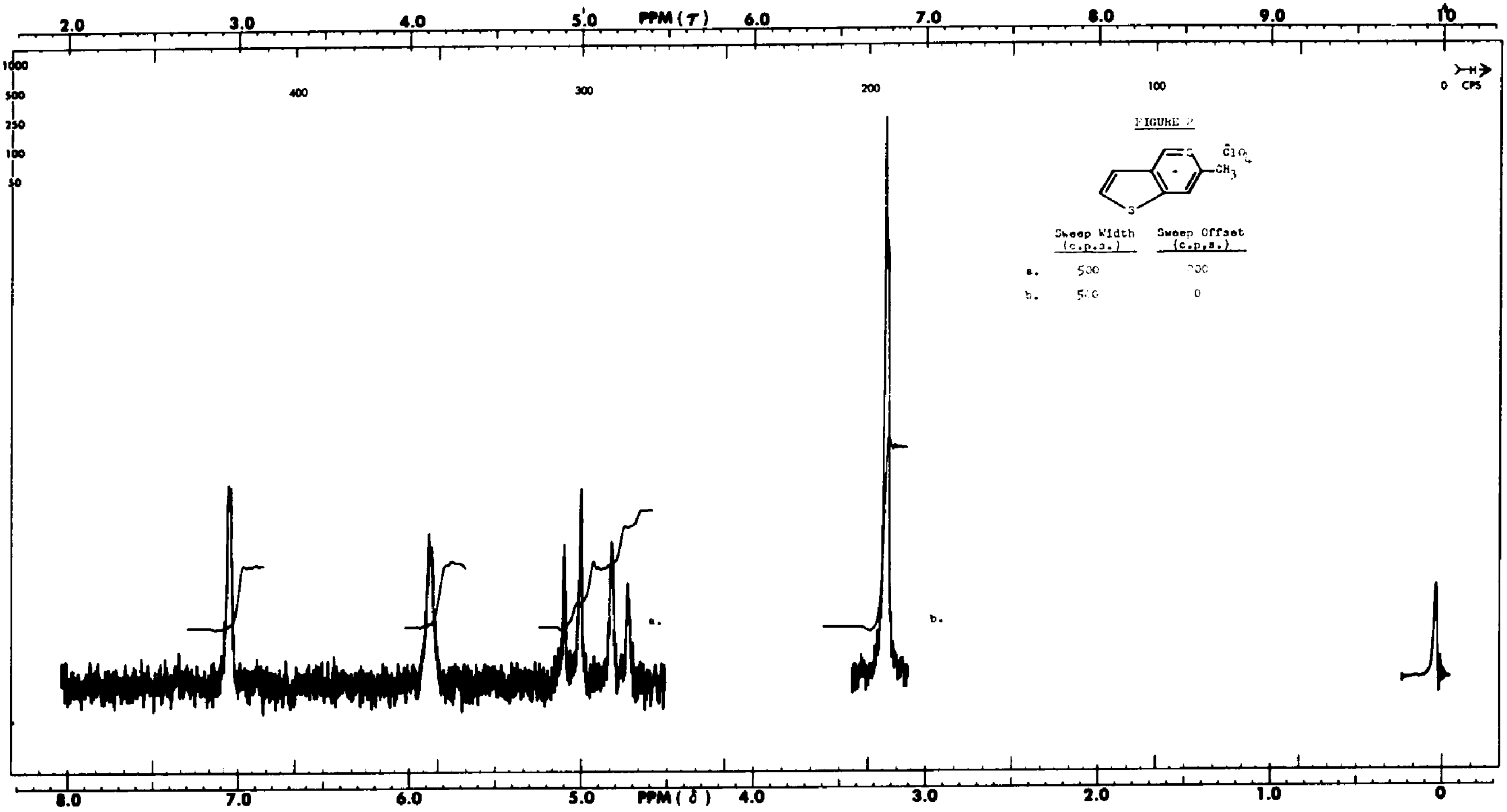


FIGURE 7

	Sweep Width (c.p.s.)	Sweep Offset (c.p.s.)
a.	500	200
b.	500	0

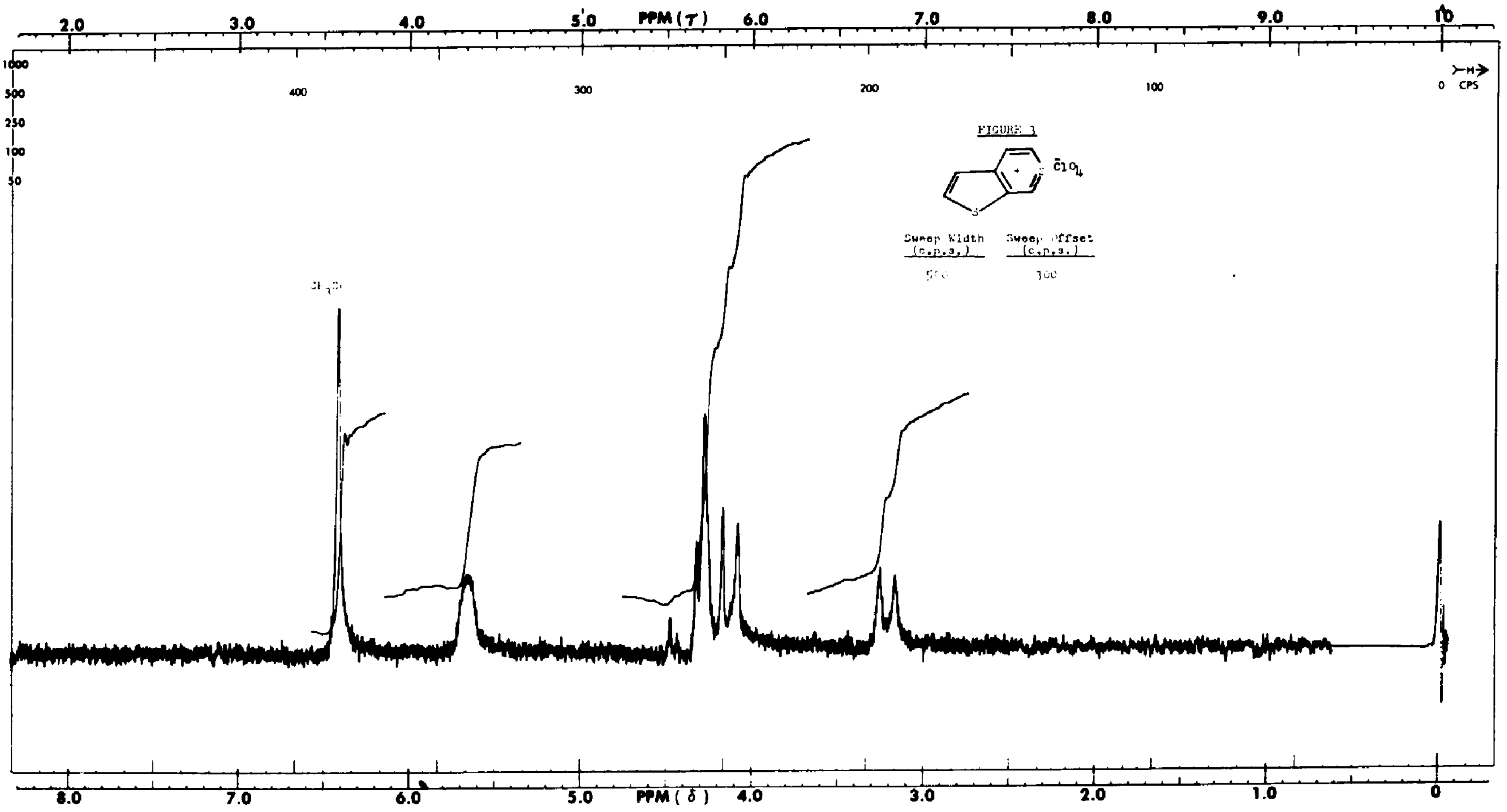
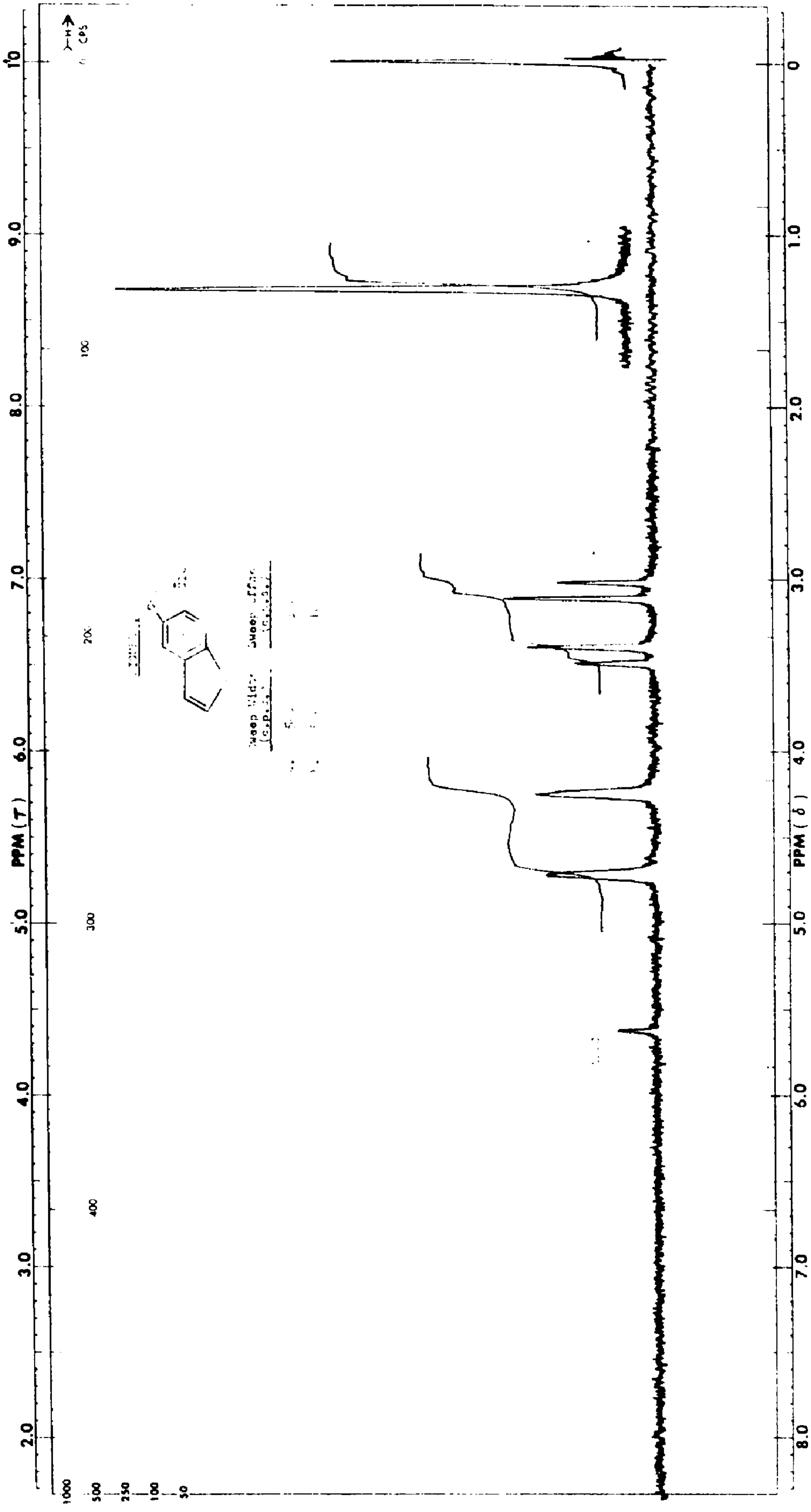
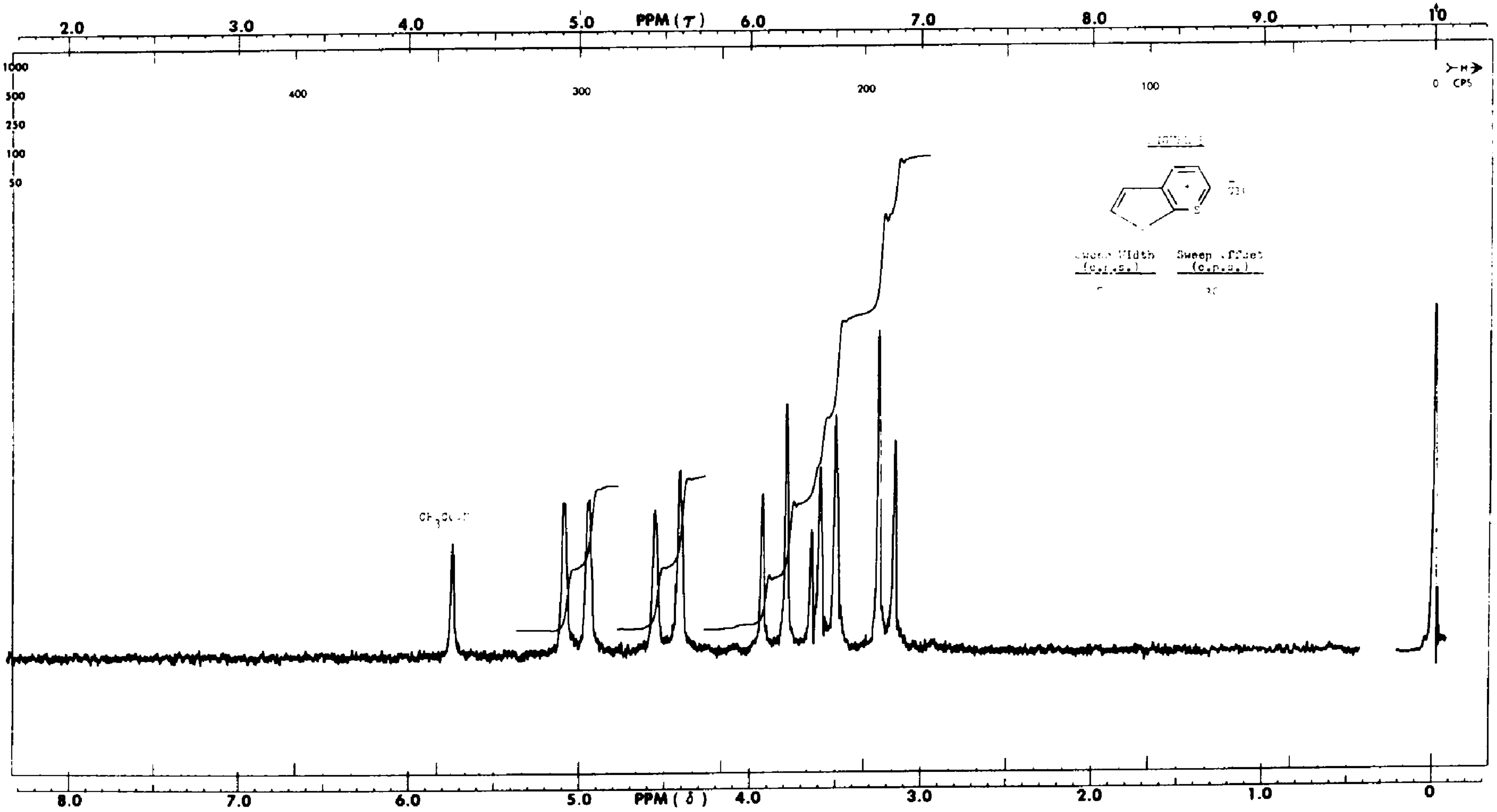


FIGURE 1

PPM (τ)
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
1000
500
250
100
50
400
300
200
100
0 CPS
H
$\bar{C}lO_4$
S
Sweep Width (c.p.s.)
500
Sweep Offset (c.p.s.)
300
CH$_3$S
PPM (δ)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0


PPM (τ)
PPM (δ)
10
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
100
200
300
400
CPS
1000
500
250
100
50
Sweep Width (c.p.s.)
Sweep Offset (c.p.s.)


2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
10
1000
500
250
100
50
400
300
200
100
0 CPS
Sweep Width (c.p.s.)
Sweep Offset (c.p.s.)
S
CH3CO2H
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0

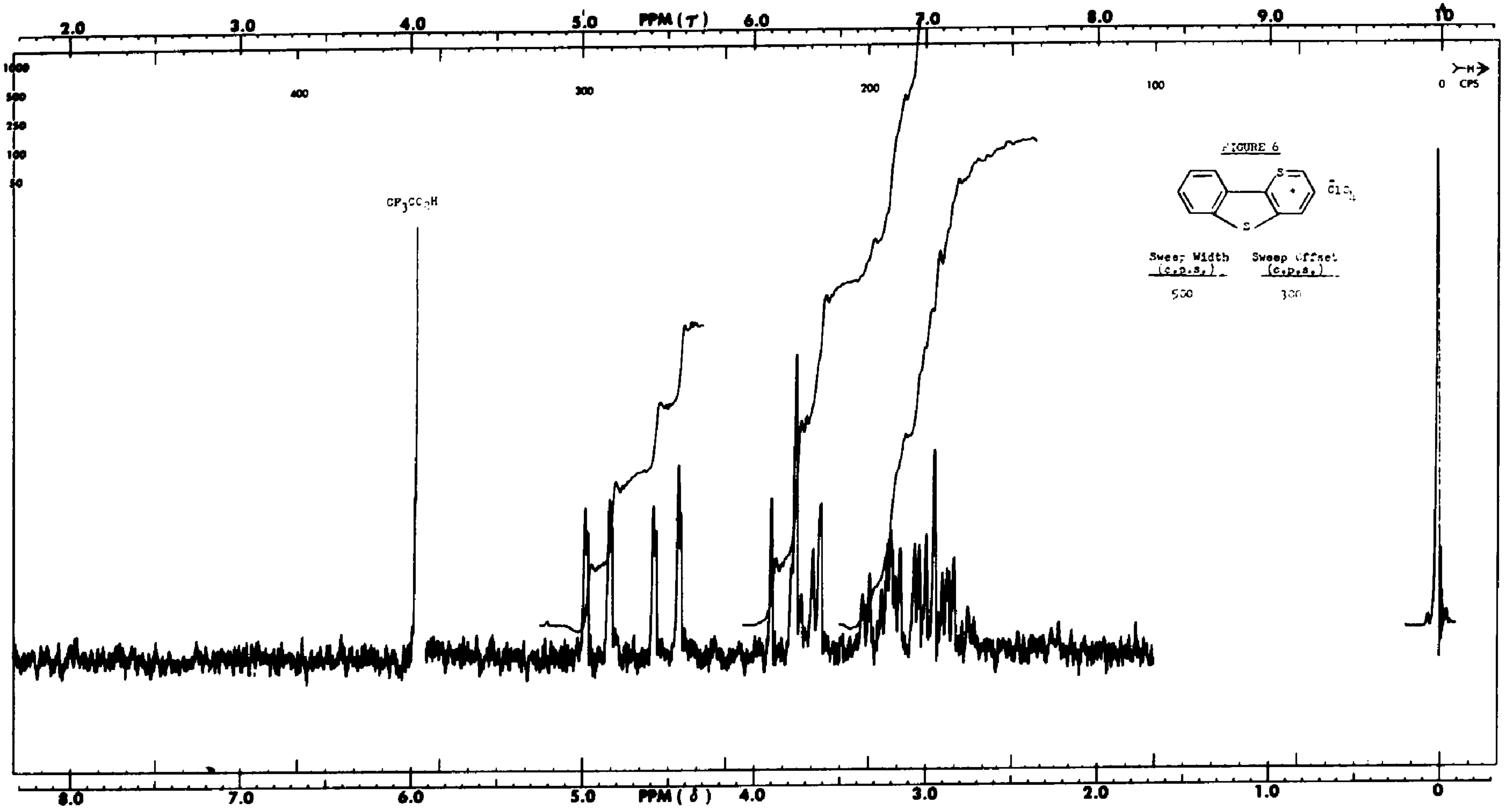


FIGURE 6

PPM (τ)
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
1000
500
250
100
50
400
300
200
100
0 CPS
CF$_3$CO$_2$H
$\bar{C}lO_4$
S
S
+
Sweep Width (c.p.s.)
500
Sweep Offset (c.p.s.)
300
PPM (δ)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0

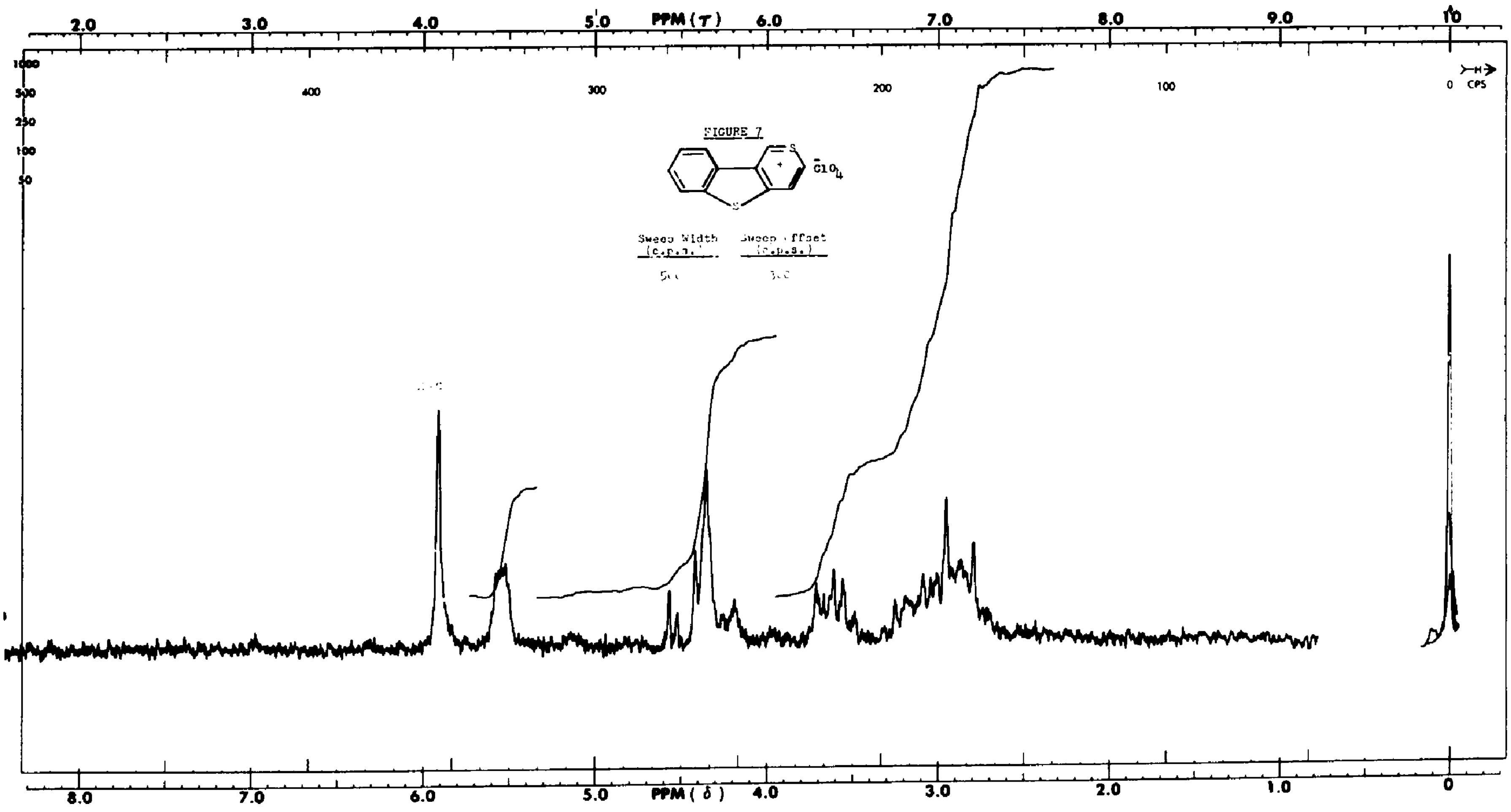


FIGURE 7

Sweep Width (c.p.s.) 500

Sweep Offset (c.p.s.) 300

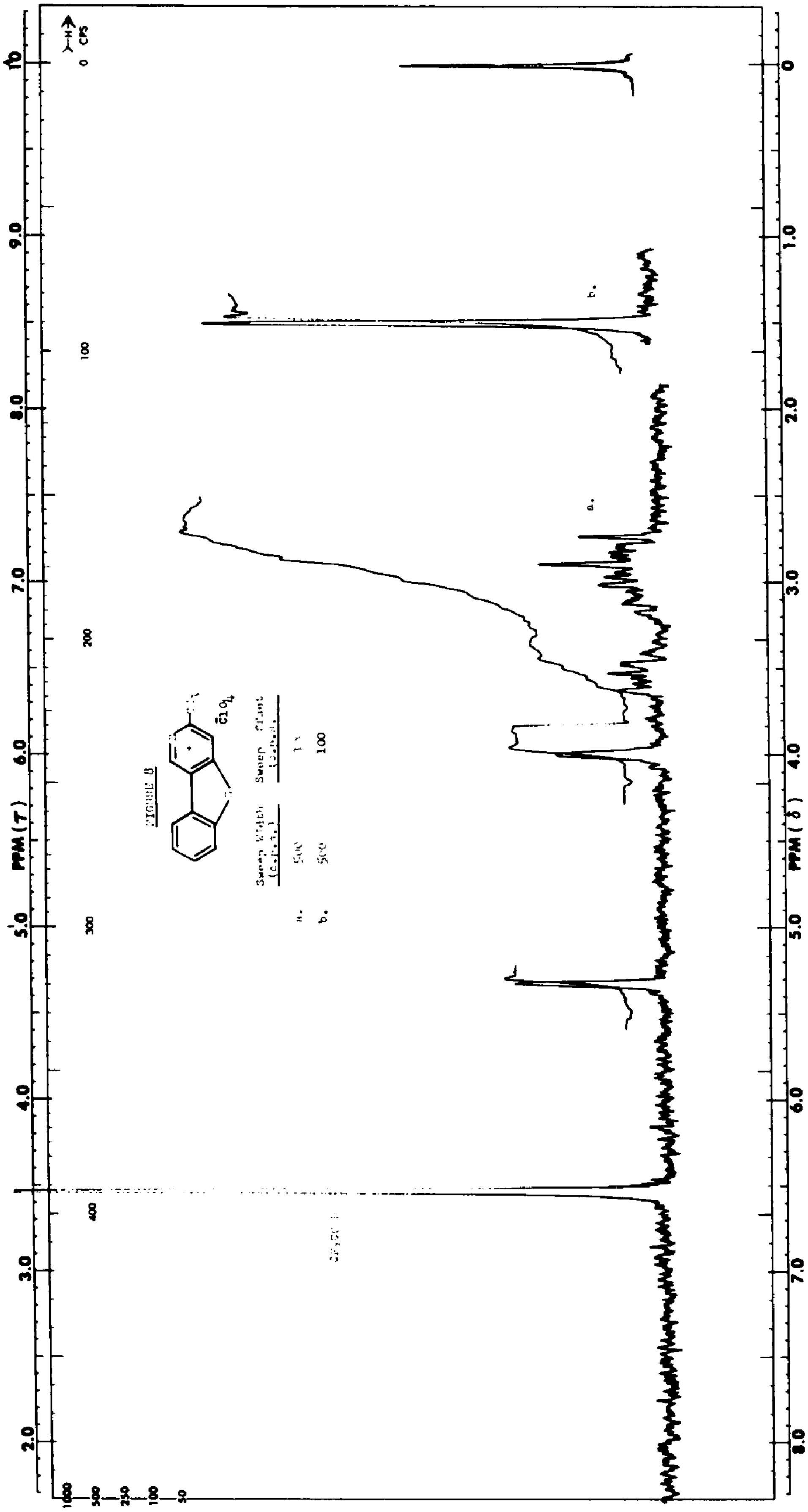


FIGURE 8

$\bar{C}lO_4$
Sweep Width (c.p.s.)
Sweep Offset (c.p.s.)
a. 500
b. 500 100
a.
b.
PPM (τ)
PPM (δ)
10
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
0 CPS
100
200
300
400
1000
500
250
100
50

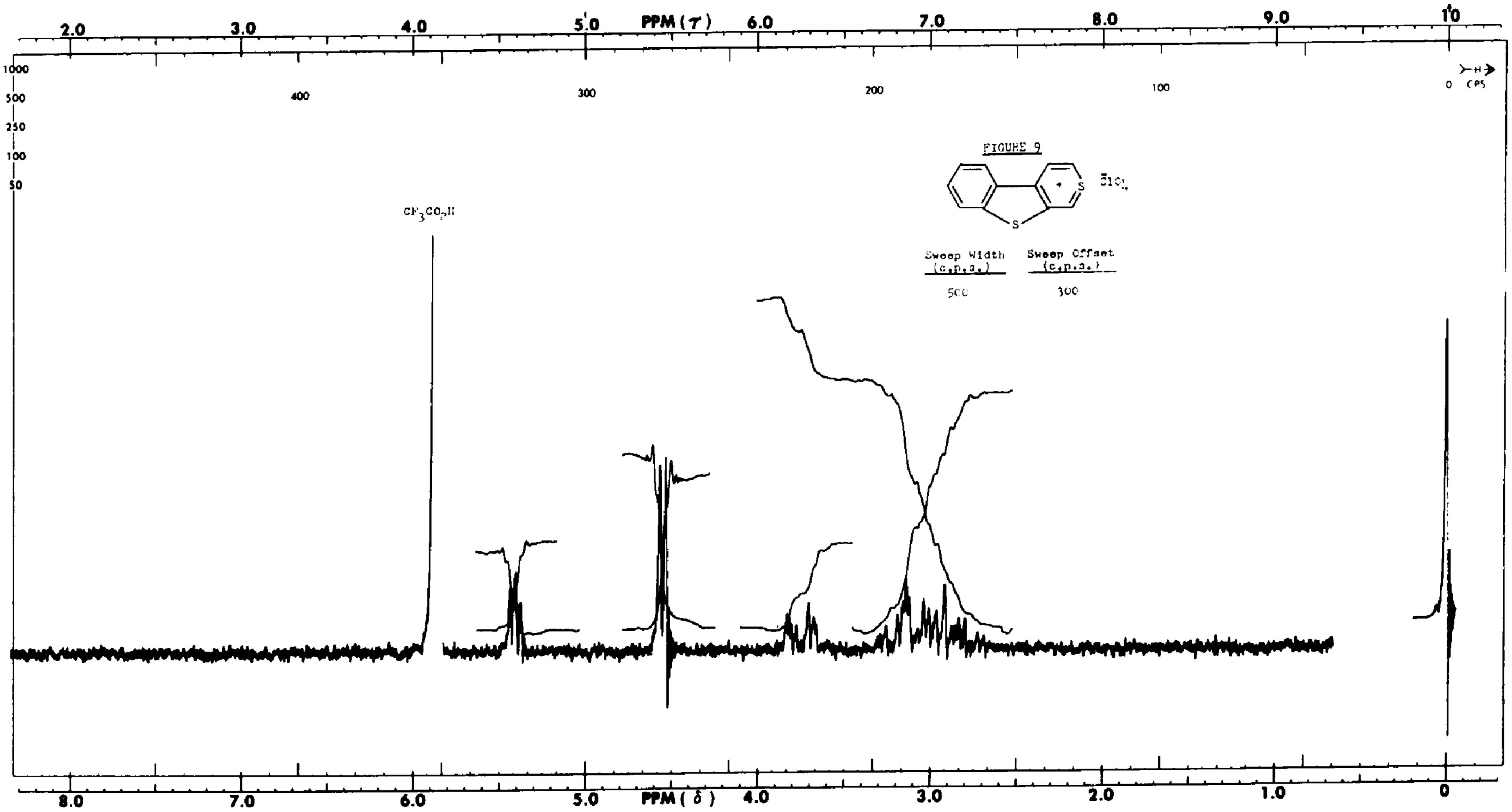


FIGURE 9

2.0
3.0
4.0
5.0
PPM (τ)
6.0
7.0
8.0
9.0
10
1000
500
250
100
50
400
300
200
100
0 CPS
$\succ$H$\rightarrow$
CF_3CO_2H
$\bar{C}lO_4$
S
S
Sweep Width (c.p.s.)
500
Sweep Offset (c.p.s.)
300
8.0
7.0
6.0
5.0
PPM (δ)
4.0
3.0
2.0
1.0
0

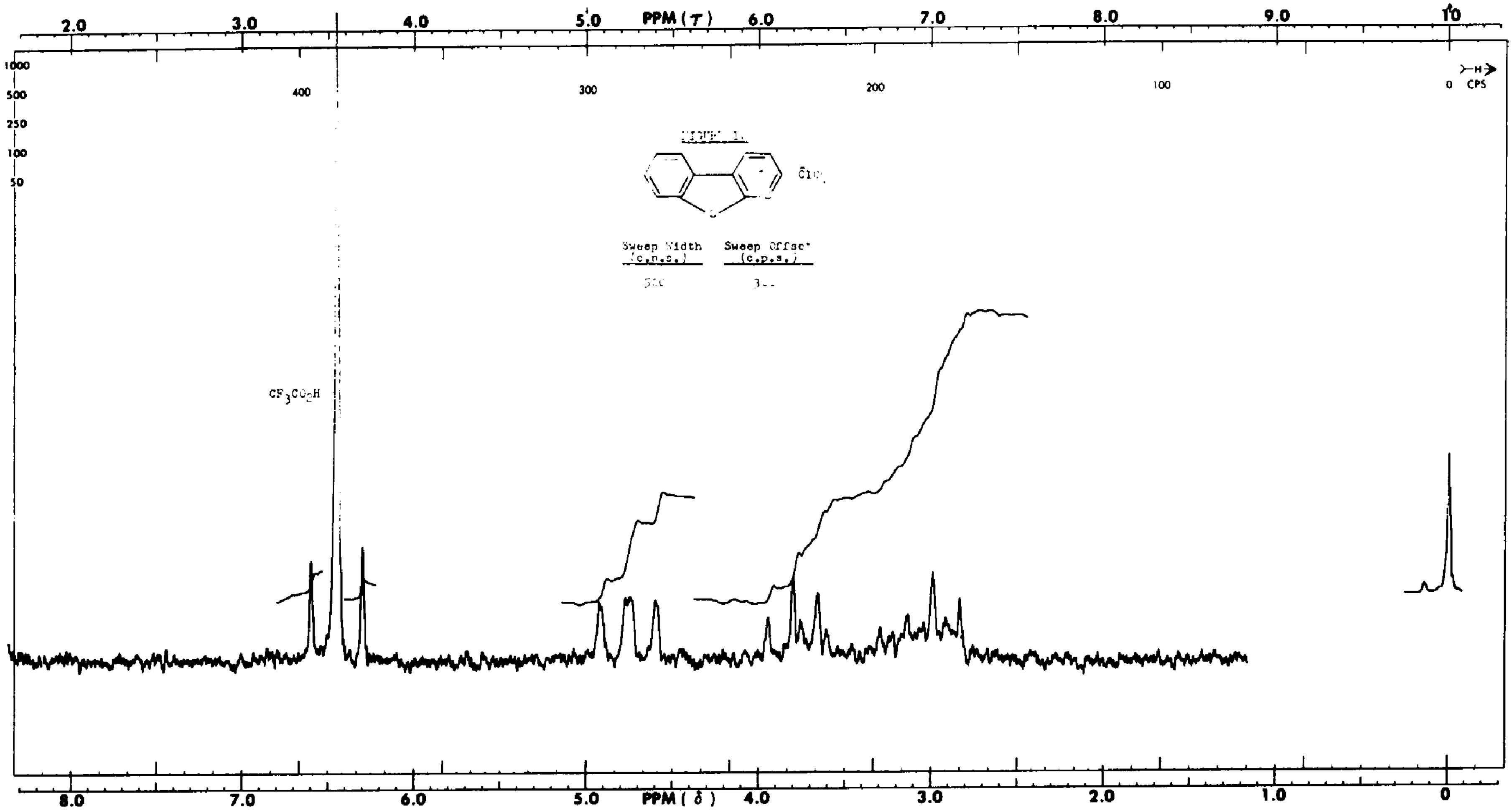


FIGURE 1.

PPM (τ)
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
1000
500
250
100
50
400
300
200
100
0 CPS
$\overline{\text{ClO}}_4$
Sweep Width (c.p.s.)
500
Sweep Offset (c.p.s.)
3[illegible]
CF_3CO_2H
PPM (δ)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0

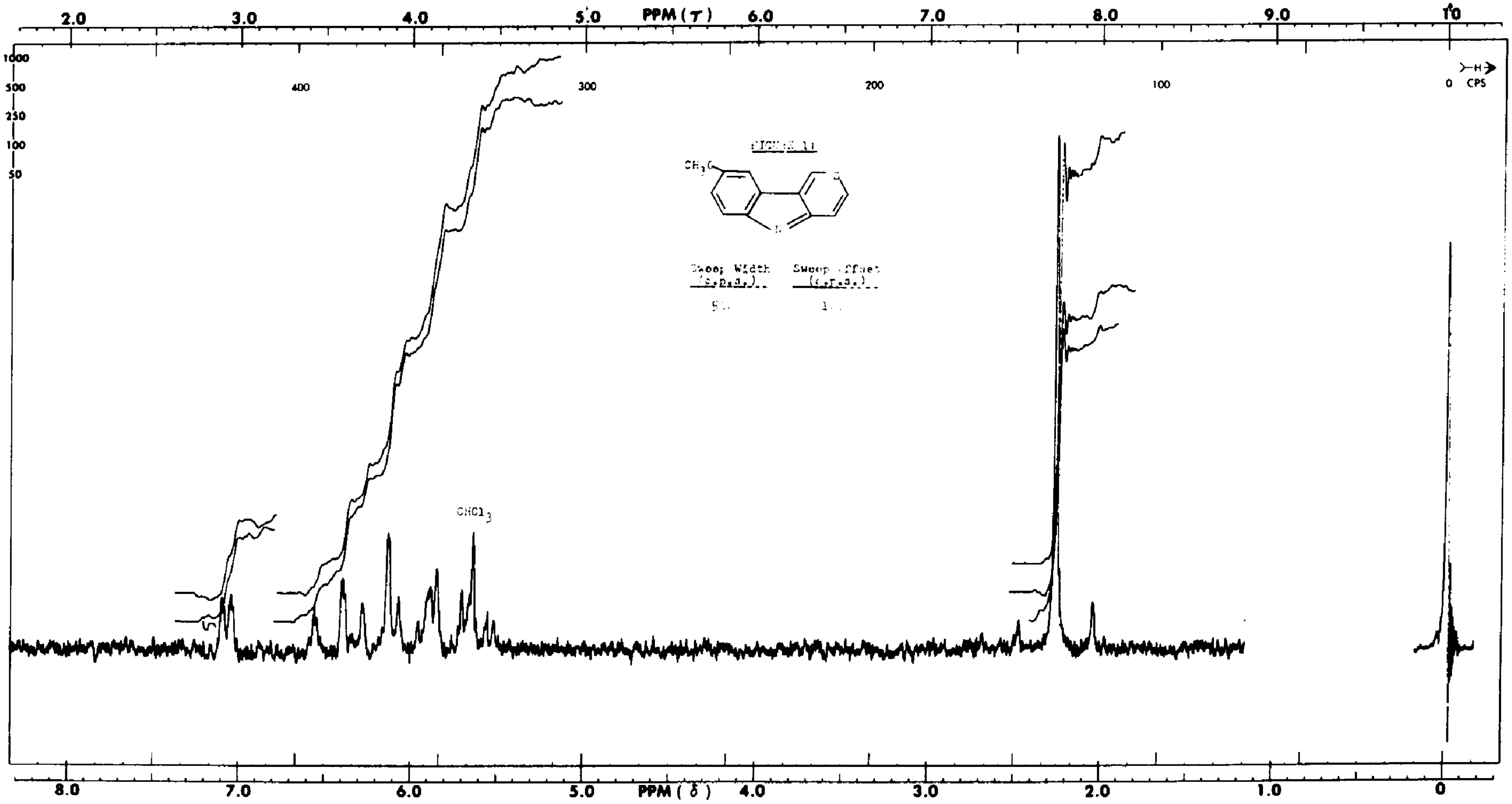


FIGURE 11

PPM (τ)
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
1000
500
250
100
50
400
300
200
100
0 CPS
CHCl3
CH3O
N
Sweep Width (C.P.S.)
Sweep Offset (C.P.S.)
PPM (δ)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0

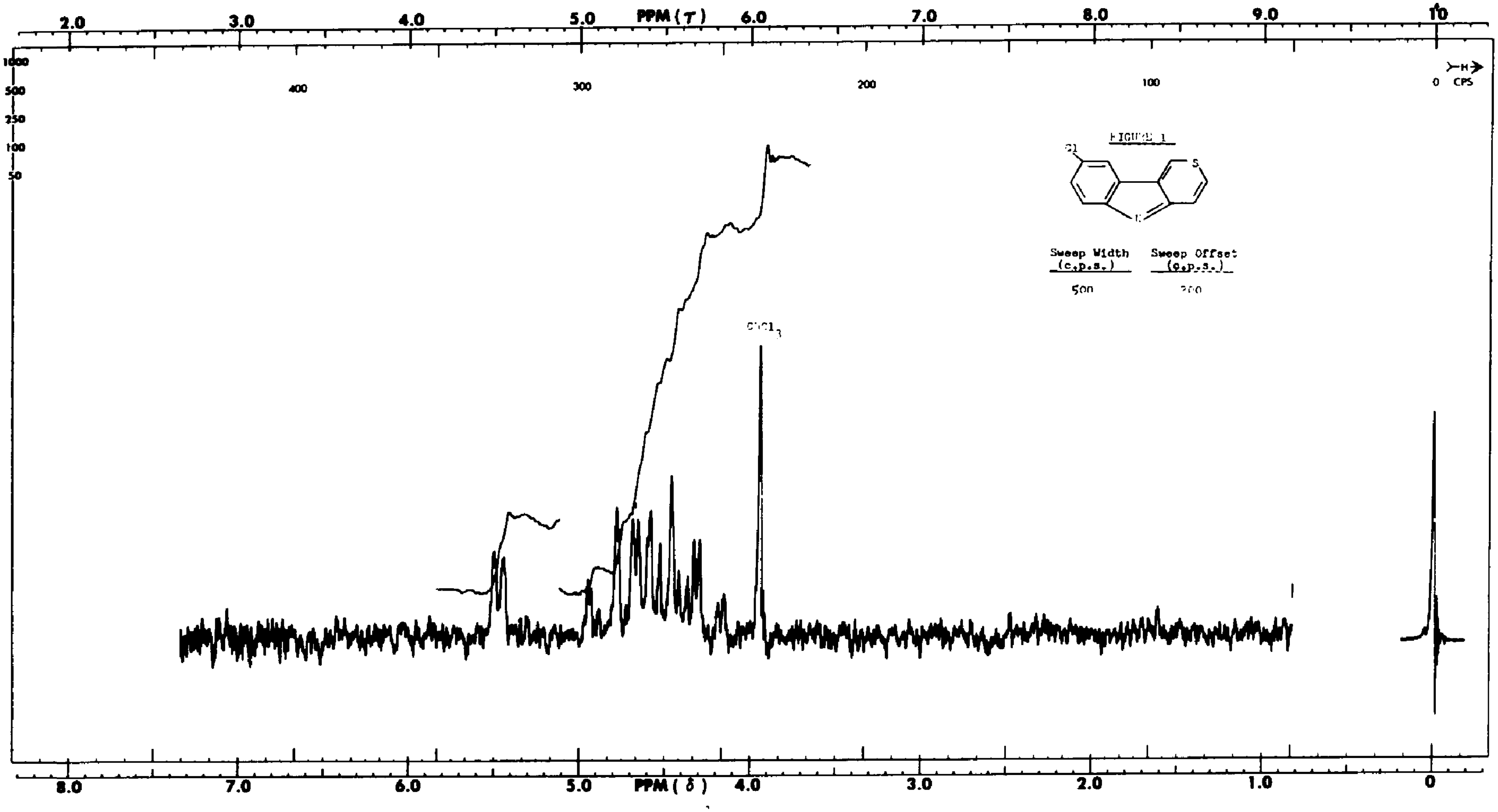


FIGURE 1

PPM (τ)
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
PPM (δ)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
400
300
200
100
0 CPS
1000
500
250
100
50
Cl
S
N
CHCl₃
Sweep Width (c.p.s.)
500
Sweep Offset (c.p.s.)
200

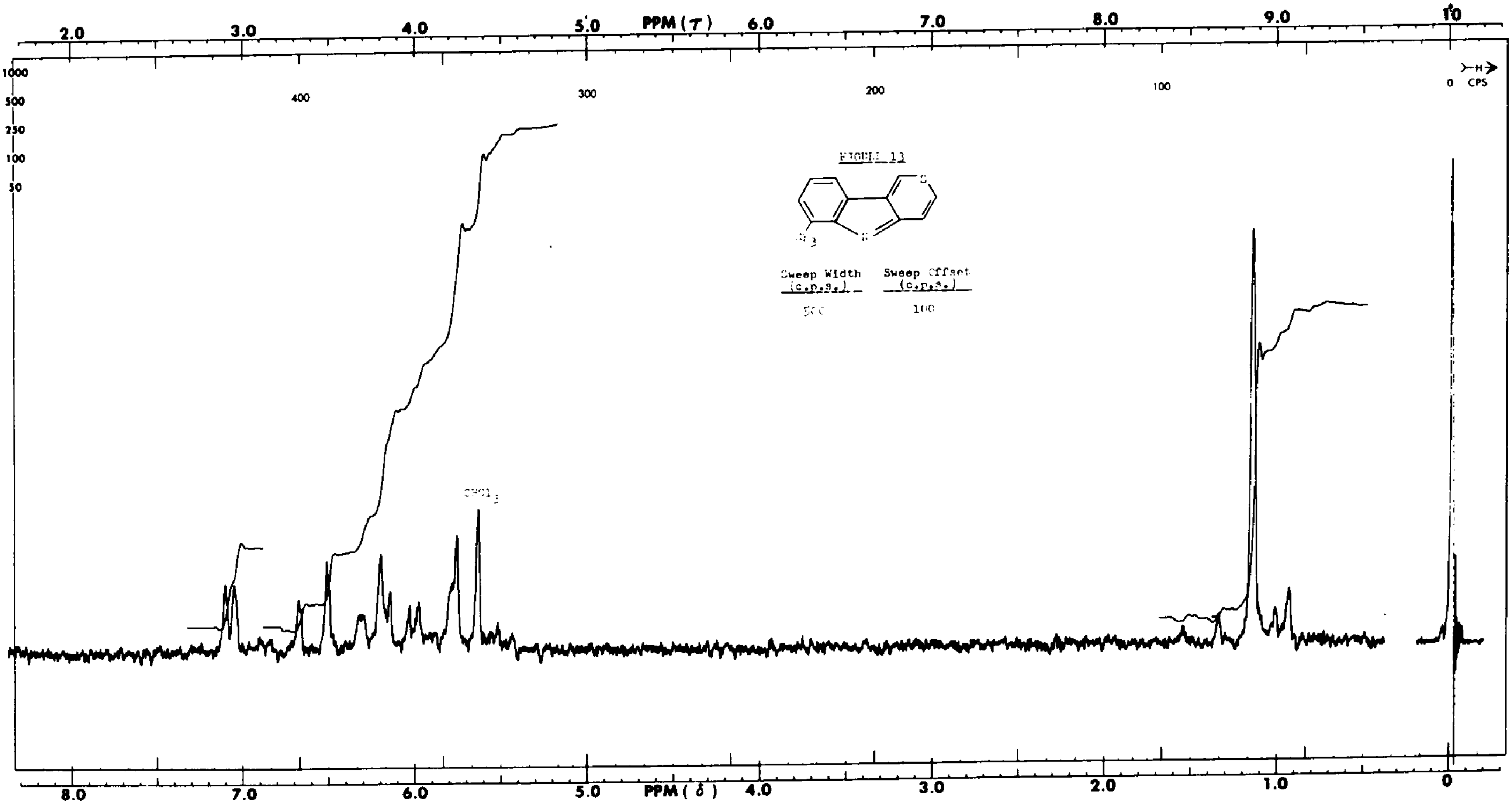


FIGURE 13

PPM (τ)
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10
1000
500
250
100
50
400
300
200
100
0 CPS
CHCl$_3$
CH$_3$
N
S
Sweep Width (c.p.s.)
500
Sweep Offset (c.p.s.)
100
PPM (δ)
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0

III. H.M.O. Calculations

H.M.O. calculations were carried out in the usual way[56] using a G.E. 225 computer and a standard eigenvalue-eigenvector program for a symmetrical matrix. A simplified model in which the coulomb and resonance integrals for sulfur were expressed (in Streitweiser's notation) as $\alpha_S = \alpha + h_S\beta$ and $\beta_{CS} = k_{CS}\beta$, respectively, in which no auxiliary inductive parameter for carbon adjacent to sulfur was employed. The parameters $h_S = 0.90$ and $k_{CS} = 0.60$ were used as determined for thionium sulfur by Ohnmacht. Later on a Fortran IV program was developed with the aid of Dr. William Hollabaugh of the Electrical Engineering Department which not only calculates the eigenvectors and eigenvalues but also computes the electron densities from these values.

The electronic spectra (Fig. 14 to 23) were measured for the perchlorate salts in acetonitrile containing 1% by volume of 70% perchloric acid and are tabulated in Tables 4 and 5. The observed wavenumber (ν, kcm^{-1}) of the longest wavelength absorption (assumed to be the L_b bands in Platt notation) was plotted against the calculated transition energies expressed as Δm, where Δm is the difference in coefficients of β between the highest occupied and the lowest unoccupied molecular orbitals. The regression line developed by Ohnmacht[57] ($\bar{\nu}=26.053\ \Delta m - 0.677$ kcm^{-1}) was superimposed on the plot. Whereas his correlations for twelve thiapyrylium perchlorate salts was excellent, the correlation using the thieno and thianaphthenothiapyrylium perchlorates is poor.

The H.M.O. calculations show that there is no large variation in the Δm values for these two series of compounds as there was for the benzenoid compounds. See Fig. 29 for the data and that of the calculated electron densities. The data for $\nu(\text{kcm}^{-1})$ vs. Δm plot are summarized in Table 7.

Assignment of the Electronic Spectral Bands of the Thieno and Thianaphthenothiapyrylium Perchlorates

The ultraviolet visible spectra of these compounds are remarkably similar to the corresponding compounds obtained by Ohnmacht. In these cases, a thiophene nucleus has been substituted for the benz-ring in the thianaphthalium salts and a benzothiophene nucleus has been substituted for the naphthalene system in the thiaphenanthrenium salts. Therefore similar band assignments can be made. The spectra are similar to that of the corresponding aromatic compounds except that all bands are red shifted.

The spectra of 12 and 18 are almost superimposable on that of 1-thianaphthalium perchlorate[58]. Therefore the bands at 262 and 264 mμ, 333 and 337 mμ, and 361 and 370 mμ for these compounds, Figures 17 and 18, correspond to the ^1B_b, ^1L_a and ^1L_b transitions of naphthalene (Platt notation). A similar assignment can be made for the remainder of the thienothiapyrylium perchlorates, *i.e.*, the band between 260 and 270 mμ corresponds to the ^1B_b transition; that between 300 and 337 mμ corresponds to the ^1L_a transition; and the longest wavelength transition between 357 and 396 mμ corresponds to the ^1L_b band. See Table 4 and Figures 14-18 for the data.

The thianaphthenothiapyrylium perchlorates have four electronic spectral band transitions which are similar to the thiaphenanthrenium perchlorates of Ohnmacht and are red shifted when compared to those of phenanthrene. The first transition (short wavelength) is possibly that of the ^1C_b band which is forbidden in the acene series but which is allowed in the less symmetrical phene series. The ^1B_b, ^1L_a and ^1L_b bands are red shifted from those of phenanthrene[59]. The ^1L_b band of 13 appears as a broad shoulder on the ^1L_a band and its exact maximum is impossible to pinpoint. A similar situation occurs with 4-thiaphenanthrenium perchlorate. The spectra of 14 and 15 show a great deal of fine structure in the ^1B_b bands, making them difficult to position exactly. The data are summarized in Table 5 and in Figures 19-23.

The electronic spectra of the thiapyrano[4,3-b]indoles are similar to that of the iso-π-electronic benz[b]-1-aza-azulene[60], which also exhibits a visible maximum at 500 mμ. The data are tabulated in Table 6 and the spectra are shown in Figures 24-27.

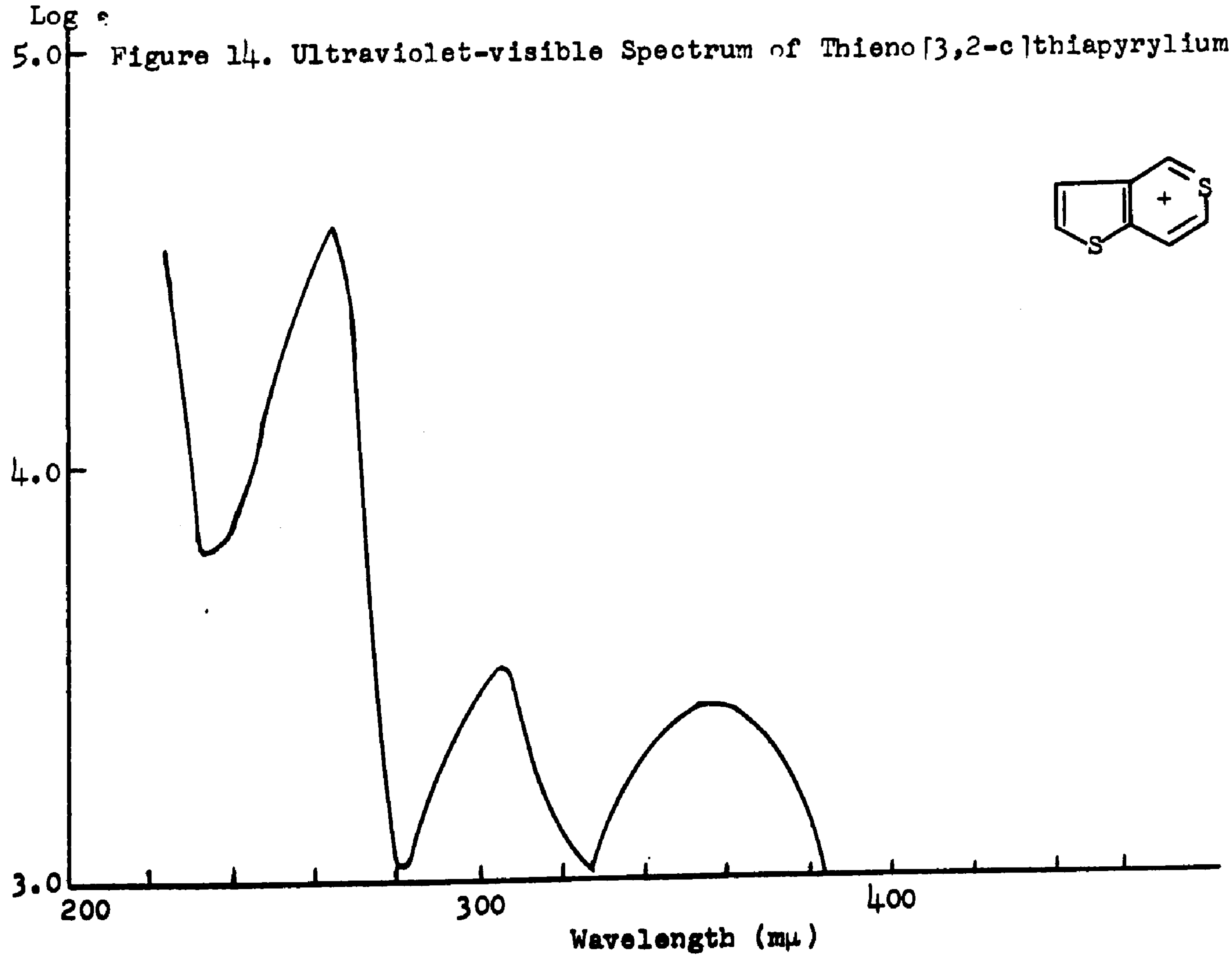


Figure 14. Ultraviolet-visible Spectrum of Thieno[3,2-c]thiapyrylium Perchlorate (9)

Figure 15. Ultraviolet-visible Spectrum of 3-Methylthieno[3,2-c]thiapyrylium Perchlorate (10)

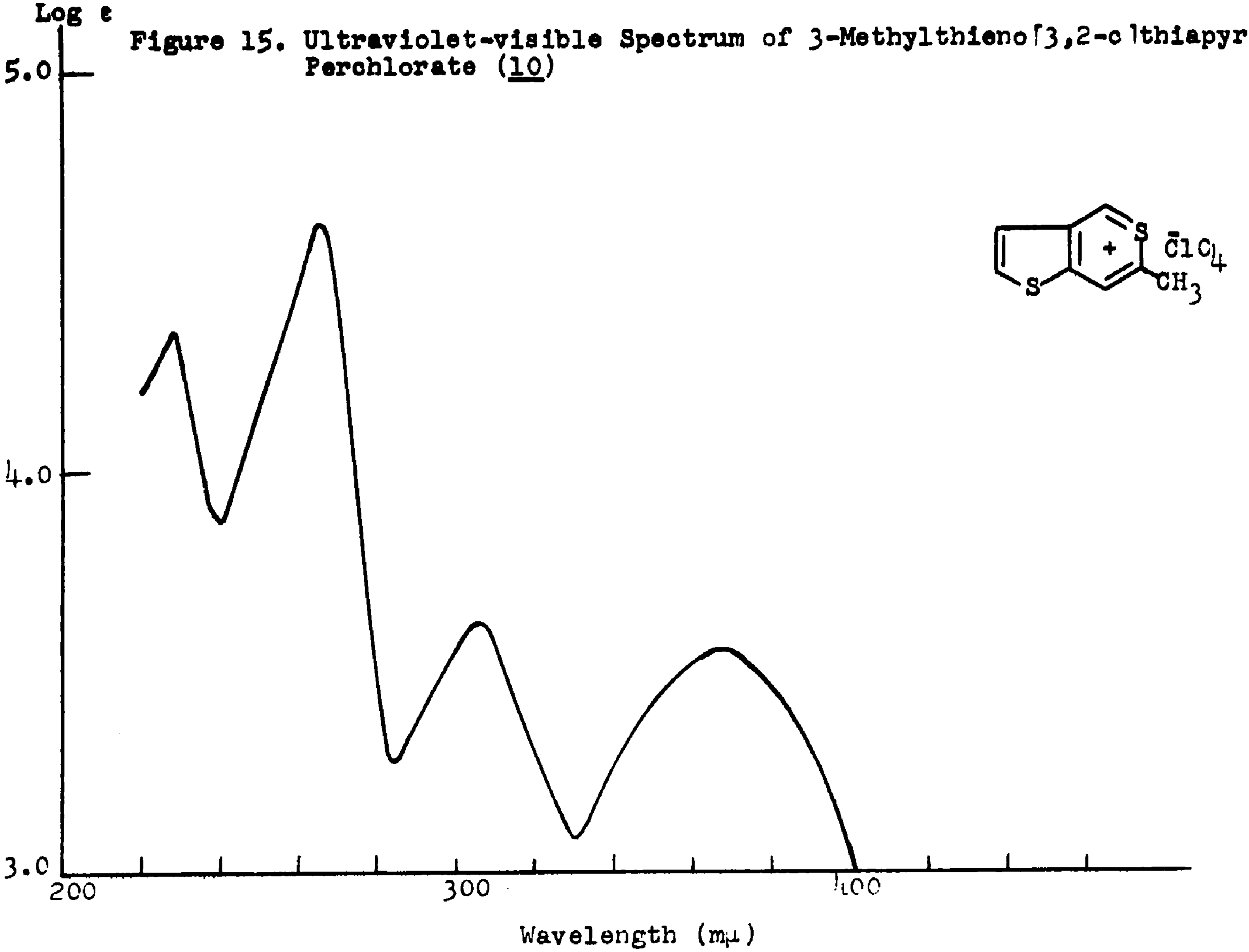
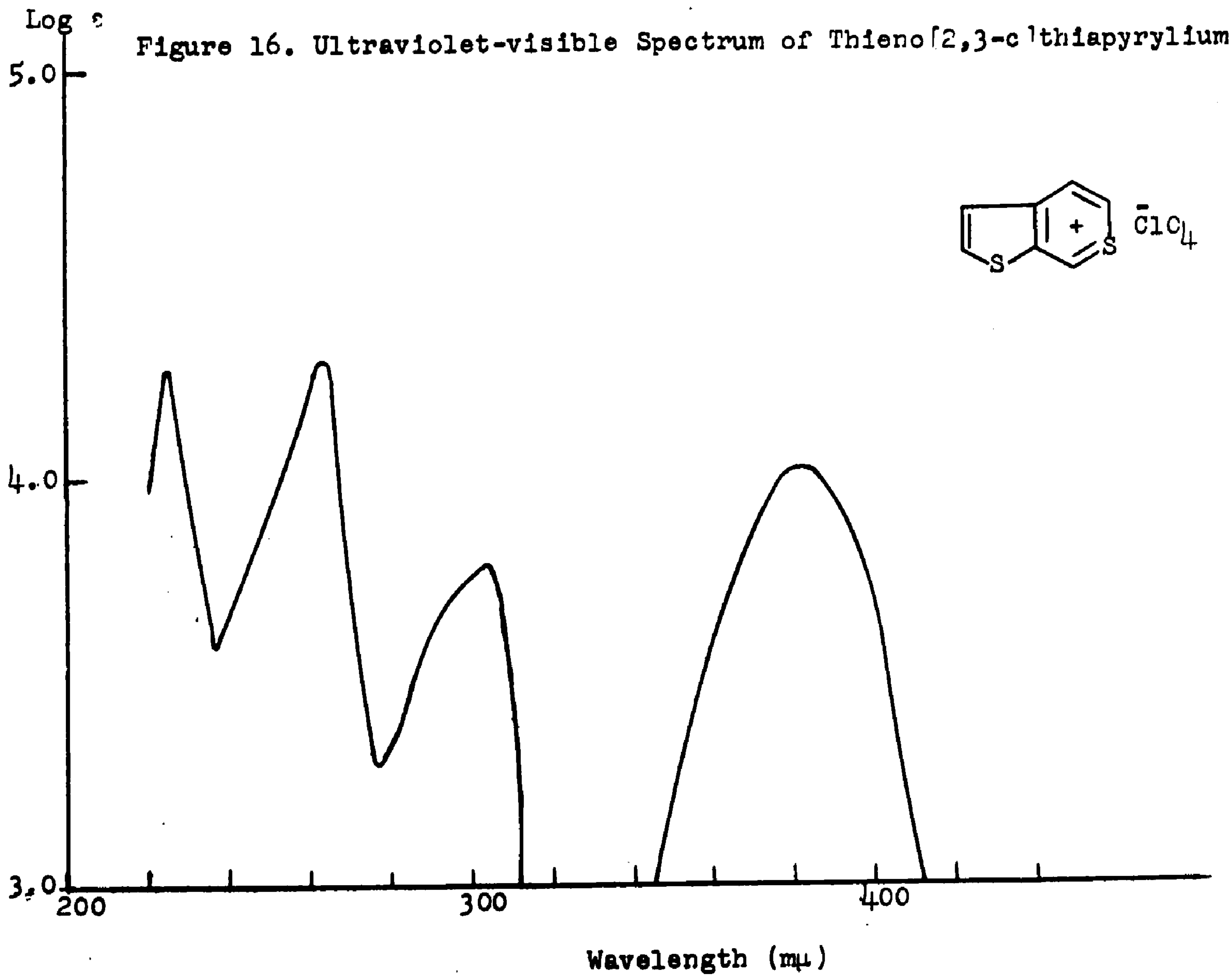


Figure 16. Ultraviolet-visible Spectrum of Thieno[2,3-c]thiapyrylium Perchlorate (11)



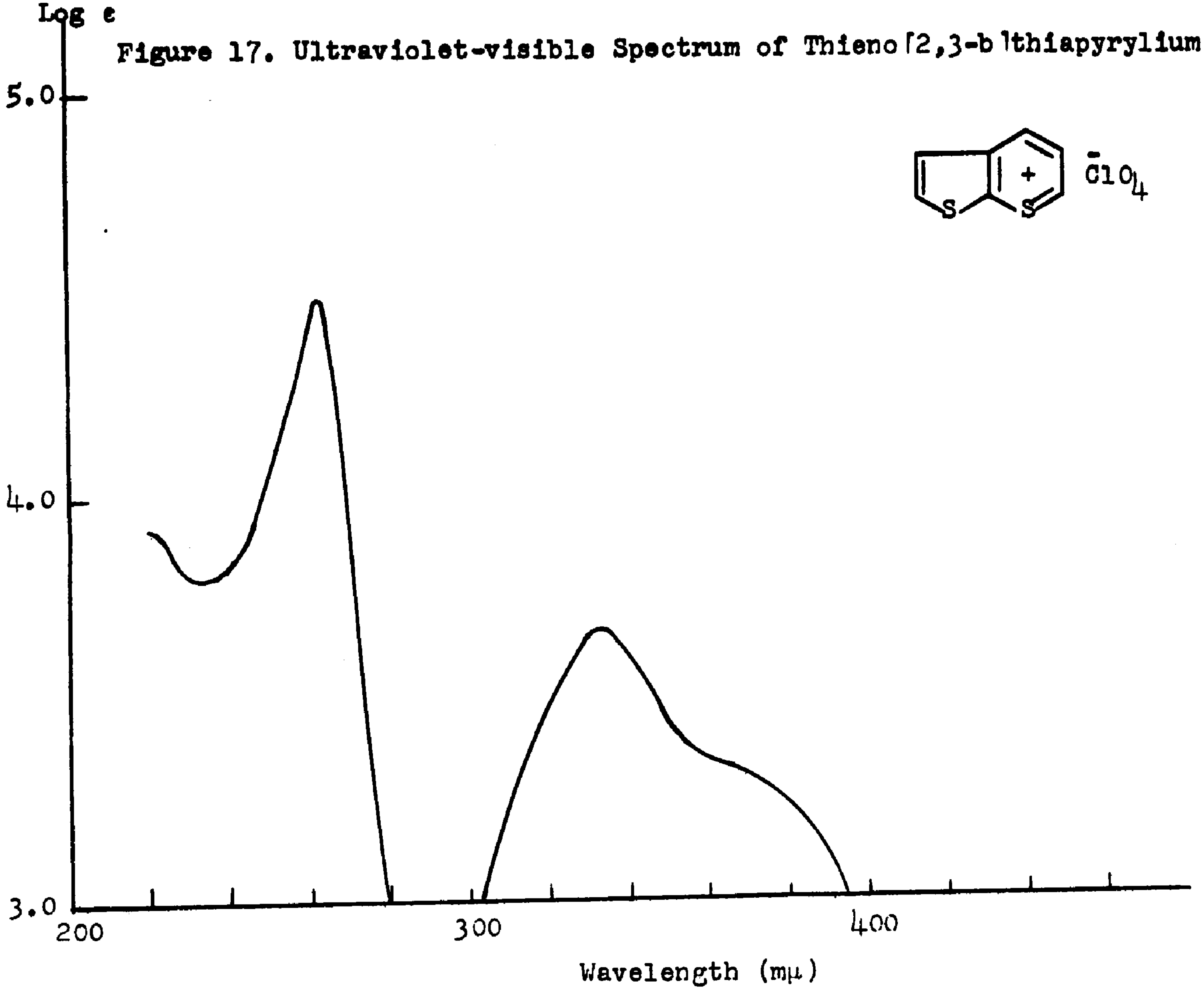
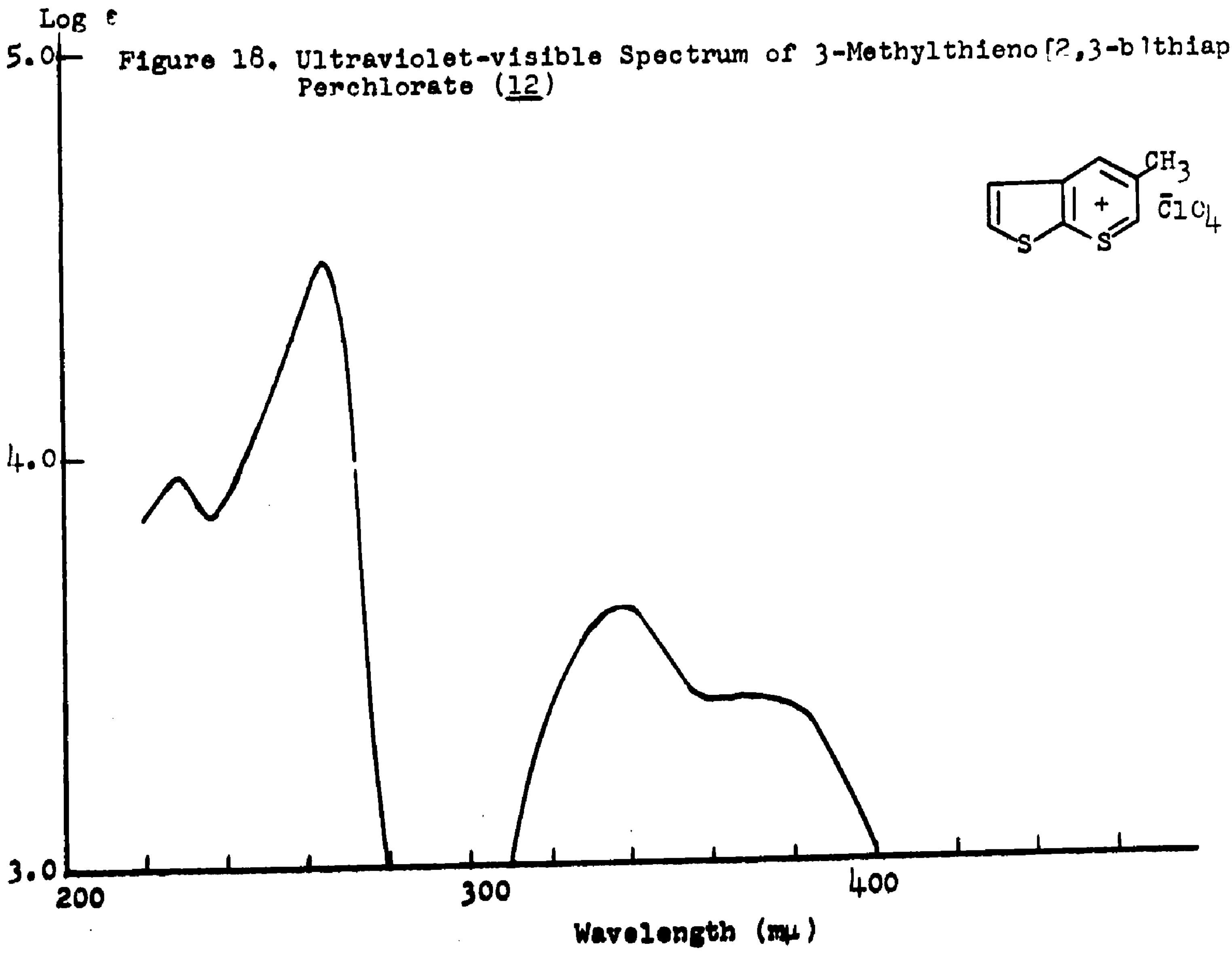


Figure 17. Ultraviolet-visible Spectrum of Thieno[2,3-b]thiapyrylium Perchlorate (18)

Figure 18. Ultraviolet-visible Spectrum of 3-Methylthieno[2,3-b]thiapyrylium Perchlorate (12)



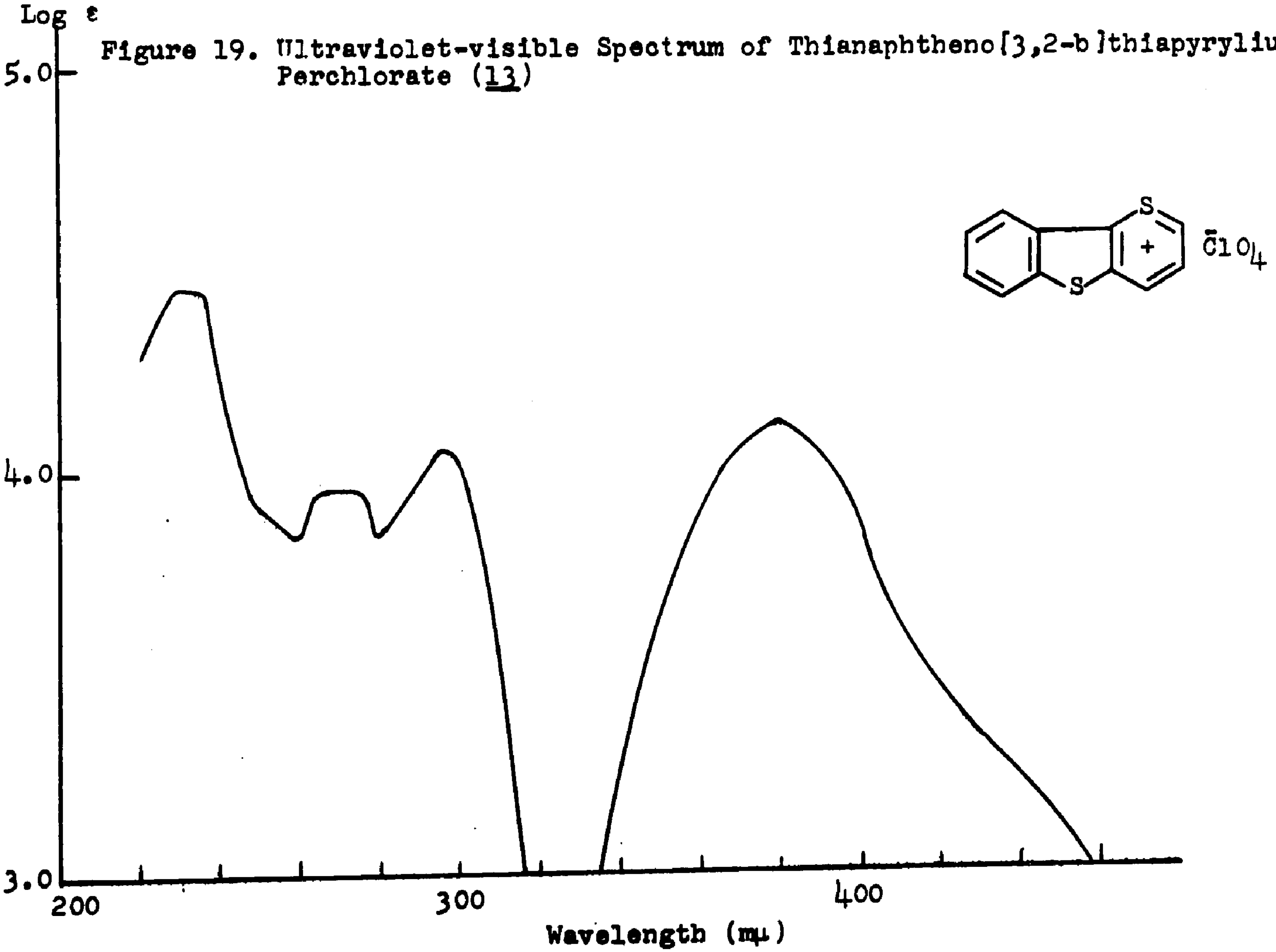


Figure 19. Ultraviolet-visible Spectrum of Thianaphtheno[3,2-b]thiapyrylium Perchlorate (13)

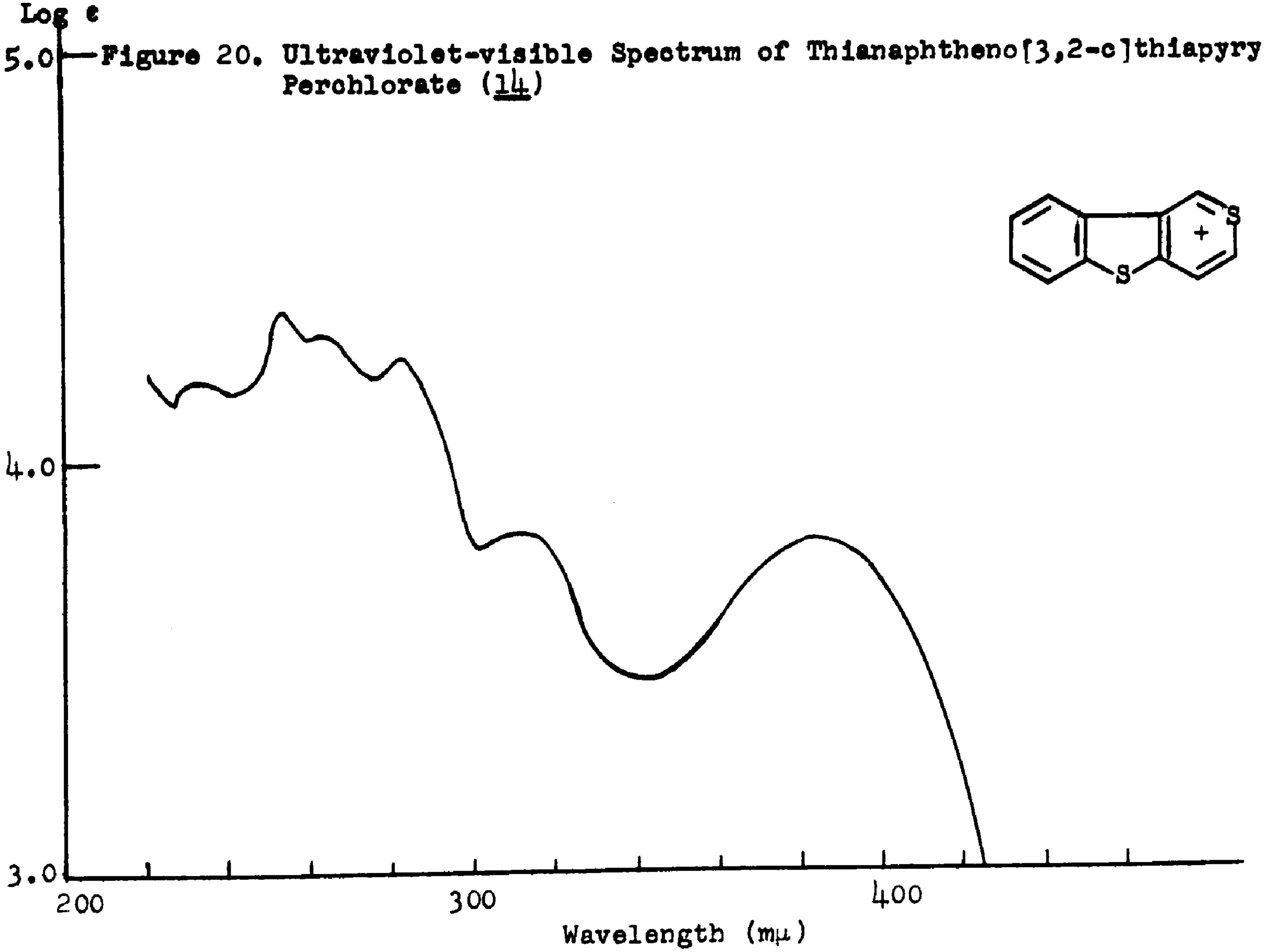


Figure 20. Ultraviolet-visible Spectrum of Thianaphtheno[3,2-c]thiapyrylium Perchlorate (14)

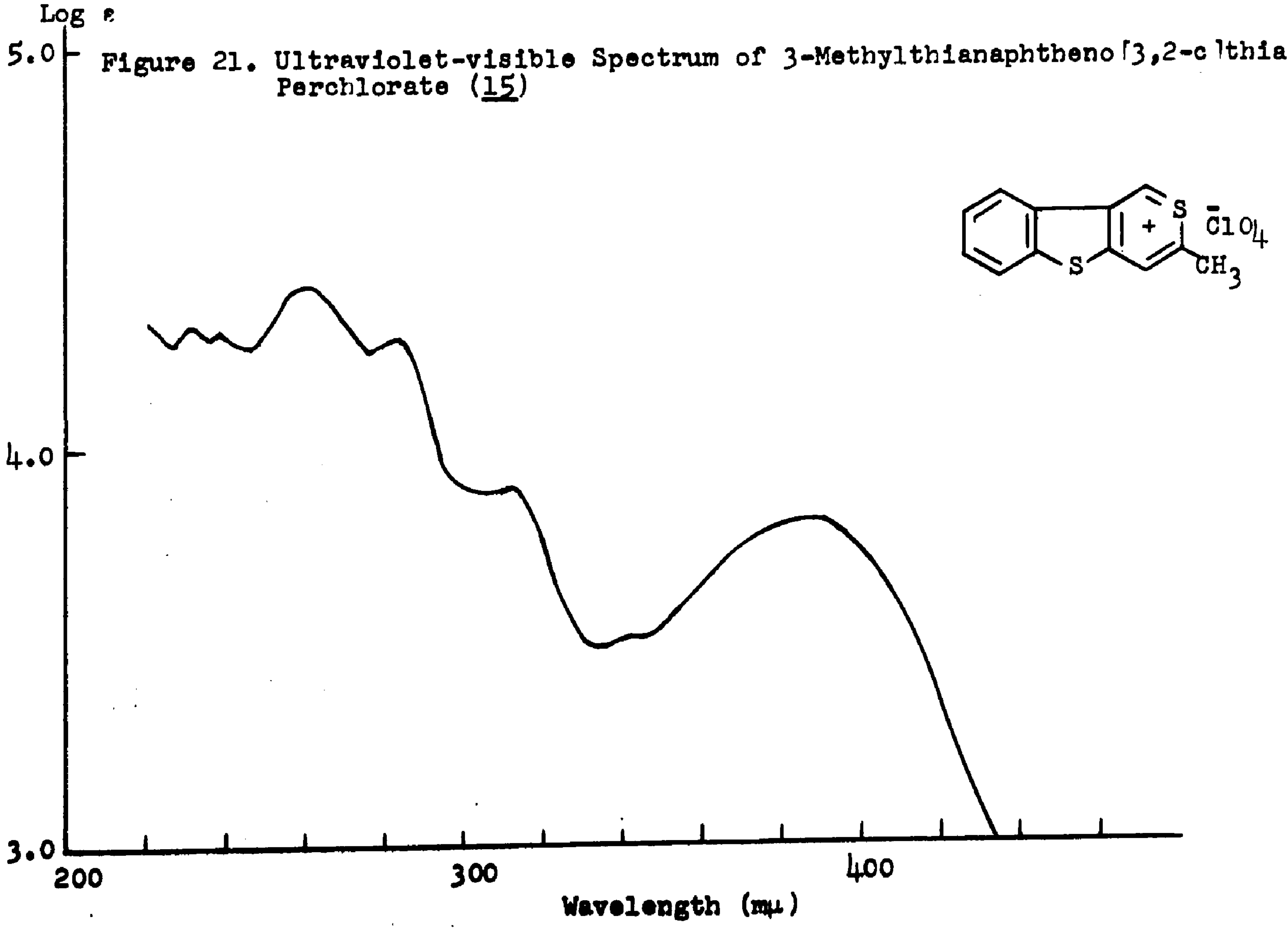


Figure 21. Ultraviolet-visible Spectrum of 3-Methylthianaphtheno[3,2-c]thiapyrylium Perchlorate (15)

Figure 22. Ultraviolet-visible Spectrum of Thianaphtheno[2,3-c]thiapyrylium Perchlorate (16)

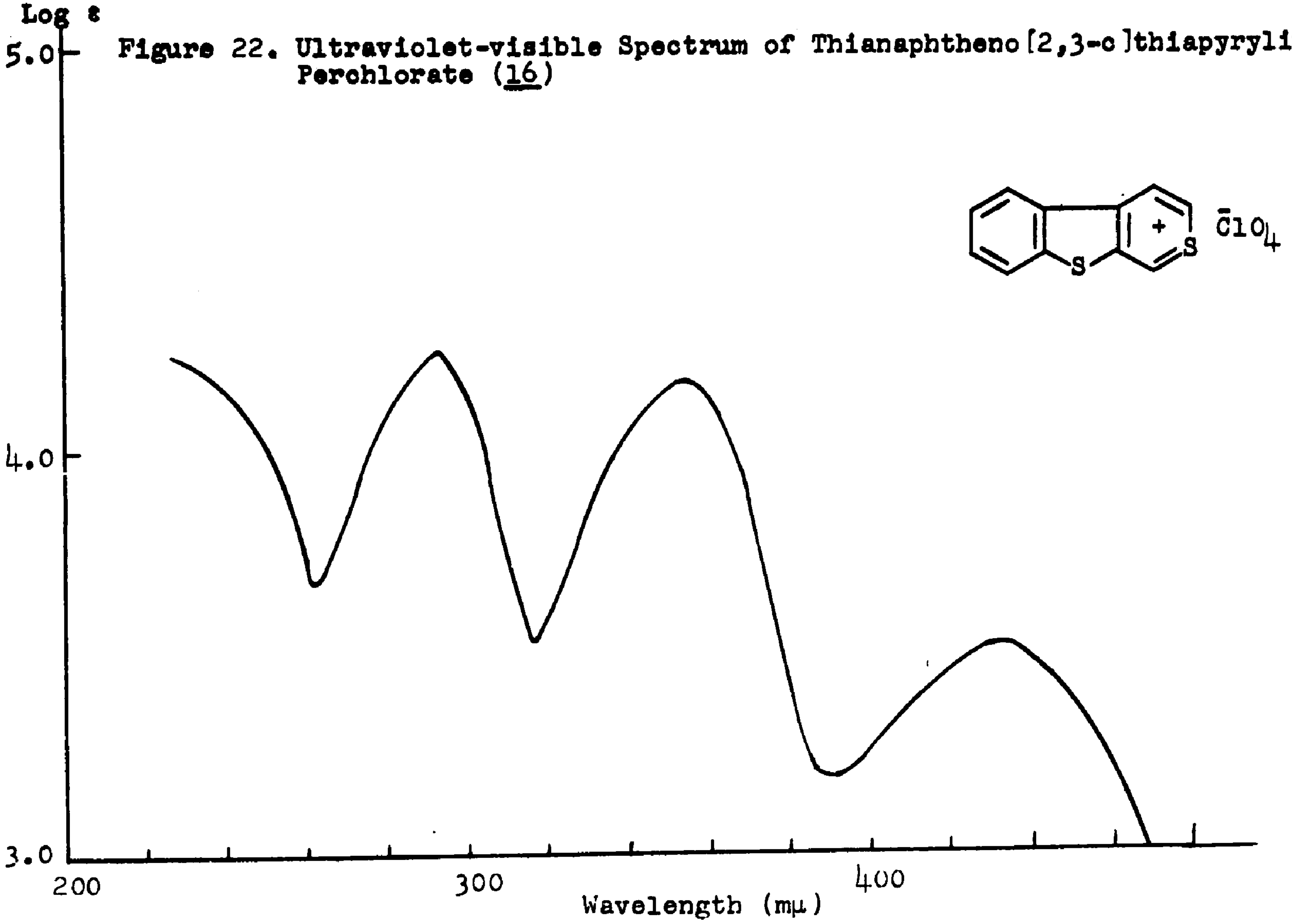


Figure 23. Ultraviolet-visible Spectrum of Thianaphtheno[2,3-b]thiapyrylium Perchlorate (17)

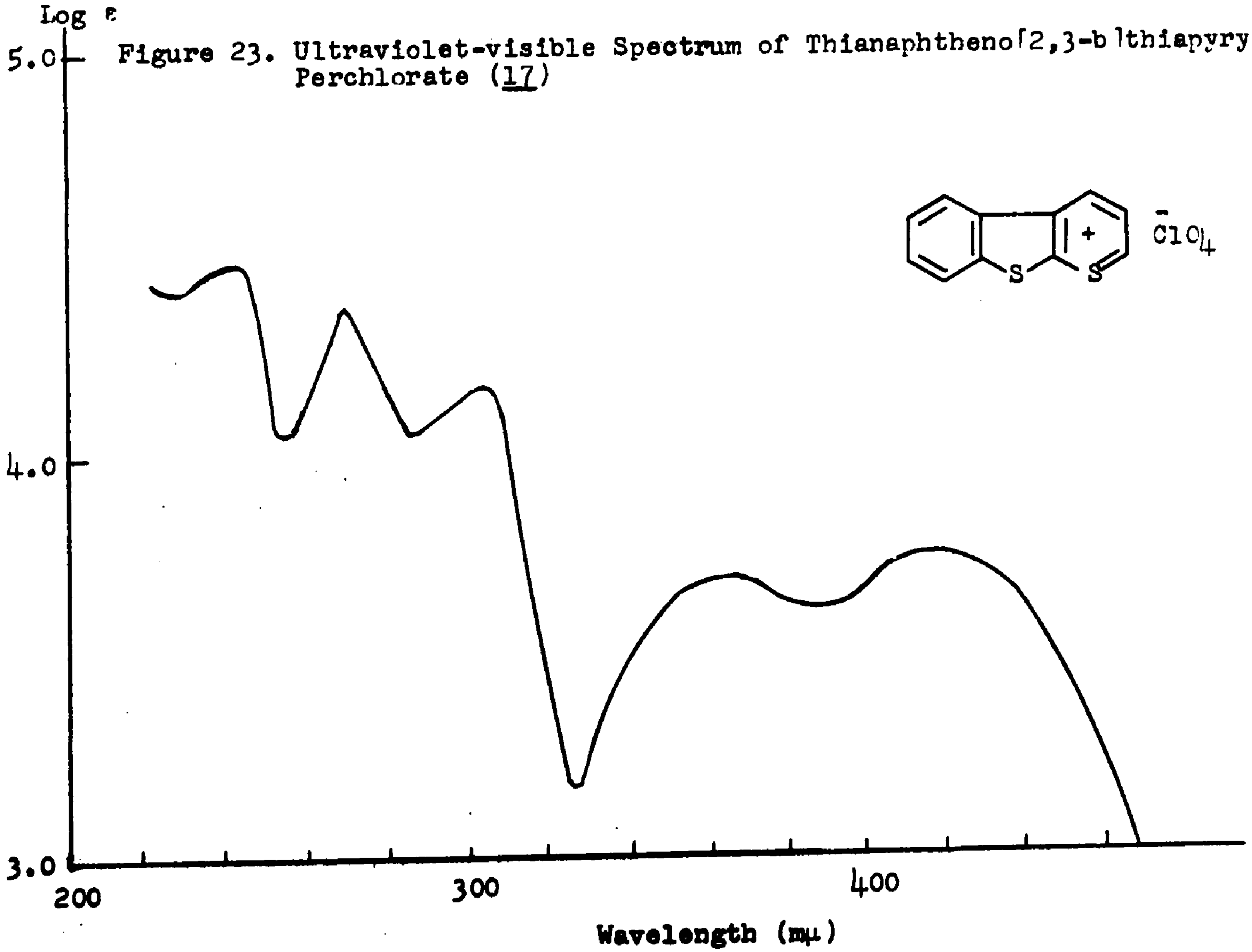
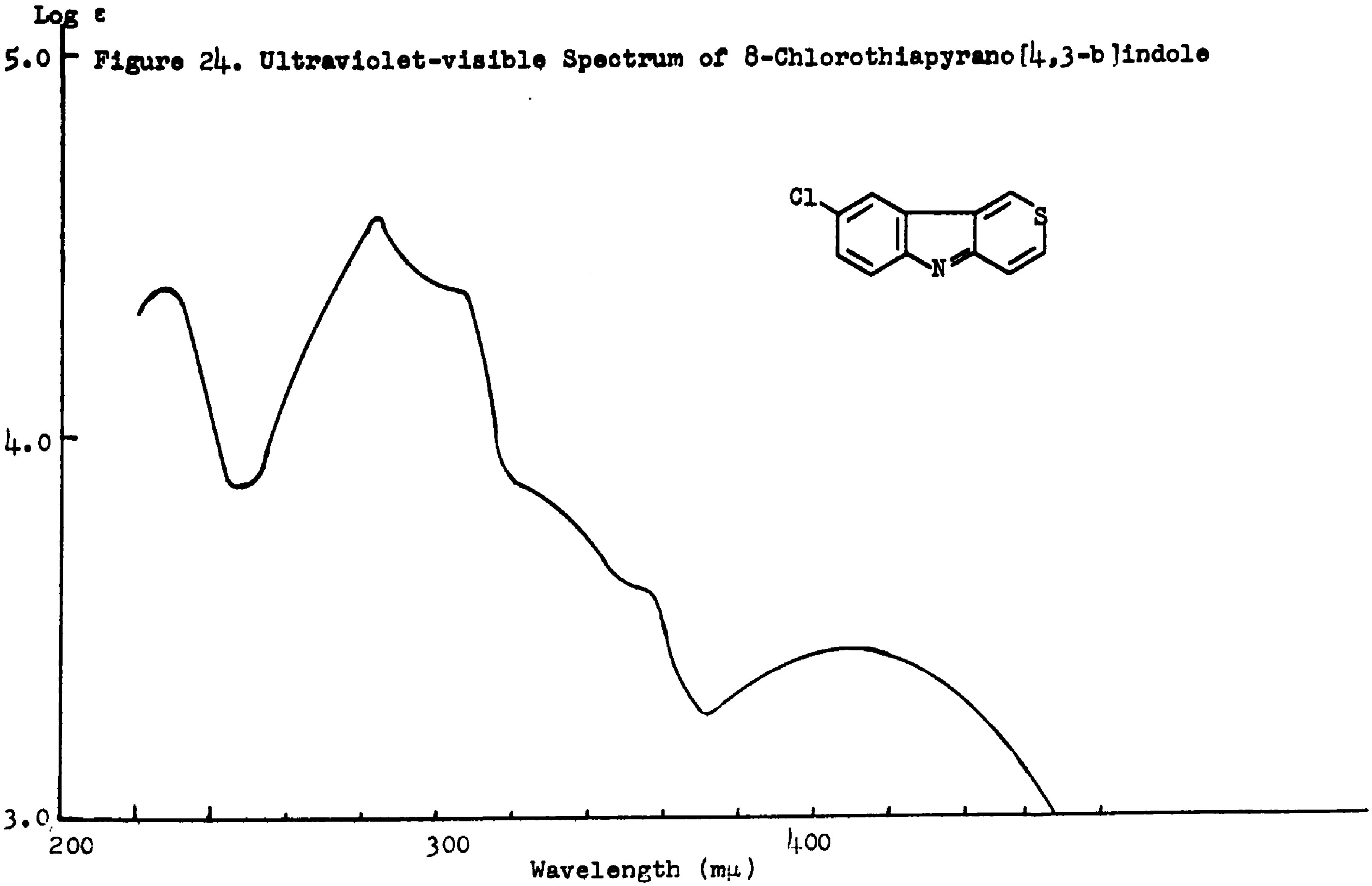


Figure 24. Ultraviolet-visible Spectrum of 8-Chlorothiapyrano[4,3-b]indole



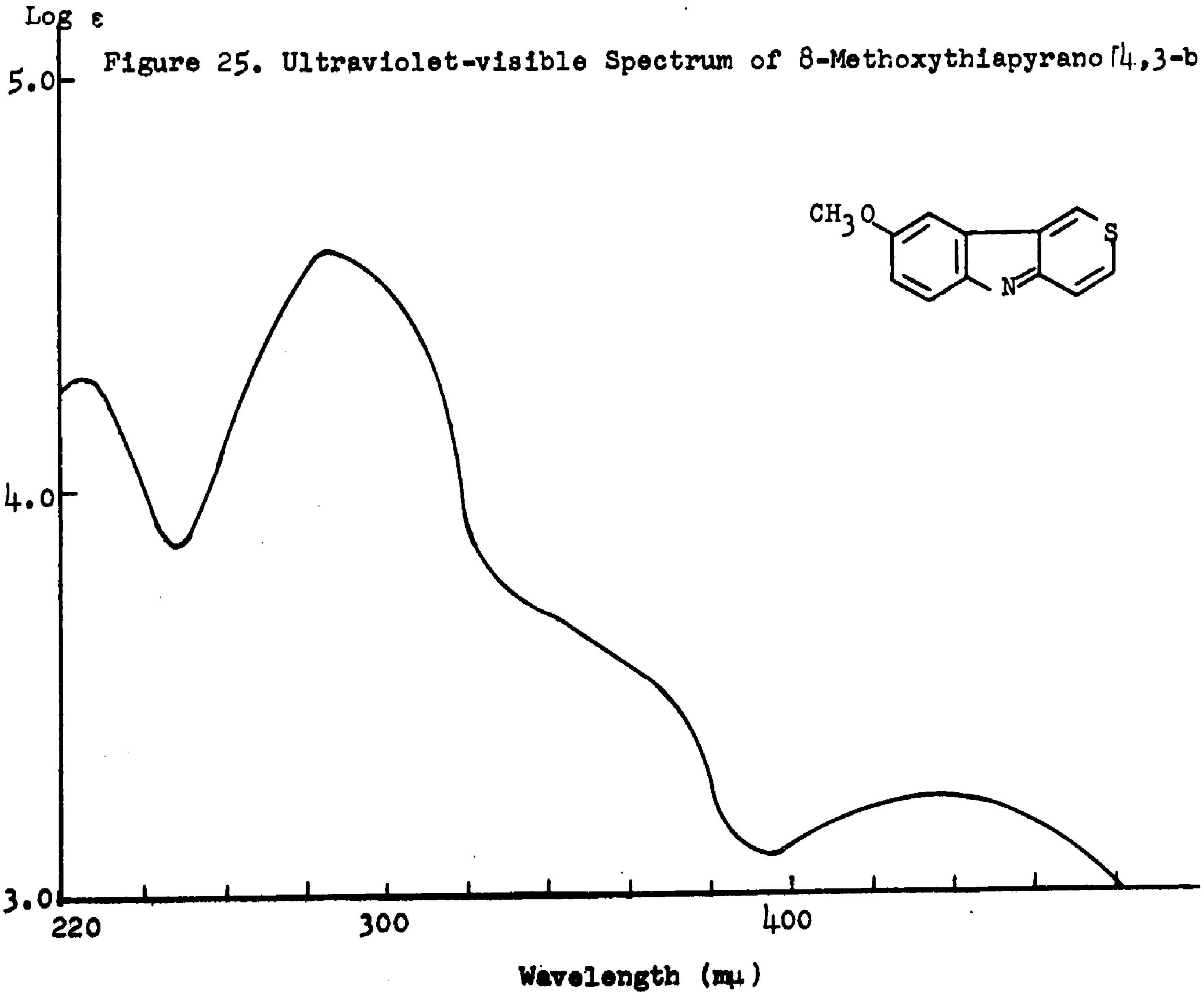


Figure 25. Ultraviolet-visible Spectrum of 8-Methoxythiapyrano[4,3-b]indole

Figure 26. Ultraviolet-visible Spectrum of 8-Nitrothiapyrano[4,3-b]indole

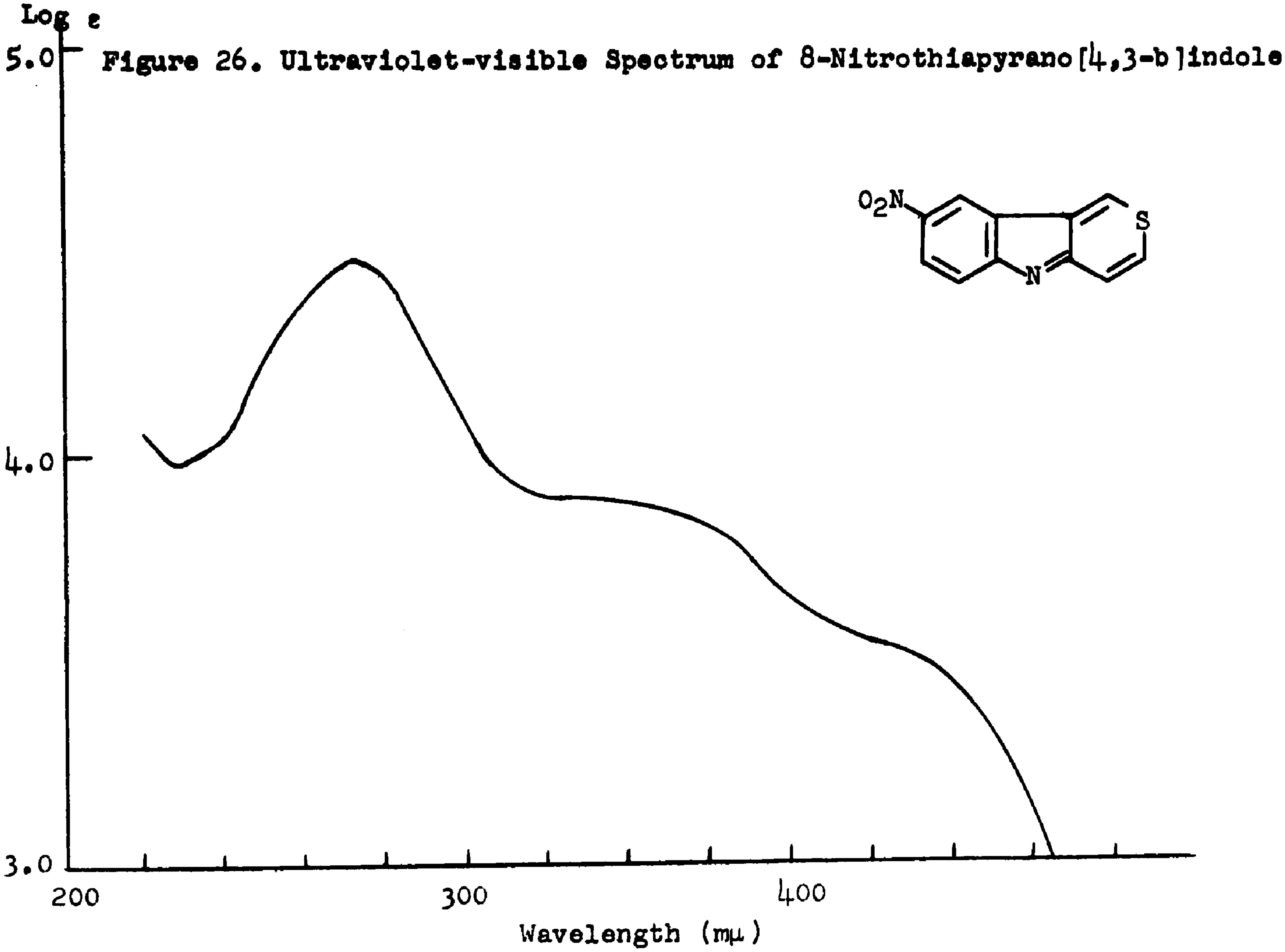


Figure 27. Ultraviolet-visible Spectrum of 6-Methylthiapyrano[4,3-b]indole

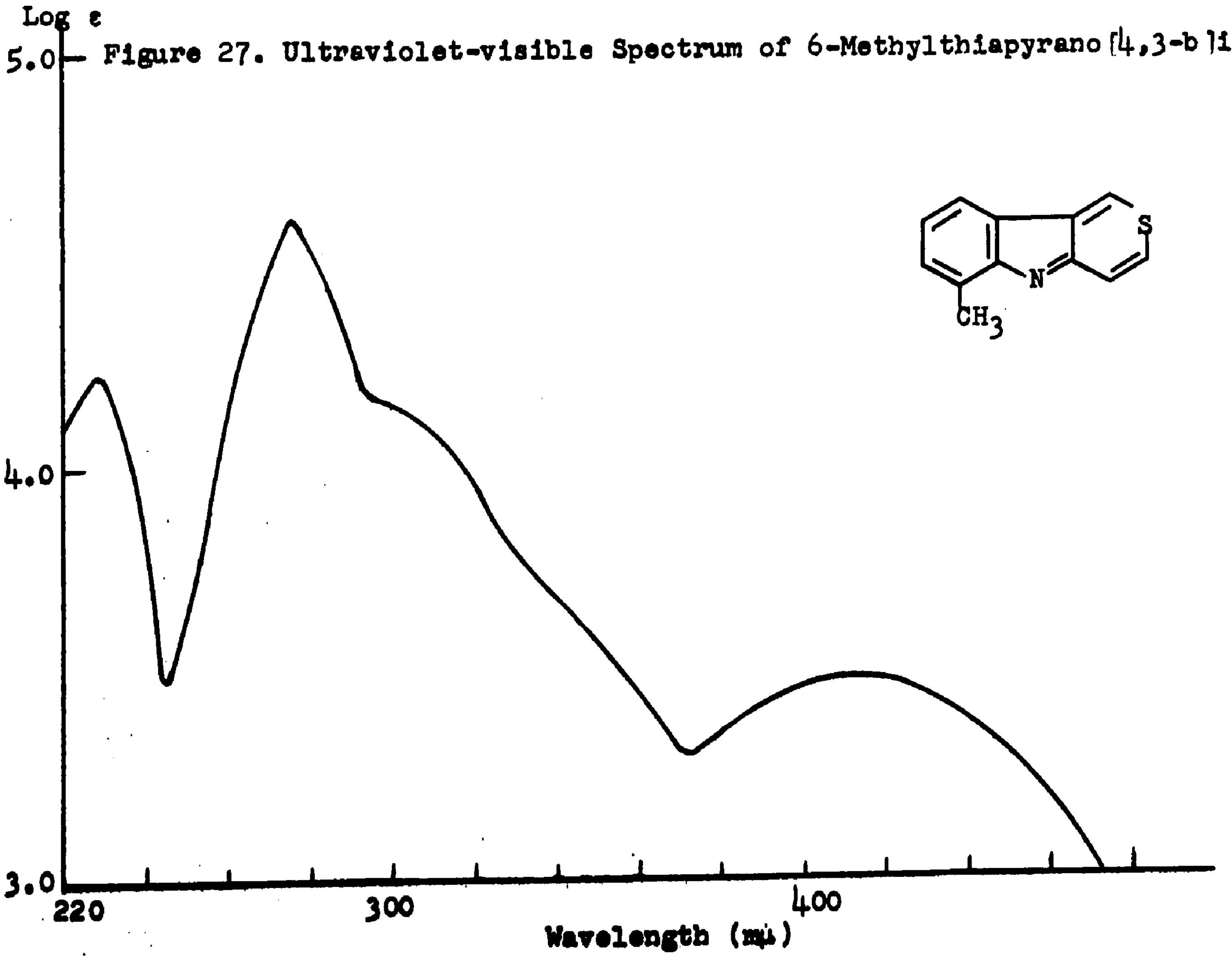


Table 4

ULTRAVIOLET AND VISIBLE SPECTRA OF THIENOTHIAPYRYLIUM PERCHLORATES

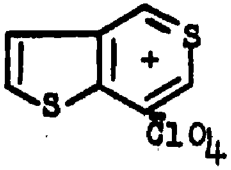
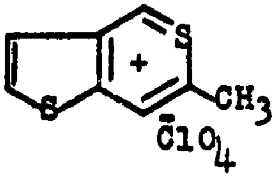
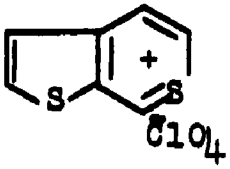
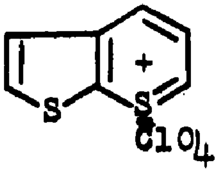
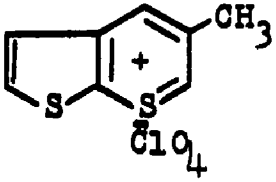
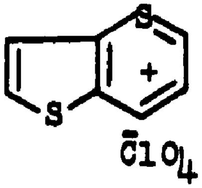
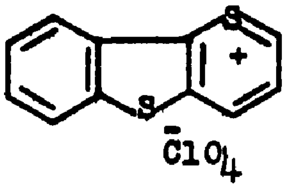
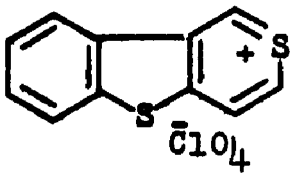
					
9	**10**	**11**	**18**	**12**	**19**
$\lambda_{m\mu}$ log ε	$\lambda_{m\mu}$ log ε	$\lambda_{m\mu}$ log ε	$\lambda_{m\mu}$ log ε	$\lambda_{m\mu}$ log ε	$\lambda_{m\mu}$ log ε
357 (3.44)	366 (3.52)	381 (4.04)	361 (3.36)	370 (3.41)	396 (3.69)
304 (3.53)	306 (4.60)	304 (3.78)	333 (3.77)	337 (3.64)	322 (3.74)
263 (4.57)	264 (4.61)	262 (4.29)	262 (4.47)	264 (4.48)	260 (4.36)
	228.5 (4.32)	224.5 (4.25)			

Table 5

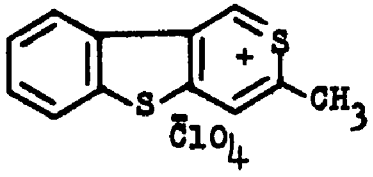
ULTRAVIOLET AND VISIBLE SPECTRA OF THIANAPHTHENOTHIAPYRYLIUM PERCHLORATES



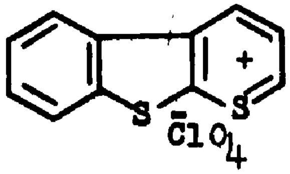
13



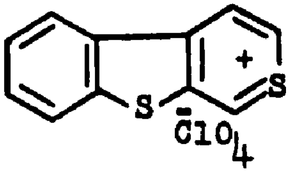
14



15



16



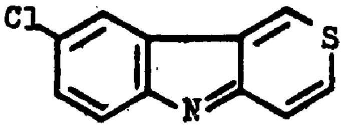
17

13		14		15		16		17	
$\lambda_{m\mu}$	log ε	$\lambda_{m\mu}$	log ε	$\lambda_{m\mu}$	log ε	$\lambda_{m\mu}$	log ε	$\lambda_{m\mu}$	log ε
379	(4.12)	384	(3.80)	385	(3.81)	423	(3.74)	433	(3.52)
297	(4.05)	314	(3.81)	312	(3.91)	361	(3.64)	354	(4.18)
232.5	(4.47)	283	(4.25)	283	(4.28)	202	(4.35)	292	(4.24)
		265	(4.32)	265_{sh}	(4.39)	268	(4.35)		
		254	(4.56)	254	(4.40)	243	(4.49)		
		237_{sh}	(4.18)	240.5	(4.28)				
		233_{sh}	(4.13)						

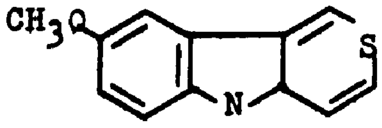
Table 6

ULTRAVIOLET AND VISIBLE SPECTRA OF THIAPYRANO[4,3-b]INDOLES

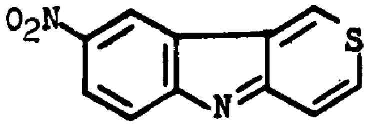
Solvent = 95% Ethanol



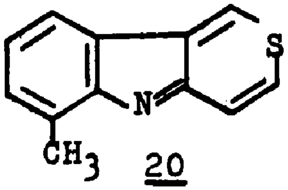
21



22



23



20

21 $\lambda_{m\mu}$ log ε	22 $\lambda_{m\mu}$ log ε	23 $\lambda_{m\mu}$ log ε	20 $\lambda_{m\mu}$ log ε
410 (3.44)	426 (3.24)	398 (3.55)	413 (3.48)
356 (3.59)	367 (3.51)$_{sh}$	320 (3.89)	359 (3.47)$_{sh}$
303 (4.40)	295 (4.55)$_{sh}$	273 (4.48)	300 (4.14)
284 (4.61)	286 (4.60)		275 (4.59)
278 (4.49)	226 (4.28)		228 (4.23)
229 (4.41)			

Table 7

λ_{max}, ΔE and Δm for Thieno and Thianaphthenothiapyrylium Perchlorates

Compound	λ_{max} (mμ)	ΔE (kcm^{-1})	Δm
18	361	27.7	1.01
11	381	26.2	1.03
9	357	28.0	1.02
19	396	25.3	1.02
16	423	23.6	1.06
17	433	23.1	0.95
14	384	26.0	1.11
13	379	26.4	0.95

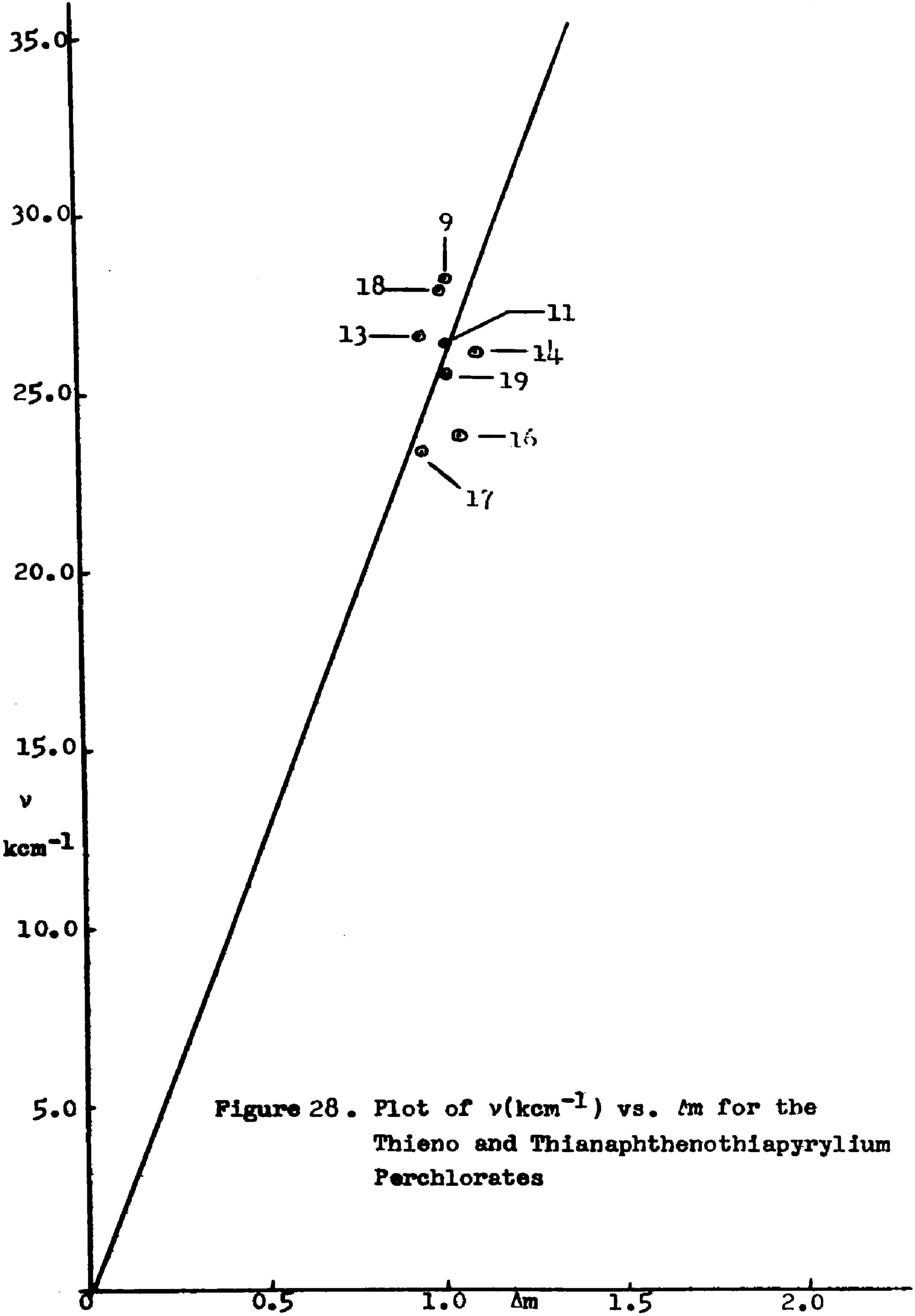
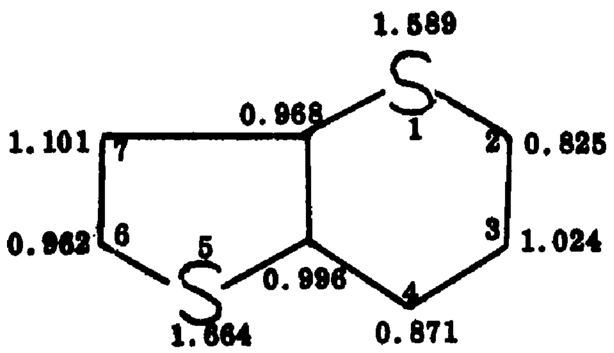


Figure 28. Plot of ν(kcm^{-1}) vs. Δm for the Thieno and Thianaphthenothiapyrylium Perchlorates

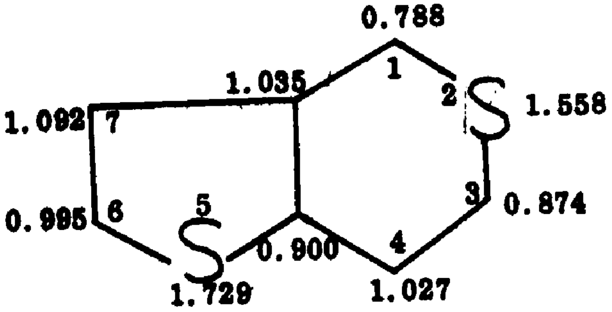
Figure 29

ELECTRON DENSITY CALCULATIONS AND EIGENVALUES (β)



19

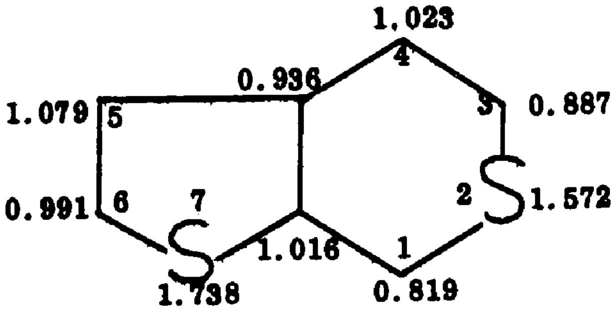
Eigenvalues
-1.956
-1.443
-1.051
-0.330
0.695
0.772
1.319
1.534
2.260



9

Eigenvalues
-2.010
-1.372
-0.802
-0.444
0.576
0.942
1.230
1.496
2.184

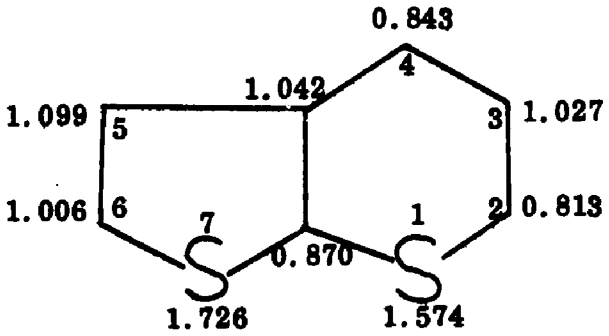
Figure 29 (continued)



11

Eigenvalues

-2.030
-1.218
-1.018
-0.372
0.661
0.854
1.240
1.495
2.188

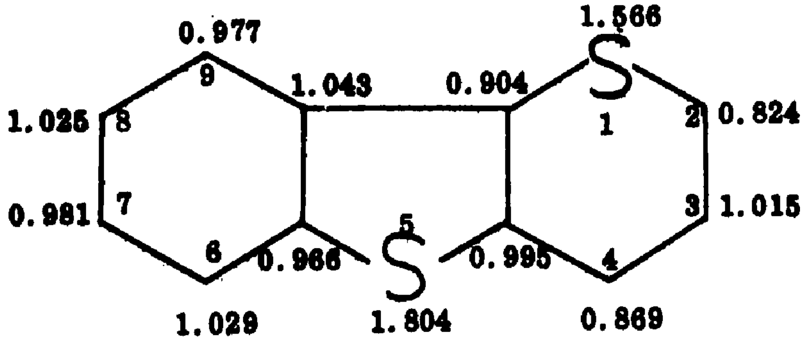


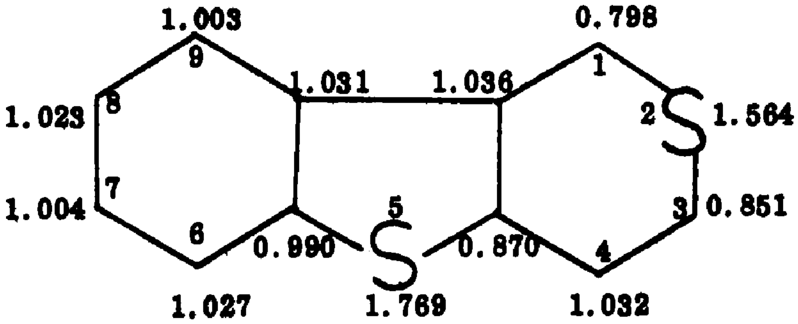
18

Eigenvalues

-2.002
-1.313
-0.946
-0.380
0.631
0.861
1.271
1.515
2.163

Figure 29 (continued)





<u>13</u>

<u>Eigenvalues</u>

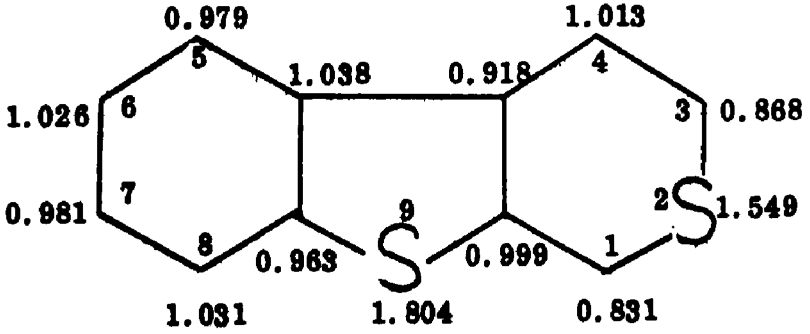
-2.178
-1.821
-1.315
-1.069
-0.879
-0.318
0.631
0.779
1.076
1.305
1.412
1.851
2.325

<u>14</u>

<u>Eigenvalues</u>

-2.243
-1.808
-1.140
-1.036
-1.000
-0.335
0.610
0.830
1.000
1.318
1.833
1.419
2.358

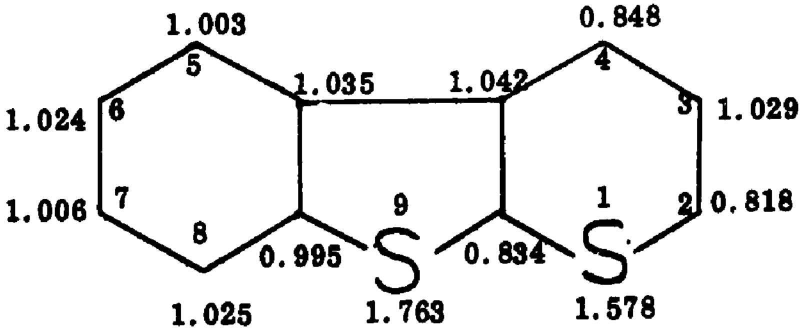
Figure 29 (continued)



16

Eigenvalues

-2.231
-1.820
-1.266
-1.050
-0.762
-0.442
0.663
0.733
1.069
1.301
1.411
1.839
2.356



17

Eigenvalues

-2.233
-1.792
-1.253
-1.073
-0.839
-0.396
0.669
0.737
1.067
1.319
1.412
1.836
2.343

Polarography

It has been shown that polarographic half-wave reduction potentials of aromatic hydrocarbons can be linearly correlated with the HMO energy of the lowest vacant molecular orbitals of the hydrocarbons[9].

In this study, polarographic half-wave reduction potentials were determined for the ten thieno and thianaphthenothiapyrylium perchlorates as well as for six of the salts prepared by Ohnmacht.

The only apparent correlation for the thieno and thianaphtheno salts is a qualitative one. When the thionium sulfur is β to the ring juncture, the half-wave reduction potential is more negative than when the thionium sulfur is α to the ring juncture. A scan of the data in Table 8 for these compounds will show that no correlation was obtained with the energy of the lowest vacant molecular orbital. The data for Ohnmacht's compounds (1 - 6 in Table 9) show a correlation as plotted in Figure 30. A least squares treatment of the data yielded the equation, $E_{1/2} = 1.85\ (m) - 0.354$. A typical polarogram is shown in Figure 31. Oxidative potentials could not be determined for the salts because the supporting electrolyte decomposed before the required voltages were reached.

Experimental

A conventional three-electrode potentiostatic polarograph with vacuum tube amplifiers constructed at Lehigh University was used. The polarograms were recorded on a fast pen-and-ink recorder, Moseley X-Y Recorder, No. 7030A (Bala-Cynwyd, Pa.) with a scan rate of 3.3 mv/sec. Potentials were measured using an Electrometer 600A, Keithly Instruments, Cleveland, Ohio. The polarograms were all run in acetonitrile which was distilled from phosphorous pentoxide and then from anhydrous potassium carbonate. The acetonitrile was 0.2N in sodium perchlorate and 1.0 mM in 70% perchloric acid and 1.0 mM in the compound on which the polarogram was to be run.

The polarographic cell was a four-ounce glass jar, 6 cm in diameter and 6 cm deep. A No. 10-1/2 rubber stopper supported the electrode and gas dispersion tube. The saturated calomel electrode (SCE) was connected to the cell by a three-compartment reference bridge constructed with fitted glass discs. The compartments were filled with: (1) acetonitrile which was 0.2N in sodium perchlorate; (2) water which was 0.5N in sodium perchlorate; and (3) saturated aqueous potassium chloride. The dropping mercury electrode (DME) was centered between the SCE and the auxiliary electrode. The auxiliary electrode was a piece of platinum wire sealed into a piece of glass tubing. The entire assembly was placed in a constant temperature bath thermostatted at 25.0 ± 0.1°. A coarse frit gas-dispersion tube was used to pass prepurified nitrogen intothe electrolysis solution for <u>ca.</u> ten minutes to displace oxygen.

Table 8

$-E_{1/2}$ and m_{m+1} for Thiapyrylium Perchlorates

Perchlorate Salts	$-E_{1/2}$ (Volts)	m_{m+1} (β Units)
9	0.34	0.4438
10	0.41	----
11	0.35	0.3717
18	0.22	0.3800
12	0.22	----
13	0.10	0.3182
14	0.35	0.3353
15	0.34	----
16	0.22	0.4424
17	0.15	0.3955

Table 9

$-E_{1/2}$ and m_{m+1} for Thiapyrylium Salts

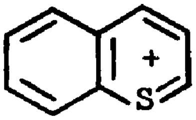
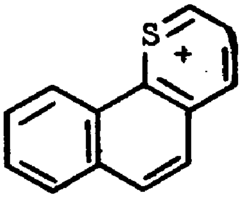
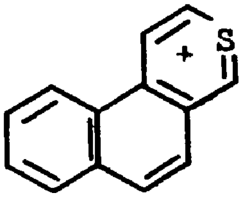
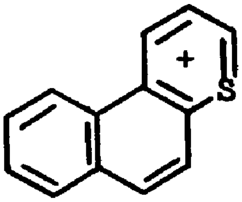
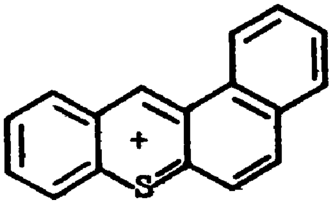
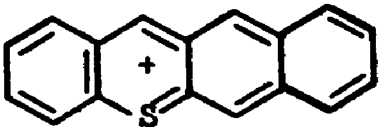
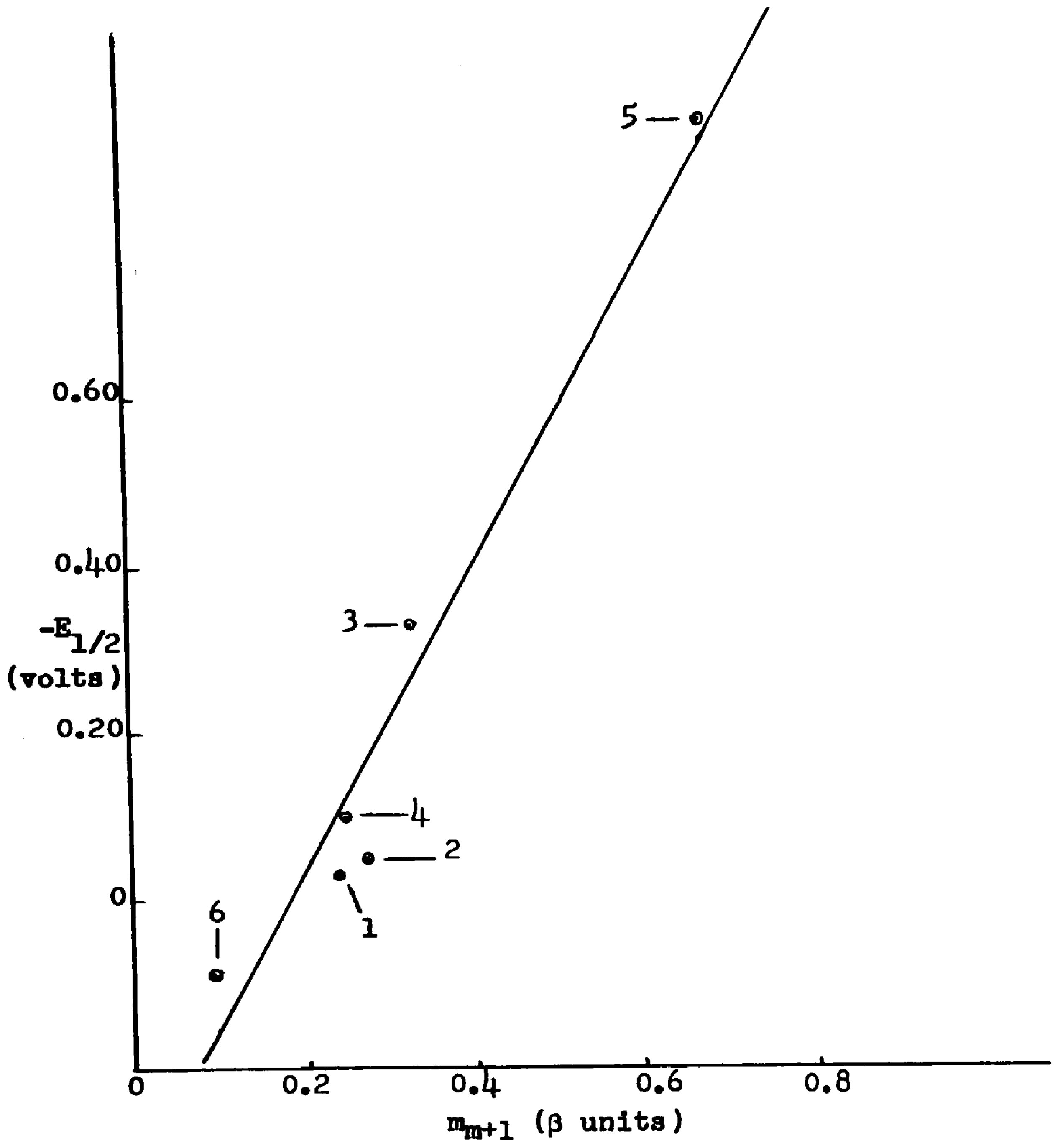
Perchlorate Salts	$-E_{1/2}$ (Volts)	m_{m+1} (β Units)
	0.03	0.2430
	0.05	0.2780
	0.33	0.3306
	0.10	0.2537
	0.94	0.6862
 as the TNBS salt	-0.09	0.0905

Figure 30. Plot of $-E_{1/2}$ vs. the Energy of the Lowest Unoccupied Molecular Orbital (β Units) for the Thiapyrylium Salts in Table 9



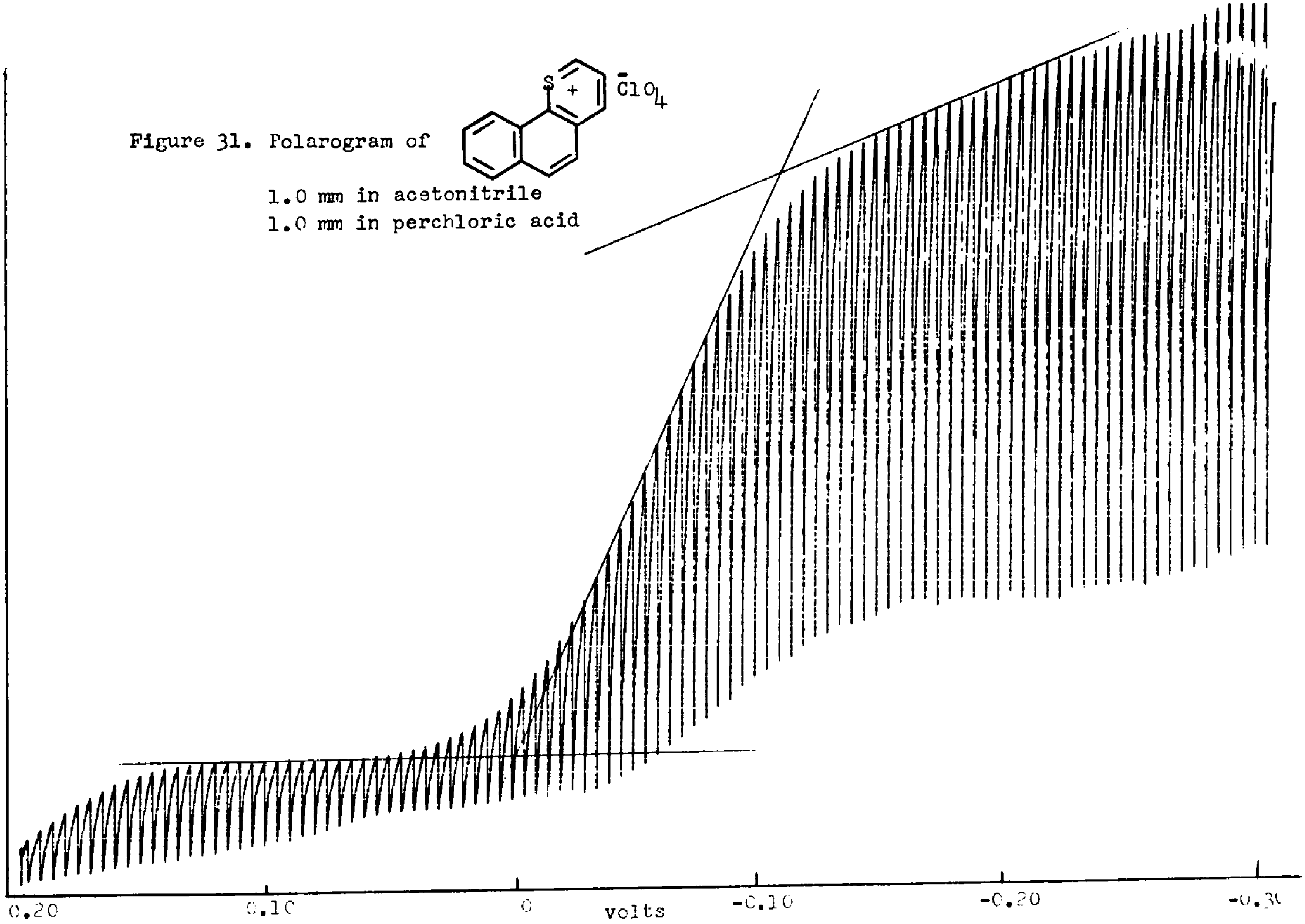


Figure 31. Polarogram of $\bar{C}lO_4$

1.0 mm in acetonitrile
1.0 mm in perchloric acid

EXPERIMENTAL

Melting points were determined in Kimax capillary tubes using a "Mel-Temp" apparatus (Laboratory Devices, Box 68, Cambridge, Massachusetts) and are uncorrected.

The microanalyses were performed by the late Dr. V. B. Fish of Lehigh University and by Galbraith Microanalytical Laboratories, Knoxville, Tennessee.

Infrared spectra were recorded on a Perkin-Elmer Model 257 instrument. Solid samples were run, at a concentration of approximately 1% by weight, in potassium bromide disks. Liquid samples were run neat between sodium chloride plates.

Ultraviolet spectra were recorded on a Beckman DK-2A spectrophotometer. The solvents are specified with the recorded spectra.

The nuclear magnetic resonance spectra were recorded on a Varian A-60 spectrometer in deuteriotrifluoroacetic acid for the salts and other specified solvents using tetramethylsilane (δ=0) as an internal standard and are presented in the order δ (multiplicity, number of protons, assignment).

The mass spectrum was run by Dr. J. E. Sturm on a Hitachi 6E high resolution instrument equipped with double focusing sector.

The petroleum ether used was the fraction boiling at 60-70° unless otherwise noted.

3-Thenylbromide(26)

This compound was prepared essentially according to a procedure of Hartough[35].

A solution of 32.0 g (0.326 mol) of 3-methylthiophene and 0.5 g benzoyl peroxide in 200 ml dry benzene (filtered from sodium ribbon) was heated to vigorous reflux with mechanical stirring and 35.4 g (0.20 mol) of N-bromosuccinimide (dried at 0.05 mm and 25° for four hrs before use) admixed with 0.5 g benzoyl peroxide and added over five min through a powder funnel which was bathed in refluxing benzene. An ultraviolet lamp was aimed at the reaction flask during this addition and for the five min reflux after completion of addition. Vigorous foaming occurred during the addition.

The resulting slurry was cooled to 0-5° in an ice bath. The succinimide was collected on a filter and washed with 2 x 50 ml of dry benzene. The solvent was evaporated on a rotary evaporator. Distillation _in vacuo_ gave 25.1 g of 3-thenylbromide (71.0% based on N-bromosuccinimide; 44.0% based on 3-methylthiophene) of material with a boiling range of 54-74° while the pressure varied from 0.3 to 0.1 mm: lit.[38] bp 78-82° (2 mm); nmr (CCl_4) δ 7.10 (m, 3, Ar_H_) and 4.36 (s, 2, C$\underline{H}_2$Br) ppm.

S - (3-thenyl)-mercaptoacetic acid (27)

To 15.9 g (0.283 mol) of potassium hydroxide dissolved in 150 ml of water was added, with ice-bath cooling, 13.05 g (0.142 mol) of mercaptoacetic acid. After the solution had cooled to 25°, 25.1 g (0.142 mol) of 3-thenylbromide was added and the two-phase mixture was stirred magnetically at 74° for eighteen hrs. The organic layer (4.6 g) was allowed to settle and was separated. The aqueous layer was extracted with three 50 ml portions of benzene (which were discarded) and then acidified with 25 ml of concentrated hydrochloric acid. The resulting oil was separated and the acidic aqueous layer was extracted with three 75 ml portions of benzene. The combined oil and benzene extracts were washed with two 100 ml portions of water, dried ($MgSO_4$), filtered and evaporated on a rotary evaporator to an oil. Distillation at 136-8° (0.12 mm) gave 15.2 g (70% after correcting for the non-reacted organic layer of S-(3-thenyl)-mercaptoacetic acid. The analytical sample distilled at 147° (0.45 mm); lit.^{25} bp 200° (14 mm); ir (neat) 3400-2500 (bonded OH), 1705 (acid C=0) and strong bands at 1420, 1295 and 782, 708 and 675 cm^{-1}; nmr (CCl_4) δ 12.13 (s, 1 $CO_2\underline{H}$), 7.12 (m, 3, Ar$\underline{H}$) 3.83 (s, 2, $C\underline{H_2}S$), and 3.00 (s, 2, $SC\underline{H_2}CO_2H$) ppm.

Anal. Calcd for $C_7H_8O_2S_2$: C, 44.66; H, 4.28; S, 34.06. Found: C, 44.93; H, 4.56; S, 33.82.

3,4-Dihydro-1H-thieno[3,2-c]thiapyran-4-one (29)

A stirred solution of 5.0 g (0.027 mol) of S-(3-thenyl)-mercaptoacetic acid, 1.9 ml (0.027 mol) of thionyl chloride and 0.2 ml of pyridine in 50 ml dry benzene (filtered from sodium ribbon) was refluxed fifteen min. Another 1.9 ml of thionyl chloride was added and reflux was continued for twenty min. Removal of the benzene and excess thionyl chloride on a rotary evaporator with two 50 ml benzene flushes to remove all the thionyl chloride produced a dark oil which was dissolved in 50 ml dry benzene. Upon cooling to 5° in an ice bath, 5.0 ml (0.043 mol) of anhydrous stannic chloride was added in one portion. The temperature rose to 25° and the resulting slurry was stirred at 25° for one hr. The slurry was poured onto 25 ml of ice and 25 ml of concentrated hydrochloric acid and the flask was rinsed with concentrated hydrochloric acid and benzene. The water-benzene mixture was stirred for one-half hr and a black tar was removed by filtration. The layers were separated and the aqueous layer was extracted with three 75 ml portions of benzene. The combined layers were washed with 100 ml of water, 100 ml of 10% sodium carbonate solution and 100 ml of a saturated sodium chloride solution. Filtration was necessary with each wash. The benzene solution was dried ($MgSO_4$), filtered, and the benzene was removed on a rotary evaporator. The residual oil was distilled at 130-5° (0.55 mm) to give 3.3 g (73%)of 3,4-dihydro-1H-thieno[3,2-c]thiapyran-4-one. Crystallization from benzene-hexane gave 1.85 g, mp 62.0-63.5°. Sublimation at 70° (0.08 mm) gave 1.5 g, mp 68-70°. Resublimation at 70° (0.08 mm) produced no change in melting point. Recrystallization from benzene-petroleum ether with a carbon treatment gave 0.5 g, mp 67.0-68.5°. Sublimation at 67° (0.05 mm) gave 0.5 g: mp 68-70° lit.[25] mp 67°;

ir (KBr) 3065 medium (aromatic H), 2950 and 2890 weak (methylene), 1640 strong (C=O) and strong bands at 1420-1380, 1305-1265, 1217, 1152, 1128, 1095, 995, 900, 848, 791, 758, and 740 cm^{-1}; nmr (C_6D_6) δ 7.62 (d, 1, J = 5 Hz, H-6), 6.98 (d, 1, J = 5 Hz, H-7), 3.85 (d, 2, J = 1.5 Hz, $C\underline{H}_2$-S) and 3.48 (d, 2, J = 1.5 Hz, $SC\underline{H}_2CO$) ppm.

Anal. Calcd for $C_7H_6OS_2$: C, 49.38; H, 3.55; S, 37.67. Found: C, 49.26; H, 3.82; S, 37.72.

3,4-Dihydro-1H-thieno[3,2-c]thiapyran-4-ol (30)

To a solution of 3.4 g (0.020 mol) of 3,4-dihydro-1H-thieno[3,2-c]thiapyran-4-one dissolved in 250 ml warm isopropanol was added 0.76 g (0.020 mol) of finely powdered sodium borohydride. The mixture was stirred magnetically at reflux overnight. Upon cooling, the reaction mixture was poured into 250 ml cold water. The aqueous isopropanol mixture was extracted with three 100 ml portions of benzene. The combined benzene extracts were washed with 100 ml of water, dried ($MgSO_4$), filtered, and evaporated to an oil on a rotary evaporator. Distillation at 107-109° (0.10 mm) yielded 3.0 g (87%) of 3,4-dihydro-1H-thieno[3,2-c]thiapyran-4-ol: ir (neat) 3600-3120 (bonded OH), 3090 medium (aromatic H), 2900 (methylene) and other strong bands at 1420-1400, 1378, 1192, 1032, 990, 710 and 680 cm^{-1}; nmr (C_6D_6) δ 6.92 (d, 1, J = 5 Hz, H-6), 6.45 (d, 1, J = 5 Hz, H-7), 4.72 (broad s, 1, $HOC\underline{H}$) 3.80 (m, 1, $\underline{H}O$-CH), 3.32 (s, 2, $C\underline{H}_2S$), and 2.65 (d, 2, J = 5 Hz, $SC\underline{H}_2CHOH$) ppm.

Anal. Calcd for $C_7H_8OS_2$: C, 48.80; H, 4.68; S, 37.23. Found: C, 48.93; H, 4.67; S, 37.42.

Thieno[3,2-c]thiapyrylium perchlorate (9) (trityl perchlorate method)

To a magnetically stirred, refluxing solution of 3.0 g (0.0174 mol) of 3,4-dihydro-1H-thieno[3,2-c]thiapyran-4-ol in 45 ml of glacial acetic acid was added 5.96 g (0.0174 mol) of trityl perchlorate in 50 ml of nitromethane over a two min period. The solution turned dark red (nearly black) as reflux was continued for fifteen min. The reaction mixture was allowed to cool ambiently with stirring to room temperature and the solvent was removed on a rotary evaporator. The resulting oil solidified on dilution to 450 ml with diethyl ether. After overnight refrigeration, the product was collected on a filter and air dried to give 5.5 g, mp 142-5°, with much prior softening. The product was slurried in 175 ml of boiling glacial acetic acid and a black, insoluble tar was removed by filtration. Upon cooling to room temperature, 1.7 g, mp 171-4°, was obtained. Two further recrystallizations from glacial acetic acid, the first with a carbon treatment, gave 0.9 g of thieno[3,2-c]thiapyrylium perchlorate (20%), mp 165-7°: visible and uv max (1% perchloric acid in acetonitrile) 263 mμ (log ε, 4.57), 304 (3.53) and 357 (3.44); ir (KBr) 3100-3000 (aromatic H), and strong bands at 1530, 1430, 1362, 1311, 1255, 1150-1000 (perchlorate), 918, 872, 804, 760 cm^{-1}; nmr (CF_3CO_2D) δ 10.60 (m, 1, H-1), 9.43 (m, 2, H-3 and H-4), 8.52 (d, 1, J = 6 Hz, H-6), and 8.20 (d, 1, J = 6 Hz, H-7) ppm.

<u>Anal</u>. Calcd for $C_7H_5ClO_4S_2$: C, 33.27; H, 1.99; Cl, 14.03. Found: C, 33.16; H, 2.06; Cl, 14.20; S, 25.27.

<u>Thieno[3,2-c]thiapyrylium perchlorate (9) (2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) and perchloric acid method)</u>

To a magnetically stirred solution at 25° of 1.5 g (0.0087 mol)of 3,4-dihydro-1H-thieno[3,2-c]thiapyran-4-ol dissolved in 40 ml of glacial acetic acid and 10 ml of nitromethane was added 1.95 g (0.0087 mol) of DDQ dissolved in 10 ml of glacial acetic acid and 10 ml of nitromethane. Then 7 ml of 70% perchloric acid was pipetted into the flask. The temperature rose to 35°. After stirring one hr at 25°, evaporation of the solvent on a rotary evaporator and dilution to 1.0 l. with diethyl ether produced a black solid. After overnight refrigeration, the solid was collected by filtration, washed with ether and dried at 25° (0.05 mm) overnight to give 2.7 g of crude material, mp 130°. The product was slurried in 150 ml of boiling glacial acetic acid and a black tar was removed by filtration. After cooling to 25°, collection of the black crystals on a filter and air drying gave 2.5 g. Recrystallization from glacial acetic acid with a massive carbon treatment gave 0.6 g (27%) of thieno[3,2-c] thiapyrylium perchlorate as beige plates, mp 165-167°.

S-(3-thenyl)-thiolactic acid

To 15.0 g (0.141 mol) of thiolactic acid dissolved in 200 ml of dry glyme (distilled from lithium aluminum hydride) was added with stirring and ice bath cooling, 15.24 g (0.282 mol) of sodium methoxide. The thick, white precipitate which formed was broken up, 25.0 g (0.141 mol) of 3-thenylbromide was added and the mixture was stirred at reflux overnight. Upon cooling, 300 ml of water was added followed by 20 ml of concentrated hydrochloric acid. The resulting oil was extracted into benzene, which was dried ($MgSO_4$), filtered, and evaporated to an oil on a rotary evaporator. Distillation gave 15.65 g (74% after correcting for a 3.8 g forerun of thiolactic acid) of S-(3-thenyl)-thiolactic acid: bp 140-3° (0.25 mm), lit.[25] 203° (15 mm); ir (neat) 3500-2500 (bonded OH), 1700 (acid C=O), and strong bands at 1450, 1410, 1280, 1240, 1195, 1075 and 780 cm^{-1}; nmr (C_6D_6) δ 12.27 (s, 1, $CO_2\underline{H}$), 7.00 (m, 3, Ar-H), 3.90 (d, 1, J = 14 Hz, $C\underline{H}_2S$), 3.55 (d, 1, J = 14 Hz, $C\underline{H}_2S$), 3.15 (q, 1, J = 7 Hz, $SC\underline{H}$) and 1.22 (d, 3, J = 7 Hz, $C\underline{H}_3$) ppm.

Anal. Calcd for $C_8H_{10}O_2S_2$: C, 47.50; H, 4.98; S, 31.70. Found: C, 47.43; H, 4.94; S, 31.45.

3-Methyl-3,4-dihydro-1H-thieno[3,2-c]thiapyran-4-one (33)

A solution of 5.0 g (0.025 mol) of S-(3-thenyl)-thiolactic acid, 1.8 ml (0.025 mol) of thionyl chloride and 0.2 ml of pyridine in 100 ml dry ether (distilled from lithium aluminum hydride) was stirred at reflux for ten min.

Another 1.8 ml of thionyl chloride was added and reflux was continued for ten min. The ether and excess thionyl chloride were removed by distillation at atmospheric pressure as benzene was added until the distillate temperature was 80°. Upon cooling to 7°, 11.6 ml (0.109 mol) of anhydrous stannic chloride was added in one portion. The temperature rose to 23° and the slurry was stirred at 25° for two hrs. The slurry was poured onto 100 ml of ice and 100 ml of concentrated hydrochloric acid and the flask was rinsed with benzene and hydrochloric acid. The water-benzene mixture was stirred for one-half hr and a black tar was removed by filtration. The layers were separated and the aqueous layer was extracted with three 75 ml portions of benzene. The combined benzene layers were washed with two 100 ml portions of water and one 100 ml portion of 10% sodium carbonate solution and 100 ml of a saturated sodium chloride solution. Filtration was necessary with each wash. The benzene solution was dried ($MgSO_4$), filtered, and evaporated to an oil on a rotary evaporator. Distillation gave 1.9 g (42%) of 3-methyl-3,4-dihydro-1H-thieno[3,2-c]thiapyran-4-one: bp 112-114° (0.15 mm); lit.[25] bp 177° (14 mm); ir (neat), 3090 medium (aromatic H), 2965, 2920 medium (methyl and methylene, 1655 strong (C=O) and other strong bands at 1418, 1402, 1248, 900, 840 and 740 cm^{-1}; nmr (CCl_4) δ 7.55 (d, 1, J = 5.5 Hz, H-6), 6.93 (d, 1, J = 5.5 Hz, H-7), 3.68 (m, 3, $C\underline{H}_2SC\underline{H}$) and 1.40 (d, 3, J = 7 Hz, $C\underline{H}_3$) ppm.

3-Methyl-3,4-dihydro-1H-thieno[3,2-c]thiapyran-4-ol (34)

To a solution of 2.4 g (0.013 mol) of 3-methyl-3,4-dihydro-1H-thieno[3,2-c]thiapyran-4-one dissolved in 250 ml of warm isopropyl alcohol was added 0.49 g (0.013 mol) of finely powdered sodium borohydride. The reaction was stirred magnetically at reflux overnight. Upon cooling, the reaction mixture was poured into 250 ml of water. The aqueous isopropanol mixture was extracted with three 100 ml portions of benzene. The combined benzene extracts were washed with 100 ml of water, dried ($MgSO_4$), filtered, and evaporated to an oil on a rotary evaporator. Distillation at 112° (0.20 mm) gave 2.05 g (84%) of 3-methyl-3,4-dihydro-1H-thieno[3,2-c]thiapyran-4-ol. Upon standing, the oil solidified to a waxy solid, mp 64-75°: nmr (C_6D_6) δ 6.82 (d, 1, J = 5.5 Hz, H-6), 6.35 (d, 1, J = 5.5 Hz, H-7), 4.40 (m, 1, HOC$\underline{H}$), 3.67-2.37 (m, 4, $C\underline{H}_2SC\underline{H}CH_3CHO\underline{H}$) and 1.28-1.07 (m, 3, $C\underline{H}_3$) ppm.

Anal. Calcd for $C_8H_{10}OS_2$: C, 51.57; H, 5.41; S, 34.43. Found: C, 51.72; H, 5.51; S, 34.17.

3-Methylthieno[3,2-c]thiapyrylium perchlorate (10)

To a magnetically stirred, refluxing solution of 1.0 g (0.0054 mol) of 3-methyl-3,4-dihydro-1H-thieno[3,2-c]thiapyran-4-ol in 16 ml of glacial acetic acid was added 1.85 g (0.0054 mol) of trityl perchlorate in 16 ml of nitromethane. Reflux was continued for fifteen min. and the reaction mixture was allowed to cool ambiently for four hrs with stirring. The solvent was removed on a rotary evaporator and the resulting oil solidified on dilution to 400 ml with ether. After overnight refrigeration, the black product was collected on a filter and air dried to give 1.75 g, mp 135-140°. Recrystallization from 100 ml of glacial acetic acid with a carbon treatment gave 0.3 g of blue-green solid, mp 155-158.5°. Recrystallization from 10 ml of acetic acid with another carbon treatment gave 0.15 g (10.5%) of 3-methylthieno 3,2-c thiapyrylium perchlorate as slightly colored (blue-green) plates: mp 156-8°; visible and uv max (1% perchloric acid in acetonitrile) 228.5 mμ (log ε = 4.32), 264 (4.61), 306 (4.60), 366 (3.52); nmr (CF_3CO_2D) δ 10.33 (s, 1, H-1), 9.17 (s, 1, H-4), 8.33 (d, 1, J = 5.5 Hz, H-6), 8.07 (d, 1, J = 5.5 Hz, H-7), and 3.23 (s, 3, C$\underline{H}_3$) ppm.

Anal. Calcd for $C_8H_7ClO_4S_2$: C, 36.02; H, 2.65; Cl, 13.29; S, 24.04. Found: C, 36.16; H, 2.87; Cl, 13.33; S, 23.93.

2-Thenylchloride (35)

This compound was prepared according to the procedure of Hartough.[43]

Hydrogen chloride gas was passed into a stirred solution of 87.5 ml (1.05 mol) of concentrated hydrochloric acid and 81 ml of aqueous 37% formaldehyde (1.0 mol) through a subsurface addition tube while 72.7 g (0.864 mol) of thiophene was added at 0-10°. The mixture was stirred for one hr at 4° and a 350 ml portion of water was added. The mixture was extracted with two 100 ml portions of ether, which was dried (K_2CO_3) and evaporated on a rotary evaporator to an oil. Distillation at 81° (18 mm) gave 53.6 g (47%) of 2-thenylchloride; lit.[43] bp 81° (18 mm); nmr (CCl_4) δ 7.30-6.80 (m, 3, Ar-H), and 4.68 (s, 2, C$\underline{H}_2$Cl) ppm.

S-(2-thenyl)-mercaptoacetic acid (36)

To 29.0 g of potassium hydroxide (0.52 mol) dissolved in 200 ml of water was added, with ice-bath cooling, 20.0 g (0.216 mol) of mercaptoacetic acid. After the solution had cooled to 25°, 28.7 g (0.216 mol) of 2-thenylchloride was added and the two-phase mixture was stirred magnetically at 74° for eighteen hrs. The reaction mixture was extracted with two 50 ml portions of carbon tetrachloride (which were discarded) and then acidified with 25 ml of concentrated hydrochloric acid. The resulting oil was separated and the acidic aqueous layer was extracted with three 50 ml portions of chloroform. The combined oil and chloroform extracts were washed with two 100 ml portions of water, dried ($MgSO_4$), filtered, and evaporated on a rotary evaporator to an oil. Distillation, with a 3.6 g forerun distilling at 50-140° (0.10 mm), gave 19.0 g (46.5%) of S-(2-thenyl)-mercaptoacetic acid: bp 138-141° (0.15 mm); lit.[24] bp 204° (17 mm); ir (neat) 3400-2500 (bonded OH), 1700 (acid C=O), and strong bands at 1420, 1300, and 700 cm^{-1}; nmr (C_6D_6) δ 12.18 (s, 1, $CO_2\underline{H}$), 7.17-6.75 (m, 3, Ar-H), 3.93 (s, 2, C$\underline{H}_2$-S), and 3.02 (s, 2, SC$\underline{H}_2CO_2H$) ppm.

3,4-Dihydro-1H-thieno[2,3-c]thiapyran-4-one (37)

A stirred solution of 9.5 g (0.051 mol) of S-(2-thenyl)-mercaptoacetic acid, 3.7 ml (0.051 mol) of thionyl chloride and 0.2 ml of pyridine in 100 ml of dry benzene (filtered from sodium ribbon) was refluxed fifteen min. Another 3.7 ml of thionyl chloride was added and reflux was continued for fifteen min. Removal of the benzene and excess thionyl chloride on a rotary evaporator with two 100 ml flushes of dry benzene produced a dark oil which was dissolved in 100 ml dry benzene. Upon cooling to 5° in an ice bath, 22.3 g (0.086 mol) of anhydrous stannic chloride was added in one portion. The temperature rose to 25° and the slurry was stirred at 25° for one hr. The slurry was poured onto 50 ml of ice and 50 ml of concentrated hydrochloric acid and the flask was rinsed with concentrated hydrochloric acid and benzene. The water-benzene mixture was stirred for one-half hr and a black tar was removed by filtration. The layers were separated and the aqueous layer was extracted with three 75 ml portions of benzene. The combined benzene layers were washed with 100 ml of water, 100 ml of 10% sodium carbonate solution and 100 ml of a saturated sodium chloride solution. Filtration was necessary with each wash. The benzene solution was dried ($MgSO_4$), filtered, and the benzene was removed on a rotary evaporator. The resulting oil was distilled at 101-5° (0.08 mm) to give 2.7 g (31%) of 3,4-dihydro-1H-thieno[2,3-c]thiapyran-4-one. Upon standing the material solidified. Sublimation at 61° (0.10 mm) produced white crystals: mp 39.5-40.5°; lit.[24] mp 42°; ir (neat) 3100, 3080 medium (aromatic H), 2960, 2880 medium (methylene), 1665 (strong (C=O) and other strong bands at 1520, 1390, 1265 and 720 cm^{-1}; nmr ($CDCl_3$) δ 7.40 (d, 1, J = 5.5 Hz, H-6), 7.07 (d, 1, J = 5.5 Hz, H-5), 3.97 (s, 2, C$\underline{H}_2$S) and 3.42 (s, 2, SC$\underline{H}_2$CO) ppm.

Anal. Calcd for $C_7H_8OS_2$: C, 49.38; H, 3.55; S, 37.67. Found: C, 49.66; H, 3.75; S, 37.56.

3,4-Dihydro-1H-thieno[2,3-c]thiapyran-4-ol (38)

To a solution of 0.90 g (0.0053 mol) of 3,4-dihydro-1H-thieno[2,3-c]thiapyran-4-one dissolved in 100 ml of warm isopropanol was added 0.22 g (0.0053 mol) of finely powdered sodium borohydride. The reaction was stirred magnetically at reflux overnight. Upon cooling, the reaction mixture was poured into 100 ml of cold water. The aqueous isopropanol mixture was extracted with three 100 ml portions of benzene. The combined benzene extracts were washed with 100 ml of water, dried ($MgSO_4$), filtered and evaporated to an oil on a rotary evaporator. Distillation yielded 0.85 g (94%) of 3,4-dihydro-1H-thieno[2,3-c]thiapyran-4-ol, bp 118.5-120° (0.28 mm); ir (neat) 3600-3120 (bonded OH), 3080 weak (aromatic H, 2900 (methylene), and other strong bands at 1415, 1195, 1030, 915, 875, 715 and 660 cm^{-1}; nmr (C_6D_6) δ 6.90 (d, 1, J = 5.5 Hz, H-6), 6.80 (d, 1, J = 5.5 Hz, H-5), 4.55 (m, 1, HOC$\underline{H}$), 3.58 (m, 1, $\underline{H}$OCH), 3.35 (s, 2, C$\underline{H}_2$S) and 2.62 (d, J = 4.5 Hz, SC$\underline{H}_2$CHOH) ppm.

Anal. Calcd for $C_7H_8OS_2$: C, 48.80; H, 4.68; S, 37.23. Found: C, 49.10; H, 4.74; S, 37.17.

Thieno[2,3-c]thiapyrylium perchlorate (11)

To a magnetically stirred, refluxing solution of 2.45 g (0.014 mol) of 3,4-dihydro-1H-thieno[2,3-c]thiapyran-4-ol in 50 ml of glacial acetic acid was added 4.88 g (0.014 mol) of trityl perchlorate in 50 ml of nitromethane over a two min period. Reflux was continued for fifteen min and the reaction mixture was allowed to cool ambiently overnight with stirring. The solvent was removed on a rotary evaporator and the resulting solids were diluted to 300 ml with diethyl ether. After three hrs refrigeration, the product was collected on a filter and air dried to give 3.3 g (92%), mp 175-182°. The product was slurried with carbon in 50 ml of boiling glacial acetic acid and a black, insoluble tar and the carbon were removed by filtration. Upon cooling to room temperature 1.7 g, mp 189-91°, was obtained. Two further recrystallizations from glacial acetic acid, the first with another carbon treatment, gave 0.8 g (22%) of thieno[2,3-c] thiapyrylium perchlorate, mp 192-4°: visible and uv max (1% perchloric acid in acetonitrile) 224.5 mμ (log $\varepsilon = 4.25$) 262 (4.29), 304 (3.78), 381 (4.01); ir (KBr) 3100-2960 (aromatic H) and other strong bands at 1530, 1430, 1360, 1310, 1253, 1150-1000 (perchlorate), 915, 870, 804 and 760 cm^{-1}; nmr (CF_3CO_2D) δ 10.67 (broad s, 1, H-1), 9.28 (m, 2, H-3 and H-4), 9.13 (d, 1, J = 5.5 Hz, H-6) and 8.22 (d, 1, J = 5.5 Hz, H-5) ppm.

<u>Anal.</u> Calcd for $C_7H_5ClO_4S_2$: C, 33.27; H, 1.99; Cl, 14.03; S, 25.38. Found: C, 33.30; H, 2.06; Cl, 14.09; S, 25.11.

2-Thiophenethiol

To 20.82 g (3.0 g-atom) of lithium metal stirred under a helium atmosphere in 800 ml dry ether (distilled from lithium aluminum hydride) was added 205.5 g (1.50 mol) of n-butyl bromide at -10 to 0° over one hr. After stirring one hr at 0°, 84.1 g (1.0 mol) of thiophene was added at <0° over fifteen min. After stirring one hr at 0°, 32.0 g (1.0 g-atom) of sulfur was added over five min (acetone-dry ice cooling). After stirring at 0° for one hr, the reaction was allowed to warm slowly to room temperature. The reaction was then heated at reflux for four hrs. Upon cooling and the cautious addition of 350 ml of water (foaming), the layers were separated and the ether layer was washed with 100 ml of water. The combined aqueous layers were made acidic with hydrochloric acid and were extracted with two 100 ml portions of ether. The combined ether layers were dried ($MgSO_4$), filtered and evaporated to an oil. Distillation gave 58.6 g (51%) of 2-thiophenethiol: bp 33° (0.75 mm), lit.[61] bp 171.1° (760 mm), ir (neat) 3100-3080 medium (aromatic H), 2525 medium (S-H), and strong bands at 1405, 1221, 845 and 695 cm^{-1}; nmr (CCl_4) δ 7.30-6.73 (m, 3, Ar-H), and 3.40 (s, 1, S<u>H</u>) ppm.

Ethyl S-(2-thienyl)-3-mercaptopropionate (39)

To 8.82 g (0.164 mol) of sodium methoxide in 200 ml dry glyme (distilled from lithium aluminum hydride) was added 19.0 g (0.164 mol) of 2-thiophenethiol and 29.6 g (0.164 mol) of ethyl 3-bromopropionate. After stirring at reflux overnight, the mixture was cooled and 100 ml of water was added.

The layers were separated and the organic layer was washed with 100 ml of water, dried ($MgSO_4$), filtered and evaporated to an oil on a rotary evaporator. Distillation at 89-92° (0.10 mm) gave 30.1 g (85%) of product. The analytical sample distilled at 90° (0.10 mm): ir (neat) 3100 weak (aromatic H), 2975, 2930 (methyl and methylene), 1730 (ester C=O), and other strong bands at 1400, 1370, 1342, 1240, 1215, 1175, 1148, 845 and 700 cm^{-1}; nmr (CCl_4) δ 7.42-6.85 (m, 3, Ar-H), 4.10 (q, 2, J = 7 Hz, $OC\underline{H}_2CH_3$), 3.13-2.37 (m, 4, $C\underline{H}_2C\underline{H}_2S$), and 1.20 (t, 3, J = 7 Hz, $CH_2C\underline{H}_3$) ppm.

Anal. Calcd for $C_9H_{12}O_2S_2$: C, 49.97; H, 5.59; S, 29.65. Found: C, 50.17; H, 5.84; S, 29.46.

S-(2-thienyl)-3-mercaptopropionic acid (40)

A mixture of 15.2 g (0.070 mol) of ethyl S-(2-thienyl)-3-mercaptopropionate and 500 ml of 20% hydrochloric acid was stirred at reflux overnight. After cooling, the mixture was extracted with three 100 ml portions of benzene which were combined, dried ($MgSO_4$), filtered and evaporated to an oil on a rotary evaporator. Distillation at 122-5° (0.20 mm) gave 10.5 g (87%) of product. The analytical sample distilled at 122° (0.15 mm); ir (neat) 3500-2500 (bonded OH), 1710 (acid C=O), and other strong bands at 1430-1400, 1260, 1218, 848, 702, and 678 cm^{-1}; nmr (CCl_4) δ 11.87 (s, 1, $CO_2\underline{H}$), 7.37-6.83 (m, 3, Ar-H), and 3.17-2.33 (m, 4, $SC\underline{H}_2C\underline{H}_2$) ppm.

Anal. Calcd for $C_7H_8O_2S_2$: C, 44.66; H, 4.28; S, 34.06. Found: C, 44.64; H, 4.34; S, 34.02.

3,4-Dihydro-2H-thieno[2,3-b]thiapyran-4-one (41)

A solution of 7.0 g (0.037 mol) of S-(2-thienyl)-3-mercaptopropionic acid, 2.65 ml (0.037 mol) of thionyl chloride and 0.2 ml of pyridine in 150 ml of dry ether (distilled from lithium aluminum hydride) was stirred at reflux for fifteen min. Another 2.65 ml of thionyl chloride was added and reflux was continued for fifteen min. The ether and excess thionyl chloride were removed by distillation at atmospheric pressure as benzene was added until the distillate temperature was 80°. Upon cooling to 5°, 21.8 ml (0.186 mol) of anhydrous stannic chloride was added in one portion. The temperature rose to 30° and the slurry was stirred at 25° for three hrs. The slurry was poured onto 100 ml of ice and 100 ml of concentrated hydrochloric acid and the flask was rinsed with benzene and concentrated hydrochloric acid. The water-benzene mixture was stirred three hrs. The layers were separated and the aqueous layer was extracted with three 100 ml portions of benzene. The combined benzene layers were washed with 100 ml of water and 100 ml of 10% sodium carbonate solution. Filtration was necessary with each wash. The benzene solution was dried ($MgSO_4$), filtered, and evaporated to an oil on a rotary evaporator. Distillation at 90-92° (0.10 mm) gave 4.4 g of 3,4-dihydro-2H-thieno[2,3-b]thiapyran-4-one (70%) as an oil which solidified on standing, mp 57.5-59.5°. The analytical sample distilled at 92° (0.10 mm): lit.[34] mp 63-4°; ir (neat) 3100, 3080 medium (aromatic H), 2910 medium (methylene), 1665 (C=O), and strong bands at

1500, 1413, 1390, 1280, 1265, 1190, 1132, 898, 730 and 682 cm^{-1}; nmr ($CDCl_3$) δ 7.47 (d, 1, J = 5.5 Hz, H-6), 7.00 (d, 1, J = 5.5 Hz, H-5), 3.35 (t, 2, J = 6 Hz, $SC\underline{H}_2CH_2CO$), and 2.80 (t, 2, J = 6 Hz, $SCH_2C\underline{H}_2CO$) ppm.

Anal. Calcd for $C_7H_6OS_2$: C, 49.38; H, 3.55; S, 37.67. Found: C, 49.42; H, 3.54; S, 37.47.

3,4-Dihydro-2H-thieno[2,3-b]thiapyran-4-ol (42)

To a solution of 2.0 g (0.012 mol) of 3,4-dihydro-2H-thieno[2,3-b]thiapyran-4-one dissolved in 200 ml of warm isopropanol was added 0.435 g (0.012 mol) of sodium borohydride. The reaction was stirred magnetically at reflux overnight. Upon cooling, the reaction mixture was poured into 250 ml of cold water. The aqueous isopropanol mixture was extracted with three 100 ml portions of benzene. The combined benzene extracts were washed with 100 ml of water, dried ($MgSO_4$), filtered and evaporated to an oil on a rotary evaporator. Distillation at 101-3° (0.10 mm) gave 1.7 g (84%) of 3,4-dihydro-2H-thieno[2,3-b]thiapyran-4-ol, which solidified on standing, mp 62-4°. The analytical sample distilled at 102° (0.10 mm): lit.[34] mp 67-8°; ir (neat) 3500-3100 (bonded OH), 2910 (methylene) and other strong bands at 1415, 1200, 1178, 1035, 1018, 915, 870 and 692 cm^{-1}; nmr ($CDCl_3$) δ 7.03 (s, 2, H-5 and H-6), 4.77 (t, 1, J = 4 Hz, $HOC\underline{H}$), 3.47-2.68 (m, 2, $SC\underline{H}_2CH_2$), 2.30 (s, 1, $\underline{H}OCH$), and 2.50-1.67 (m, 2, $SCH_2C\underline{H}_2$) ppm.

Anal. Calcd for $C_7H_8OS_2$: C, 48.80; H, 4.68; S, 37.23. Found: C, 49.02; H, 4.57; S, 37.09.

Thieno[2,3-b]thiapyrylium perchlorate (18)

A mixture of 1.8 g (0.011 mol) of 3,4-dihydro-2H-thieno-[2,3-b]thiapyran-4-ol and 1.0 g of potassium pyrosulfate were placed in a 25 ml pear shaped flask which was fitted with a normal vacuum distillation apparatus. The system was evacuated to 1.75 mm and the flask was heated to 200° over ten min. The reaction yielded 0.4 g (25%) of 2-H-thieno[2,3-b] thiapyran as shown by the following: bp 89° (1.75 mm); lit.[34] bp 81-2° (0.6 mm); ir (neat) 3100, 3035 (aromatic H), 2875 (methylene), and other bands at 1611, 1405, 1208, 1198, 1158, 1095, 1041, 831, 778, 721 and 670 cm^{-1}; nmr (CCl$_4$) δ 6.92 (d, 1, J = 5 Hz, H-6), 6.78 (d, 1, J = 5 Hz, H-5), 6.43 (d, 1, J_{3-4} = 10 Hz, J_{2-4} = 1 Hz, H-4), 7.32 (m, 1, J = 5 Hz, H-3), and 3.42 (q, 2, J = 5 Hz, J = 1 Hz, SC$\underline{H}_2$); mass spectrum (80 eV) *m/e* 154 (P), calcd 154, 153 (P-1).

The material was used immediately for the synthesis of the thiapyrylium salt.

To a stirred solution of 0.4 g (0.0026 mol) of 2-H thieno[2,3-b]thiopyran in 25 ml acetonitrile was added 0.885 g (0.0026 mol) of trityl perchlorate in 15 ml of acetonitrile. The solution was stirred at 25° for one hr and then was evaporated to near dryness on a rotary evaporator to yield a solid which was diluted to 100 ml with diethyl ether. After three hrs refrigeration, the solid was collected on a filter and air dried to yield 0.55 g (84%) of product, mp 248-52°, dec. Two recrystallizations from glacial acetic acid, the first with a carbon treatment, gave 0.24 g (37%) of thieno[2,3-b]thiapyrylium perchlorate: mp 255-7°, dec.; lit.[34] mp 142°; visible and uv max (1% perchloric acid in acetonitrile), 262 mμ (log ε = 4.47), 333 (3.66), 361 sh (3.36); nmr (CF_3CO_2D) δ 10.02 (d, 1, J = 8.5 Hz, H-2), 9.48 (d, 1, J = 8.5 Hz, H-4), 8.78 (t, 1, J = 8.5 Hz, H-3), 8.55 (d, 1, J = 5.5 Hz, H-6) and 8.20 (d, 1, J = 5.5 Hz, H-5) ppm.

Anal. Calcd for $C_7H_5ClO_4S_2$: C, 33.27; H, 1.99; S, 25.28. Found: C, 33.55; H, 1.93; S, 25.14.

Methyl S-(2-thienyl)-2-methyl-3-mercaptopropionate (44)

To 19.0 g (0.164 mol) of 2-thiophenethiol was added with stirring and ice bath cooling, 1 ml of 30% aqueous triethylamine. The viscosity of the mixture increased rapidly and 16.5 g (0.164 mol) of methyl methacrylate was added rapidly while keeping the temperature under 40°. After stirring at room temperature for 48 hrs, distillation at 85° (0.10 mm) yielded 34.0 g (96%) of a slightly yellow oil. An analytical sample distilled at 79° (0.08 mm); ir (neat) 3095 weak (aromatic H), 2970 and 2940 medium (methyl and methylene), 1735 (ester C=0), and other strong bands at 1455, 1430, 1215, 1160, 845 and 700 cm^{-1}; nmr (CCl_4) δ 7.42-6.85 (m, 3, Ar-H), 3.63 (s, 3, $CO_2C\underline{H}_3$), 3.22-2.45 (m, 3, $C\underline{H}_2SC\underline{H}$), and 1.23 (d, 3, J = 7 Hz, $CHC\underline{H}_3$) ppm.

Anal. Calcd for $C_9H_{12}O_2S_2$: C, 49.97; H, 5.59; S, 29.95. Found: C, 50.13; H, 5.67; S, 29.64.

S-(2-thienyl)-2-methyl-3-mercaptopropionic acid (45)

A stirred mixture of 15 g (0.069 mol) of methyl S-(2-thienyl)-2-methyl-3-mercaptopropionate and 500 ml of 20% hydrochloric acid was stirred at reflux overnight. After cooling, the mixture was extracted with three 100 ml portions of benzene, which were combined, dried ($MgSO_4$), filtered and evaporated to an oil on a rotary evaporator. Distillation at 122-4° (0.12 mm) yielded 11.0 g (78%) of S-(2-thienyl)-2-methyl-3-mercaptopropionic acid. The analytical sample distilled at 123° (0.12 mm): ir (neat) 3500-2500 (bonded OH), 1710 (acid C=O) and strong bands at 1460, 1410, 1240, 1218, 845 and 700 cm^{-1}; nmr (CCl_4) δ 12.07 (s, 1, $CO_2\underline{H}$), 7.42-6.85 (m, 3, Ar-H), 3.38-2.47 (m, 3, $SC\underline{H}_2C\underline{H}$), and 1.30 (d, 3, 6.5 Hz, $CHC\underline{H}_3$) ppm.

Anal. Calcd for $C_8H_{10}O_2S_2$: C, 47.50; H, 4.98; S, 31.70. Found: C, 47.44; H, 5.10; S, 31.66.

3-Methyl-3,4-dihydro-2H-thieno[2,3-b]thiapyran-4-one (46)

A solution of 7.0 g (0.035 mol) of S-(2-thienyl)-2-methyl-3-mercaptopropionic acid, 2.40 ml (0.035 mol) of thionyl chloride and 0.2 ml of pyridine in 150 ml of dry ether (distilled from lithium aluminum hydride) was stirred at reflux for fifteen min. Another 2.40 ml of thionyl chloride was added and reflux was continued for fifteen min. The ether and excess thionyl chloride were removed by distillation at atmospheric pressure as benzene was added until the distillate temperature was 80°. Upon cooling to 5°, 20.2 ml

(0.173 mol) of anhydrous stannic chloride was added in one portion. The temperature rose to 30° and the slurry was stirred at 25°for three hrs. The slurry was poured onto 100 ml of ice and 100 ml of concentrated hydrochloric acid. The water-benzene mixture was stirred three hrs. The layers were separated and the aqueous layer was extracted with three 100 ml portions of benzene. The combined benzene layers were washed with 100 ml of water and 100 ml of 10% sodium carbonate solution. Filtration was necessary with each wash. The benzene solution was dried ($MgSO_4$), filtered and evaporated to an oil on a rotary evaporator. Distillation at 86-89° (0.10 mm) gave 3.7 g (58%) of an oil which solidified on standing, mp 28-31°. The analytical sample distilled at 87° (0.10 mm): ir (neat) 3100 and 3080 medium (aromatic H), 2960 and 2920 (methyl and methylene), 1660 (C=O), and strong bands at 1498, 1413, 1388, 1265, 1242, 1229, 1034, 868 and 695 cm^{-1}; nmr ($CDCl_3$) δ 7.47 (d, 1, J = 5.5 Hz, H-6), 7.00 (d, 1, J = 5.5 Hz, H-5), 3.27 (d, 2, J = 7 Hz, $SC\underline{H_2}$), 2.80 (q, 1, J = 7 Hz, $C\underline{H}CH_3$), and 1.32 (d, 3, J = 7 Hz, $CHC\underline{H_3}$) ppm.

Anal. Calcd for $C_8H_8OS_2$: C, 52.14; H, 4.38; S, 34.80. Found: C, 52.30; H, 4.59; S, 34.60.

3-Methyl-3,4-dihydro-2H-thieno[2,3-b]thiapyran-4-ol (47)

To a solution of 2.0 g (0.011 mol) of 3-methyl-3,4-dihydro-2H-thieno[2,3-b]thiapyran-4-one dissolved in 250 ml warm isopropanol was added 0.41 g (0.011 mol) of sodium borohydride. The reaction was stirred magnetically at reflux overnight. Upon cooling, the reaction mixture was poured into 250 ml of cold water. The aqueous isopropanol mixture was extracted with three 100 ml portions of benzene. The combined benzene extracts were washed with 100 ml of water, dried ($MgSO_4$), filtered and evaporated to an oil on a rotary evaporator. Distillation at 98° (0.10 mm) gave 1.8 g (89%) of 3-methyl-3,4-dihydro-2H-thieno[2,3-b]thiapyran-4-ol, which solidified on standing, mp 47-75°. The analytical sample distilled at 98° (0.10 mm): ir (neat) 3600-3140 (bonded OH), 3100 weak (aromatic H), 2960, 2920, 2900 and 2870 medium (methyl and methylene), and strong bands at 1422, 1410, 1028, 830 and 698 cm^{-1}; nmr ($CDCl_3$) δ 7.05 (s, 2, Ar-H), 4.50 (m, 1, HOC$\underline{H}$), 3.50-1.67 (m, 4, $\underline{H}$OCHC$\underline{H}$C$\underline{H}_2$), and 1.30-1.00 (m, 3, C$\underline{H}_3$)ppm.

Anal. Calcd for $C_8H_{10}OS_2$: C, 51.57; H, 5.41; S, 34.43. Found: C, 51.71; H, 5.37; S, 34.39.

3-Methylthieno[2,3-b]thiapyrylium perchlorate (12)

A mixture of 1.0 g of finely powdered potassium pyrosulfate and 2.8 g (0.015 mol) of 3-methyl-3,4-dihydro-2H-thieno[2,3-b]thiapyran-4-ol was placed in a 15 ml pear shaped flask connected to a vacuum distillation apparatus which was immediately evacuated to 2.5 mm. The temperature was raised to 200° over fifteen min with an oil bath initially at 150°. The product, 3-methyl-2H-thieno[2,3-b]thiapyran, 1.2 g (48%) distilled at 110-112° (2.5 mm); ir (neat) 3100 medium (aromatic H), 2960, 2920, 2900 and 2870 strong (methyl and methylene) and strong bands at 1444, 1410, 1212, 831, 695 and 630 cm^{-1}.

Because of the instability of the product (immediately turned yellow on exposure to air and then further darkening even under a nitrogen atmosphere) it was used immediately.

To 1.2 g (0.0071 mol) of 3-methyl-2H-thieno[2,3-b] thiapyran in 45 ml of acetonitrile was added 2.44 g (0.0071 mol) of trityl perchlorate in 45 ml of acetonitrile. After stirring at 25° for one-half hr, evaporation to near dryness on a rotary evaporator and dilution to 450 ml with diethyl ether produced solids. After two hrs refrigeration, the product was collected on a filter and air dried to yield 1.80 g (95%) of 3-methylthieno[2,3-b]thiapyrylium perchlorate, mp 168-71°. Two recrystallizations from glacial acetic acid, the first with a carbon treatment, gave 0.38 g (20%); mp 175-77°; visible and uv max (1% perchloric acid in acetonitrile, 264 mμ (log ε = 4.48), 337 (3.64), 370 (3.41); nmr (CF_3CO_2D) δ 9.72 (s, 1, H-2), 9.25 (s, 1, H-4), 8.45 (d, 1, J = 5.5 Hz, H-6), 8.07 (d, 1, J = 5.5 Hz, H-5) and 2.98 (s, 3, $C\underline{H}_3$) ppm.

Anal. Calcd for $C_8H_7ClO_4S_2$: C, 36.02; H, 2.65; S, 24.04. Found: C, 33.26; H, 2.90; S, 23.90.

3-Bromothianaphthene (51)

To a stirred solution of 67.1 g (0.50 mol) of thianaphthene and 68.5 g (0.83 mol) of anhydrous sodium acetate in 380 ml of chloroform was added 26.2 ml (0.51 mol) of bromine in 70 ml of chloroform over 45 min with water bath cooling so that the temperature did not rise above 33°. After stirring for 90 min at 25°, 100 ml of water was added and the layers were separated. The chloroform layer was washed with 200 ml of water, 100 ml of 5% sodium hydroxide, 200 ml of water and 200 ml of saturated sodium chloride solution. After drying ($MgSO_4$) and filtration, the solvent was removed on a rotary evaporator. The resulting oil yielded 84.3 g (79%) of 3-bromothianaphthene distilling at 73-90° (0.5-0.2 mm). Redistillation gave 76 g of a pale, yellow liquid: bp 60-5° (0.05 mm); lit.[48] bp 90-105° (1.5 mm).

3-Mercaptothianaphthene (53)

To 9.7 g (0.40 g-atom) of magnesium in 750 ml dry ether (distilled from lithium aluminum hydride) at 30° was added 42.62 g (0.20 mol) of 3-bromothianaphthene and 21.60 g (0.20 mol) of ethyl bromide. After some initial difficulty, the reaction proceeded and was refluxed for two hr. After cooling to 15°, 12.84 g (0.40 g-atom) of sulfur was added slowly. The mixture was refluxed for three hrs and allowed to stand overnight and 20.4 g of sulfuric acid in 300 ml of water was cautiously added. The layers were separated and the aqueous layer was extracted with two 100 ml portions of ether. The combined ether layers were washed with 100 ml of water, dried ($MgSO_4$), filtered and evaporated to an oil on a rotary evaporator. Distillation *in vacuo* resulted in 23.3 g of residue with no 2535 cm^{-1} (-SH) band in the infrared.

On the assumption that this material was the disulfide, it was dissolved in dry ether (distilled from lithium aluminum hydride) and added over one-half hr to 2.03 g (0.054 mol) of lithium aluminum hydride in dry ether with external cooling, so that no reflux occurred. The reaction mixture was warmed with a water bath to reflux and refluxed for one hr. After cooling to 4°, 50 ml of water was added and 15% sulfuric acid was added at 4° until the aqueous layer was acidic. Saturated sodium sulfate was added for coagulation and the slurry was filtered. The layers were separated and the ether layer was washed with 100 ml of water. The aqueous layers were saturated with sodium chloride and extracted with 100 ml of ether. The combined ether layers were dried ($MgSO_4$), filtered and evaporated to an oil on a rotary evaporator. Distillation gave 9.0 g (27%) of 3-mercaptothianapththene; bp 99° (1.15 mm); lit.[52] bp 77-80° (0.20 mm); ir (neat) 3100 and 3060 (aromatic H), 2540 medium (SH), and strong bands at 1455, 1422, 1315, 1258, 1062, 1020, 828, 758, 729 and 704 cm^{-1}; lit. ν SH = 2535 cm^{-1}; nmr (CCl_4) δ 7.77-7.47 (m, 2, Ar-H), 7.32-7.05 (m, 3, ArH) and 3.00 (d, 1, J = 1 Hz, S<u>H</u>) ppm.

S-(3-thianaphthenyl)-3-mercaptopropionic acid (54)

To 9.0 g (0.054 mol) of 3-mercaptothianaphthene in 250 ml of absolute ethanol was added 13.6 g (0.162 mol) of sodium bicarbonate and 8.3 g (0.054 mol) of 3-bromopropionic acid. After a six hr reflux, the reaction mixture was cooled and evaporated to near dryness on a rotary evaporator. An emulsion formed upon water addition. Concentrated hydrochloric acid was added until the aqueous layer was red to litmus (foaming). The resulting oil was extracted into benzene, which was dried ($MgSO_4$), filtered and evaporated to an oil on a rotary evaporator. Dilution with petroleum ether and scratching produced solids, which were collected on a filter and air dried to yield 9.2 g (72%) of S-(3-thianaphthenyl)-3-mercaptopropionic acid: mp 61-5°. Sublimation at 90° (0.12 mm) gave an analytical sample: mp 70-2°; ir (KBr) 3300-2300 (bonded OH), 1695 (acid C=O) and strong bands at 1438, 1420, 1400, 1335, 1256, 1198, 938, 838, 752 and 731 cm^{-1}; nmr ($CDCl_3$) δ 11.55 (s, 1, $CO_2\underline{H}$), 8.08-7.70 (m, 2, Ar-H), 7.58-7.18 (m, 3, Ar-H), 3.22-2.92 (m, 2, $SC\underline{H}_2$), and 2.72-2.42 (m, 2, $C\underline{H}_2CO_2H$) ppm.

Anal. Calcd for $C_{11}H_{10}O_2S_2$: C, 55.43; H, 4.23; S, 26.91. Found: C, 55.61; H, 4.45; S, 26.99.

3,4-Dihydro-2H-thianaphtheno[3,2-b]thiapyran-4-one (55)

A stirred solution of 5.0 g (0.021 mol) of S-(3-thianaphthenyl)-3-mercaptopropionic acid, 1.5 ml of thionyl chloride (0.021 mol) and 0.2 ml of pyridine was refluxed fifteen min. Another 1.5 ml of thionyl chloride was added and reflux was continued for fifteen min. The solvent was exchanged for benzene at atmospheric pressure. Upon cooling to 5°, 12.3 ml (0.105 ml) of anhydrous stannic chloride was added in one portion. The temperature rose to 23° and the red slurry was stirred for three hrs. The slurry was poured onto 100 ml of concentrated hydrochloric acid and 100 ml of ice and the flask was rinsed with benzene and concentrated hydrochloric acid. The water-benzene mixture was stirred one hr and the layers were separated. The aqueous layer was extracted with three 100 ml portions of benzene. The benzene layers were combined and washed with 100 ml of 10% sodium carbonate. After drying ($MgSO_4$), filtration and evaporation on a rotary evaporator, the resulting solids were slurried with petroleum ether, collected on a filter and air dried to yield 4.25 g (97%) of 3,4-dihydro-2H-thianaphtheno[3,2-b]thiapyran-4-one: mp 121-4° with prior shrinking. Recrystallization from methanol-water with a carbon treatment gave the analytical sample: mp 123.5-125.0°; ir (KBr) 1630 (C=O), and strong bands at 1480, 1290, 1275, 1188, 931, 754 and 724 cm^{-1}; nmr ($CDCl_3$) δ 7.90-7.20 (m, 4, Ar-H), 3.38-3.27 (m, 2, $S\underline{CH_2}$), and 3.08-2.80 (m, 2, $\underline{CH_2}CO$) ppm.

Anal. Calcd for $C_{11}H_8OS_2$: C, 59.97; H, 3.66; S, 29.11. Found: C, 60.06; H, 3.87; S, 28.99.

3,4-Dihydro-2H-thianaphtheno[3,2-b]thiapyran-4-ol (56)

To a solution of 2.0 g (0.009 mol) of 3,4-dihydro-2H-thianaphtheno[3,2-b]thiapyran-4-one dissolved in 500 ml of warm isopropanol was added 0.342 g (0.009 mol) of sodium borohydride. The reaction mixture was stirred magnetically at reflux overnight. Upon cooling, the solvent was evaporated to near dryness on a rotary evaporator. After dilution with water, the mixture was extracted with three 100 ml portions of benzene. The combined benzene layers were washed with 50 ml of water, dried ($MgSO_4$), filtered and evaporated to an oil on a rotary evaporator. On dilution with petroleum ether, the oil became a solid which was collected on a filter and air dried to yield 2.0 g (100%) of 3,4-dihydro-2H-thianaphtheno[3,2-b]thiapyran-4-ol: mp 104-5°. Sublimation at 92° (0.07 mm) gave an analytical sample: mp 104-5°; ir (KBr) 3440-3060 (bonded OH), 3050 (aromatic H), 2910 (methylene), and strong bands at 1430, 1257, 1155, 1050, 1020, 758 and 730 cm^{-1}; nmr ($CDCl_3$) δ 7.87-7.08 (m, 4, Ar-H), 4.87 (t, 1, J = 4.5 Hz, HOC$\underline{H}$), 3.45-2.83 (m, 2, C$\underline{H_2}$S), 2.68 (s, 1, CHO$\underline{H}$, disappears on exchange with D_2O) and 2.50-1.83 (m, 2, C$\underline{H_2}$CHOH) ppm.

Anal. Calcd for $C_{11}H_{10}OS_2$: C, 59.42; H, 4.58; S, 28.85. Found: C, 59.69; H, 4.57; S, 28.85.

Thianaphtheno[3,2-b]thiapyrylium perchlorate (13)

To 1.0 g (0.0045 mol) of 3,4-dihydro-2H-thianaphtheno[3,2-b]thiapyran-4-ol in 20 ml of refluxing glacial acetic acid was added 1.54 g (0.0045 mol) of trityl perchlorate in 20 ml of nitromethane. Reflux was continued for fifteen min and the reaction mixture was allowed to cool to room temperature. Evaporation on a rotary evaporator produced an oil, which solidified on dilution with ether. After three hrs refrigeration, the solid was collected on a filter and air dried to yield 1.2 g (88%) of thianaphtheno[3,2-b]thiapyrylium perchlorate. Four recrystallizations from glacial acetic acid, the first with a carbon treatment, gave the analytical sample: mp 199.0-200.5°; visible and uv max (1% perchloric acid in acetonitrile) 232.5 mμ (log ε = 4.47), 297 (4.05), and 379 (4.12); nmr (CF_3CO_2D) δ 9.92 (d, 1, J = 8 Hz, H-2), 9.52 (d, 1, J = 8 Hz, H-4), 8.75 (t, 1, J = 8 Hz, H-3) and [8.75-8.60 (m, 1) and 8.40-7.70 (m, 3, H's-6,7,8,9)] ppm

__Anal.__ Calcd for $C_{11}H_7ClO_4S_2$: C, 43.64; H, 2.33; S, 21.18. Found: C, 43.89; H,2.52; S, 20.95.

__3-Thianaphthenyl chloride (57)__

Hydrogen chloride gas was passed into a stirred mixture of 65.25 g (0.485 mol) of thianaphthene, 48.5 g (0.600 mol) of aqueous 47% formaldehyde and 48.5 ml (0.58 mol) of concentrated hydrochloric acid through a subsurface addition tube. The temperature rose to 60° and was held there for five hrs. After one hr, the gas flow was set at a slow rate. The mixture was cooled to 30° and was poured into 500 ml of water. The layers were separated as well as possible and the aqueous layer was extracted with three 100 ml portions of benzene. The combined organic layers were washed with two 100 ml portions of water, one 100 ml portion of 10% sodium carbonate solution (emulsion removed by filtration) and one 100 ml portion of water. The benzene solution was dried (K_2CO_3), filtered and evaporated to an oil on a rotary evaporator. Distillation at 117-8° (3 mm); lit.[51] bp 125-7° (2 mm) gave 58.5 g (71%) of 3-thianaphthenyl chloride after allowing for a 7.6 g forerun of unreacted thianaphthene. The nmr spectrum in CCl_4 consisted of δ 7.80-7.50 (m, 2, Ar-H), 7.40-7.10 (m, 3, Ar-H), and 4.53 (s, 2, $C\underline{H_2}Cl$) ppm.

S-(3-thianaphthenyl)-mercaptoacetic acid (58)

To 14.1 g (0.153 mol) of mercaptoacetic acid dissolved in 100 ml of dry glyme (distilled from lithium aluminum hydride) was added with stirring and ice-bath cooling, 16.5 g (0.306 mol) of sodium methoxide. The resulting thick white precipitate was broken up, 28.0 g (0.153 mol) of 3-thianaphthenyl chloride was rinsed into the flask with 100 ml of dry glyme. The mixture was stirred at reflux overnight. Upon cooling, the thick, white precipitate was dissolved by 100 ml of water. After addition of 50 ml of concentrated hydrochloric acid, the two-phase system was evaporated to an oily solid on a rotary evaporator. The oil was taken up in 500 ml of benzene, which was washed with two 100 ml portions of water, dried ($MgSO_4$), filtered and evaporated to an oil on a rotary evaporator. After dilution with petroleum ether, scratching and overnight refrigeration, 19.6 g, mp 75-95°, of a gummy semi-solid was collected on a filter and washed with petroleum ether. Recrystallization from cyclohexane gave 11.5 g (31.6%), mp 91-103°. Sublimation at 100° (0.10 mm) gave an analytical sample: mp 103-105.5°; ir (KBr) 3630-2500 (bonded OH), 1690 (acid C=O), and strong bands at 1420, 1290, 1128, 930, 760 and 730 cm^{-1}; nmr ($CDCl_3$) δ 11.80 (s, 1, $CO_2\underline{H}$), 8.00-7.67 (m, 2, Ar-H), 7.53-7.20 (m, 3, Ar-H), 4.10 (s, 2, $C\underline{H}_2S$) and 3.07 (s, 2, $SC\underline{H}_2$) ppm.

Anal. Calcd for $C_{11}H_{10}O_2S_2$: C, 55.43; H, 4.23, S, 26.91. Found: C, 55.32; H, 4.47; S, 27.01.

3,4-Dihydro-1H-thianaphtheno[3,2-c]thiapyran-4-one (59)

A solution of 10.5 g (0.044 mol) of S-(3-thianaphthenyl)-mercaptoacetic acid, 4.0 ml (0.055 mol) of thionyl chloride and 0.2 ml of pyridine in 200 ml of dry ether (distilled from lithium aluminum hydride) was stirred at reflux for one-half hr. The mixture was evaporated to dryness in vacuo on a steam bath and flushed with dry benzene at atmospheric pressure. Upon cooling to <10°, 26.4 ml (0.225 mol) of anhydrous stannic chloride was added in one portion. The temperature rose to 30°. The slurry was stirred at 25° for three hrs and then was poured onto 100 ml of ice and 100 ml of concentrated hydrochloric acid. The flask was rinsed with benzene and concentrated hydrochloric acid. The water-benzene mixture was stirred five hrs and let stand for two days. The mixture was filtered and the layers separated. The benzene layer was washed with 100 ml of water and 100 ml of 10% sodium carbonate solution. Filtration was necessary with each wash. The benzene solution was dried ($MgSO_4$), filtered,and evaporated to a solid on a rotary evaporator. The solid was slurried in petroleum ether, collected on a filter and air dried to yield 6.9 g (71%) of 3,4-dihydro-1H-thianaphtheno[3,2-c]thiapyran-4-one, mp 153-5°. Recrystallization from carbon tetrachloride-benzene with a carbon treatment gave 4.2 g (43%), mp 158-161°. Sublimation of 1.0 g at 130° (0.09 mm) gave 0.85 g, mp 158-161°. Recrystallization from carbon tetrachloride-benzene with a carbon treatment, sublimation at 132° (0.18 mm) and recrystallization from methanol-water with a carbon treatment gave 0.1 g: mp 159-160°; ir (KBr) 1640 (C=O), and strong bands at 1355, 1280, 1255, 989 and 760 cm^{-1}; nmr ($CDCl_3$ and CCl_4) δ 8.00-7.25 (m, 4, Ar-H), 4.02 (s, 2, $C\underline{H}_2S$), and 3.60 (s, 2, $C\underline{H}_2S$), and 3.60 (s, 2, $SC\underline{H}_2CO$) ppm.

Anal. Calcd for $C_{11}H_8OS_2$: C, 59.97; H, 3.66; S, 29.11. Found: C, 60.25; H, 3.49; S, 28.93.

3,4-Dihydro-1H-thianaphtheno[3,2-c]thiapyran-4-ol (60)

To a solution of 2.20 g (0.01 mol) of 3,4-dihydro-1H-thianaphtheno[3,2-c]thiapyran-4-one dissolved in 200 ml of isopropyl alcohol was added 0.38 g (0.01 mol) of sodium borohydride. The reaction was stirred magnetically at reflux overnight. Upon cooling, the reaction mixture was poured into 200 ml of cold water. The aqueous isopropanol mixture was extracted with three 200 ml portions of 1:1 benzene-ether. The combined benzene-ether extracts were washed with 100 ml of water, dried ($MgSO_4$), filtered and evaporated to a solid on a rotary evaporator. The solids were slurried in petroleum ether, collected on a filter and air dried to yield 1.9 g (86%) of 3,4-dihydro-1H-thianaphtheno[3,2-c]thiapyran-4-ol, mp 128-132°. Sublimation at 110° (0.20 mm) followed by recrystallization from methanol-water with a carbon treatment gave an analytical sample: mp 139.0-140.5°; ir (KBr) 3500-3140 (bonded OH), 3040 weak (aromatic H), 2880 medium (methylene), and strong bands at 1430, 1408, 1378, 1260, 1188, 1150, 1060, 1040, 755 and 728 cm^{-1}; nmr ($CDCl_3$) δ 7.95-7.27 (m, 4, Ar-H), 5.00 (m, 1, $HOC\underline{H}$), 3.80 (s, 2, $C\underline{H}_2S$), 3.12

(m, 2, SC$\underline{H}_2$CHOH), and 2.75 (m, 1, O$\underline{H}$, exchanges with D_2O) ppm.

Anal. Calcd for $C_{11}H_{10}OS_2$: C, 59.42; H, 4.53; S, 28.85. Found: C, 59.62; H, 4.57; S, 28.83.

Thianaphtheno[3,2-c]thiapyrylium perchlorate (14)

To a magnetically stirred, refluxing solution of 1.0 g (0.0045 mol) of 3,4-dihydro-1H-thianaphtheno[3,2-c]thiapyran-4-ol in 16 ml of glacial acetic acid was added 1.54 g (0.0045 mol) of trityl perchlorate in 16 ml of nitromethane. Reflux was continued for fifteen min and the reaction mixture was allowed to cool ambiently for four hrs with stirring. The solvent was removed on a rotary evaporator and the resulting oil solidified on dilution to 500 ml with ether. After overnight refrigeration, the yellow product was collected on a filter and air dried to give 1.45 g, mp 173-6°. Recrystallization of 0.5 g from 40 ml of glacial acetic acid with a carbon treatment gave 0.3 g of yellow needles, mp 178-80°, after drying over P_2O_5 at 25° (0.07 mm): visible and uv max (1% perchloric acid in acetonitrile), 233 sh (log $\varepsilon = 4.13$), 237 sh (4.18), 254 (4.56), 2.65 (4.32), 283 (4.25), 314 (3.81), 384 (3.80); nmr (CF_3CO_2D) δ 10.57 (m, 1, H-1), 9.60-9.15 (m, 2, H-3 and H-4), 8.73-8.47 (m, 1, Ar-H), and 8.27-7.67 (m, 3, Ar-H) ppm.

Anal. Calcd for $C_{11}H_7ClO_4S_2$: C, 43.64; H, 2.33; S, 21.18. Found: C, 43.78; H, 2.63; S, 21.28.

S-(3-thianaphthenyl)-thiolactic acid (61)

To 16.25 g (0.153 mol) of thiolactic acid dissolved in 100 ml of dry ether (distilled from lithium aluminum hydride) was added with stirring and ice-bath cooling, 16.5 g (0.306 mol) of sodium methoxide. The resulting thick, white precipitate was broken up and 28.0 g (0.153 mol) of 3-thianaphthenyl chloride was washed into the flask with 100 ml of dry glyme. The mixture was stirred at reflux overnight. Upon cooling, the thick, white precipitate was dissolved in 100 ml of water. After addition of 50 ml of concentrated hydrochloric acid, the two-phase system was evaporated to an oil on a rotary evaporator. Trituration with petroleum ether, refrigeration and collection on a filter resulted in 33.8 g (88%) of solid product, mp 75-90°. Recrystallization, with a carbon treatment, from cyclohexane gave 19.8 g (51%), mp 93.5-96.0°. Sublimation at 90° (0.05 mm) gave an analytical sample: mp 94.0-97.0°; ir (KBr) 3300-2500 (bonded OH), 1680 (acid C=O), and strong bands at 1445, 1420, 1281, 1231, 1059, 925, 758 and 730 cm^{-1}; nmr ($CDCl_3$) δ 12.15 (s, 1, $CO_2\underline{H}$), 8.13-7.70 (m, 2, Ar-H), 7.50-7.18 (m, 2, Ar-H), 4.33 (d, 1, J = 14 Hz, $C\underline{H_2}S$), 4.05 (d, 1, J = 14 Hz, $C\underline{H_2}S$), 3.40 (q, 1, J = 7 Hz, $S\text{-}C\underline{H}CH_3$), and 1.43 (d, 3, J = 7 Hz, $C\underline{H_3}$) ppm.

Anal. Calcd for $C_{12}H_{12}O_2S_2$: C, 57.11; H, 4.79, S, 25.41. Found: C, 57.33; H, 4.78; S, 25.40.

3-Methyl-3,4-dihydro-1H-thianaphtheno[3,2-c]thiapyran-4-one (62)

A solution of 10.09 g (0.04 mol) of S-(3-thianaphthenyl)-thiolactic acid, 3.56 ml (0.05 mol) of thionyl chloride and 0.5 ml of pyridine in 200 ml dry ether (distilled from lithium aluminum hydride) was stirred at reflux for 45 min. The mixture was evaporated to dryness on a rotary evaporator and flushed with dry benzene at atmospheric pressure. Upon cooling to 8°, 23.5 ml (0.20 mol) of anhydrous stannic chloride was added in one portion. The temperature rose to 15°. The slurry was stirred at 25° for three hrs and then was poured onto 100 ml of ice and 100 ml of concentrated hydrochloric acid. The flask was rinsed with benzene and concentrated hydrochloric acid. The water-benzene mixture was stirred overnight. The mixture was filtered and the layers separated. The aqueous layer was extracted with two 100 ml portions of benzene. The combined benzene layers were washed with 100 ml of water, 100 ml of 10% sodium carbonate solution and 100 ml of water. The benzene solution was dried ($MgSO_4$), filtered and evaporated to a solid on a rotary evaporator. The solid was slurried in petroleum ether, collected on a filter and air dried to yield 7.4 g (79%) of 3-methyl-3,4-dihydro-1H-thianaphtheno[3,2-c]thiapyran-4-one, mp 97-103°. Recrystallization from carbon tetrachloride with a carbon treatment gave 5.2 g (55%), mp 103.0-105.5°. Sublimation of 1.0 g at 105° (0.10 mm) followed by recrystallization with a carbon treatment from methanol gave 0.45 g; mp 105.0-106.5°; ir (KBr) 2960, 2920, 2880 weak (methyl and methylene), 1650 strong (C=O), and strong bands at 1525, 1425, 1360, 1300, 1242, 912, 882, 753, and 725 cm^{-1}; nmr ($CDCl_3$) δ 7.98-7.28 (m, 4, Ar-H), 4.37-3.60 (m, 3, C$\underline{H}_2$SC$\underline{H}$), and 1.57 (d, 3, J = 7 Hz, C$\underline{H}_3$) ppm.

Anal. Calcd for $C_{12}H_{10}OS_2$: C, 61.52; H, 4.30; S, 27.35. Found: C, 61.30; H, 4.27; S, 27.09.

3-Methyl-3,4-dihydro-1H-thianaphtheno[3,2-c]thiapyran-4-ol (63)

To a solution of 2.0 g (0.0086 mol) of 3-methyl-3,4-dihydro-1H-thianaphtheno[3,2-c]thiapyran-4-one dissolved in 250 ml of warm isopropanol was added 0.323 g (0.0086 mol) of finely powdered sodium borohydride. The reaction was stirred magnetically at reflux overnight. Upon cooling, the reaction mixture was poured into 250 ml of cold water. The aqueous isopropanol mixture was extracted with three 150 ml portions of benzene. The combined benzene extracts were washed with 100 ml of water, dried ($MgSO_4$), filtered and evaporated on a rotary evaporator to an oil which solidified on standing. The solid was slurried in petroleum ether, collected on a filter and air dried to yield 1.9 g (94%) of 3-methyl-3,4-dihydro-1H-thianaphtheno[3,2-c]thiapyran-4-ol, mp ca. 70-115°. Recrystallization from methanol-petroleum ether with a carbon treatment gave an analytical sample: mp 120-132°; ir (KBr) 3500-3100 (bonded OH), 3040 weak (aromatic H), 2850 weak (methyl and methylene), and strong bands at 1430-1370, 1015, 750 and 728 cm^{-1}; nmr (C_6D_6 and $CDCl_3$) δ 7.98-7.15 (m, 4, Ar-H), 4.67 (d, 1, J = 2 Hz, $\underline{H}$COH), 4.42-2.90 (m, 3, C$\underline{H}_2$-S-C$\underline{H}$CH$_3$), 2.77 (s, 1, O$\underline{H}$), exchanges with D_2O, and 1.75-1.08 (m, 3, C$\underline{H}_3$) ppm.

Anal. Calcd for $C_{12}H_{12}OS_2$: C, 60.98; H, 5.12; S, 27.13. Found: C, 61.09; H, 5.08; S, 26.96.

3-Methylthianaphtheno[3,2-c]thiapyrylium perchlorate (15)

To a magnetically stirred, refluxing solution of 1.0 g (0.0042 mol) of 3-methyl-3,4-dihydro-1H-thianaphtheno[3,2-c]thiapyran-4-ol in 16 ml of glacial acetic acid was added 1.45 g (0.0042 mol) of trityl perchlorate in 16 ml of nitromethane. Reflux was continued for 15 min and the reaction mixture was allowed to cool ambiently for four hrs with stirring. The solvent was removed on a rotary evaporator and the resulting oil solidified on dilution to 400 ml with ether. After overnight refrigeration, the black product was collected on a filter and air dried to give 1.2 g (90%), mp 204-6°. Recrystallization from boiling glacial acetic acid gave an analytical sample: mp 211-12°, dec.; visible and uv max (1% perchloric acid in acetonitrile), 240.5 mμ (log ε = 4.28), 258 (4.40), 265 sh (4.39), 283 (4.28), 312 (3.91), 385 (3.81); nmr (CF_3CO_2D) δ 10.33 (s, 1, H-1), 9.00 (s, 1, H-4), 8.50 (m, 1, Ar-H), 8.20-7.70 (m, 3, Ar-H), and 3.17 (s, 3, C$\underline{H}_3$) ppm.

Anal. Calcd for $C_{11}H_7ClO_4S_2$: C, 45.50, H, 2.86; S, 20.24. Found: C, 45.68; H, 3.09; S, 20.26.

2-Methylthianaphthene (64)

To 6.94 g (1.0 g-atom) of lithium metal stirred under a helium atmosphere in 250 ml of dry ether (distilled from lithium aluminum hydride) was added 68.5 g (0.50 mol) of n-butyl bromide at -10 to 0° over two hrs. After stirring one hr at 0°, 44.7 g (0.333 mol) of thianaphthene in 50 ml of ether was added over one-half hr at <0°. After stirring for one hr at 0°, 62.2 g (0.333 mol) of methyl tosylate was added over twenty min as the temperature rose to 20°. After stirring one hr at 10° and two hrs at 25°, the mixture was heated at reflux for one-half hr. The mixture was cooled and 100 ml of water was added slowly with much foaming. After another 300 ml of water was added, the layers were separated. The aqueous layer was extracted with three 100 ml portions of ether. The combined ether layers were dried ($MgSO_4$), filtered and the ether removed at atmospheric pressure. Distillation at 80 mm, followed by recrystallization from ethanol, gave 33.5 g (64%) of 2-methylthianaphthene: mp 49.5-51.5°; lit.[22] mp 51.5-52°; nmr (CCl_4) δ 7.70-6.82 (m, 5, Ar-H), and 2.45 (s, 3, C$\underline{H}_3$) ppm.

2-Bromomethylthianaphthene (65)

To 10.0 g (0.068 mol) of doubly distilled 2-methylthianaphthene in 250 ml of carbon tetrachloride was added 12.0 g (0.068 mol) of recrystallized N-bromosuccinimide (dried over P_2O_5 at 0.1 mm) and 2.0 g of benzoyl peroxide. After stirring at reflux for two hrs, all the solids were floating on top of the solvent. After cooling to 10° and filtration, the solvent was removed on a rotary evaporator, yielding an oil. The oil was dissolved in benzene, which was washed with 100 ml of 10% sodium carbonate solution and 100 ml of water. After drying ($MgSO_4$), filtration, and solvent removal, the oil was distilled at 118-20° (0.20 mm), mp 51-4°; lit.[62] 46°; nmr (CCl_4) δ 8.27-7.17 (m, Ar-H), and 4.68 (s, $C\underline{H}_2Br$) ppm in the ratio of 3.65/1, calcd 2.5/1.

S-(2-thianaphthenyl)-mercaptoacetic acid (66)

To 4.80 g (0.052 mol) of mercaptoacetic acid dissolved in 300 ml dry glyme (distilled from lithium aluminum hydride) was added 5.62 g (0.104 mol) of sodium methoxide. The thick white precipitate was broken up and 11.8 g (0.052 mol) of 2-bromomethylthianaphthene was washed into the flask with 100 ml of dry glyme. The mixture was stirred at reflux for twenty hrs. Upon cooling, the white precipitate was dissolved in 100 ml of water and the solution was evaporated to 100 ml on a rotary evaporator. After the addition of 50 ml of 10% sodium carbonate solution, the solution was extracted with two 100 ml portions of benzene. After acidification with concentrated hydrochloric acid, the mixture was extracted with two 100 ml portions of benzene. After drying ($MgSO_4$), filtration and evaporation to an oil on a rotary evaporator, dilution with petroleum ether gave a solid. After 24 hrs refrigeration, the solid was collected on a filter, washed with petroleum ether and air dried to yield 6.0 g

(48%) of S-(2-thianaphthenyl)-mercaptoacetic acid, mp 60-70°. Recrystallization from benzene-cyclohexane gave 3.0 g, mp 71-3°. Sublimation of 1.0 g at 110° (0.07 mm) gave an analytical sample: mp 95-96.5° (with prior softening); ir (neat) 3400-2500 (bonded OH), 1705 (acid C=O), and strong bands at 1432, 1295, 748, 728 and 679 cm^{-1}; nmr ($CDCl_3$) δ 11.35 (s, 1, $CO_2\underline{H}$), 7.87-7.50 (m, 2, Ar-H), 7.47-7.12 (m, 3, Ar-H), 4.12 (s, 2, $C\underline{H}_2S$), and 3.17 (s, 2, $SC\underline{H}_2$) ppm.

Anal. Calcd for $C_{11}H_{10}O_2S_2$: C, 55.43, H, 4.23; S, 29.61. Found: C, 55.66; H, 3.98; S, 26.67.

3,4-Dihydro-1H-thianaphtheno[2,3-c]thiapyran-4-one (67)

A solution of 2.0 g (0.0084 mol) of S-(3-thianaphthenyl)-mercaptoacetic acid, 0.6 ml (0.0084 mol) of thionyl chloride and 0.2 ml of pyridine in 150 ml of dry ether (distilled from lithium aluminum hydride) was stirred at reflux for fifteen min; another 0.6 ml of thionyl chloride was added and reflux was continued for fifteen min. The solvent was exchanged for benzene at atmospheric pressure. Upon cooling to 6°, 4.9 ml (0.042 mol) of anhydrous stannic chloride was added in one portion. The resulting slurry was stirred at 25° for three hrs and then poured onto 100 ml of ice and 100 ml of concentrated hydrochloric acid and the flask was rinsed with concentrated hydrochloric acid and benzene. The water-benzene mixture was stirred for one hr and a black tar was removed by filtration. The layers were separated and the aqueous layer was extracted with two 100 ml portions of benzene. The combined benzene layers were washed with 100 ml of water and 100 ml of 10% sodium carbonate solution with a filtration before each separation. The benzene solution was dried ($MgSO_4$), filtered and evaporated on a rotary evaporator to a maroon solid. After slurrying with petroleum ether, the solids were collected on a filter, washed with petroleum ether and air dried to give 0.75 g (41%) of 3,4-dihydro-1H-thianaphtheno[2,3-c]thiapyran-4-one, mp 110-120°. Recrystallization from carbon tetrachloride-methanol, sublimation at 110° (0.18 mm) and two recrystallizations from methanol-water, the second with a carbon treatment, gave an analytical sample: mp 120.0-121.5°; ir (KBr) 3060 weak (aromatic H), 2970 and 2890 weak (methylene), 1650 (C=O) and strong bands at 1455, 1428, 1365, 1200, 760 and 724 cm^{-1}; nmr ($CDCl_3$) δ 8.60 (m, 1, Ar-H), 7.70 (m, 1, Ar-H), 7.47-7.18 (m, 2, ArH), 3.92 (d, 2, J = 1.5 Hz, $C\underline{H}_2S$), and 3.44 (d, 2, J = 1.5 Hz, $SC\underline{H}_2CO$) ppm.

Anal. Calcd for $C_{11}H_8O_2S_2$: C, 59.97; H, 3.66; S, 29.11. Found: C, 60.15; H, 3.70; S, 29.17.

3,4-Dihydro-1H-thianaphtheno[2,3-c]thiapyran-4-ol (68)

To 1.75 g (0.008 mol) of 3,4-dihydro-1H-thianaphtheno[2,3-c]thiapyran-4-one in 250 ml warm isopropanol (which required filtration for clarification of a non-soluble haze) was added 0.30 g (0.008 mol) of finely powdered sodium borohydride. The reaction was stirred magnetically at reflux overnight. Upon cooling, 10 ml of water was added and the solution was evaporated to 125 ml on a rotary evaporator. After addition of 125 ml of water and 125 ml of benzene, the layers were separated and the aqueous layer was extracted with three 100 ml portions of benzene. The combined benzene layers were dried ($MgSO_4$), filtered and evaporated to an oil on a rotary evaporator. The oil solidified on dilution with petroleum ether and overnight refrigeration. The solids were collected on a filter and air dried to yield 1.3 g (74%) of 3,4-dihydro-1H-thianaphtheno[2,3-c]thiapyran-4-ol, mp 78-84°. Recrystallization from methanol-water with a carbon treatment, followed by sublimation at 95° (0.10 mm) gave an analytical sample: mp 89-91°; ir (KBr) 3500-3100 (bonded OH), 2875 medium (methylene), and strong bands at 1435, 1411, 1190, 1045-1018 and 740-720 cm^{-1}; nmr ($CDCl_3$) δ 8.00-7.55 (m, 2, Ar-H), 7.48-7.22 (m, 2, Ar-H), 5.00 (m, 1, HOC$\underline{H}$), 4.00 (d, 2, J = 17 Hz, C$\underline{H_2}$S), 3.50 (d, 2, J = 17 Hz, C$\underline{H_2}$S), 3.03 (m, 2, SC$\underline{H_2}$CHOH) and 2.77 (m, 1, CHO$\underline{H}$, disappears on exchange with D_2O) ppm.

<u>Anal</u>. Calcd for $C_{11}H_{10}OS_2$: C, 59.42; H, 4.53; S, 28.85. Found: C, 59.35; H, 4.71; S, 28.58.

<u>Thianaphtheno[2,3-c]thiapyrylium perchlorate (16)</u>

To a magnetically stirred, refluxing solution of 0.88 g (0.004 mol) of 3,4-dihydro-1H-thianaphtheno[2,3-c]thiapyran-4-ol in 15 ml of glacial acetic acid was added 1.37 g (0.004 mol) of trityl perchlorate in 15 ml of nitromethane. After a fifteen minute reflux, the reaction mixture was allowed to cool ambiently to room temperature and the solvent was removed on a rotary evaporator. After dilution to 400 ml with ether and overnight refrigeration, the solid was collected on a filter and air dried to give 1.1 g (91%) of thianaphtheno[2,3-c]thiapyrylium perchlorate. After several recrystallizations from glacial acetic acid, an analytical sample was obtained: mp 207.0-208.0°; visible and uv max (1% perchloric acid in acetonitrile), 292 mμ (log $\varepsilon = 4.24$), 354 (4.18), and 433 (3.52); nmr (CF_3CO_2D) δ 10.40 (m, 1, $J = 2$ Hz, H-1), 9.55 (two singlets, 2, H-3 and H-4), 8.77 (m, 1) and 8.32-7.68 (m, 3, H's 6, 7, 8, 9) ppm.

Anal. Calcd for $C_{11}H_7ClO_4S_2$: C, 43.64; H, 2.33; S, 21.18. Found: C, 43.82; H, 2.37; S, 21.10.

Ethyl S-(2-thianaphthenyl)-3-mercaptopropionate (69)

To 3.47 g (0.50 g-atom) of lithium metal stirred under a helium atmosphere in 250 ml dry ether (distilled from lithium aluminum hydride) was added, at -10 to 0°, 27.4 g (0.20 mol) of n-butyl bromide over one hr. After the reaction was stirred at 0° for one hr, the remaining lithium wire was removed with tweezers and 40.26 g (0.30 mol) of thianaphthene in 50 ml dry ether was added at 0° over one hr. The reaction was stirred at 0° for one hr and 6.4 g (0.20 g-atom) of sulfur was added. The temperature rose to 26°. Reflux at 24° was continued for three hrs and 36.2 g (0.20 mol) of ethyl 3-bromopropionate was added. Reflux was continued overnight. After cooling to 25°, 100 ml of water was added over one hr, so that the vigorous reaction was kept under control. The layers were separated and the ether layer was washed with three 10 ml portions of water (neutral to litmus). The aqueous layers were re-extracted with two 100 ml portions of ether which were combined and washed with three 50 ml portions of water. The combined ether layers were dried ($MgSO_4$), filtered and evaporated to an oil on a rotary evaporator. The distillation temperature varied from 128-164° as the oil bath temperature varied from 170-210°. The distillation temperature was about 40-50° below the oil bath temperature. Distillation at 0.2 mm gave 30.8 g (58%) of ethyl S-(2-thianaphthenyl)-3-mercaptopropionate. Redistillation gave an analytical sample: ir (neat) 3050 weak (aromatic H), 2950, 2920 strong and 2865 medium (methyl and methylene), 1730 (ester C=O), and other strong bands at 1452, 1420, 1370, 1345, 1278, 1242, 1178, 747 and 725 cm^{-1}; nmr (C_6D_6) δ 7.70-7.05 (m, 5, Ar-H), 4.00 (q, 2, J = 7.5 Hz, $OC\underline{H_2}CH_3$), 3.05 (t, 2, J = 7 Hz, $SC\underline{H_2}$), 2.53 (t, 2, J = 7 Hz $SCH_2C\underline{H_2}$), and 1.02 (t, 3, J = 7.5 Hz, $CH_2C\underline{H_3}$) ppm.

<u>Anal</u>. Calcd for $C_{13}H_{14}O_2S_2$: C, 58.61; H, 5.30; S, 24.08. Found: C, 58.71; H, 5.21; S, 24.20.

<u>S-(2-thianaphthenyl)-3-mercaptopropionic acid (70)</u>

A mixture of 12.0 g (0.045 mol) of ethyl S-(2-thianaphthenyl)-3-mercaptopropionate and 1.0 l. of 50% hydrochloric acid was stirred at reflux overnight. Upon cooling, the oil solidified and was collected by filtration. The gummy solid was taken up in 400 ml of benzene, which was washed with three 75 ml portions of water, dried ($MgSO_4$), filtered, carbon treated, filtered and evaporated to an oil on a rotary evaporator. Dilution with petroleum ether produced a solid which was collected on a filter and dried to give 6.0 g, mp 60-90°. Recrystallization from cyclohexane gave 2.7 g (25%) of S-(2-thianaphthenyl)-3-mercaptopropionic acid, mp 109-114°. Sublimation at 166° (0.05 mm) gave an analytical sample: mp 115.5-118.0°; ir (KBr) 3300-2500 (bonded OH), 1684 (acid C=O), and strong peaks at 1418, 1392, 1233, 923, 918, 813, 749, 740 and 722 cm^{-1}; nmr ($CDCl_3$) δ 11.37 (s, 1, $CO_2\underline{H}$), 7.78 (m, 2, Ar-H), 7.50-7.25 (m, 3, ArH), 3.30-3.03 (m, 2, $S\underline{CH_2}CH_2$), and 2.90-2.55 (m, 2, $SCH_2\underline{CH_2}$) ppm.

Anal. Calcd for $C_{11}H_{10}O_4S_2$: C, 55.43; H, 4.23; S, 26.91. Found: C, 55.53; H, 4.31; S, 26.68.

3,4-Dihydro-2H-thianaphtheno[2,3-b]thiapyran-4-one (71)

A solution of 3.0 g (0.012 mol) of S-(2-thianaphthenyl)-3-mercaptopropionic acid, 1.8 ml (0.025 mol) of thionyl chloride and 0.5 ml of pyridine in 30 ml of ether (distilled from lithium aluminum hydride) was stirred at reflux. The solvent and the excess thionyl chloride were removed by distillation at atmospheric pressure as benzene was added until the distillate temperature was 80°. Upon cooling to 5°, 7.0 ml (0.06 mol) of anhydrous stannic chloride was added in one portion. The temperature rose to 15° and the slurry was stirred at 30° for one hr. The slurry was poured onto 100 ml of ice and 100 ml of concentrated hydrochloric acid and the flask was rinsed with benzene and hydrochloric acid. The water-benene mixture was stirred one-half hr, filtered, and the layers separated. The aqueous layer was extracted with two 75 ml portions of benzene. The combined benzene layers were washed with 100 ml of water, 100 ml of 10% sodium carbonate solution and 100 ml of water. Filtration was necessary with each wash. The benzene solution was dried ($MgSO_4$), filtered and evaporated to a solid. The solid was slurried in petroleum ether and collected on a filter. Recrystallization from benzene-petroleum ether with a carbon treatment gave 2.2 g (79%) of 3,4-dihydro-2H-thianaphtheno[2,3-b]thiapyran-4-one, mp 122-5°. Sublimation at 120° (0.15 mm) followed by two recrystallizations from ethanol-water (the last with a carbon treatment) gave an analytical sample: mp 123.5-125.0°; ir (KBr) 1640 (C=O) and strong bands at 1445, 1402, 1358, 1162, 740 and 736 cm^{-1}; nmr (CCl_4) δ 8.67-8.47 (m, 1, Ar-H), 7.75-7.20 (m, 3, Ar-H), 3.58-3.27 (m, 2, $SC\underline{H}_2$) and 3.03-2.72 (m, 2, $SCH_2C\underline{H}_2$) ppm.

Anal. Calcd for $C_{11}H_8OS_2$: C, 59.97; H, 3.66; S, 29.11. Found: C, 60.16; H, 3.69; S, 29.05.

3,4-Dihydro-2H-thianaphtheno[2,3-b]thiapyran-4-ol (72)

To a solution of 1.9 g (0.0086 mol) of 3,4-dihydro-2H-thianaptheno[2,3-b]thiapyran-4-one dissolved in 150 ml of isopropanol was added 0.325 g (0.0086 mol) of sodium borohydride. The reaction was stirred magnetically at reflux overnight. Upon cooling, the reaction mixture was poured into 100 ml of cold water. The aqueous isopropanol mixture was extracted with three 100 ml portions of benzene. The combined benzene extracts were washed with 100 ml of water, dried ($MgSO_4$), filtered and evaporated to a solid on a rotary evaporator. The solid was slurried with petroleum ether, collected on a filter and air dried to give 1.7 g (83%) of 3,4-dihydro-2H-thianaphtheno[2,3-b]thiapyran-4-ol, mp 115.0-116.5°. Sublimation at 103° (0.12 mm) gave an analytical sample: mp 115.0-118.0°; ir (KBr) 3400-3000 (bonded OH), 2880 weak (methylene), and strong bands at 1400, 1260, 1240, 1018, 905 and 728 cm^{-1}; nmr ($CDCl_3$) δ 7.82-7.55 (m, 2, Ar-H), 7.48-7.08 (m, 2, Ar-H), 5.05 (m, 1, HOC$\underline{H}$), and 3.75-1.72 (m, 5, $\underline{H}OCHC\underline{H}_2C\underline{H}_2$) ppm.

Anal. Calcd for $C_{11}H_{10}OS_2$: C, 59.42; H, 4.53; S, 28.85. Found: C, 59.62; H, 4.61; S, 28.97.

Thianaphtheno[2,3-b]thiapyrylium perchlorate (17)

To a magnetically stirred, refluxing solution of 0.60 g (0.0027 mol) of 3,4-dihydro-2H-thianaphtheno[2,3-b]thiapyran-4-ol in 16 ml of glacial acetic acid was added 0.93 g (0.0027 mol) of trityl perchlorate in 16 ml of nitromethane. Reflux was continued for fifteen min and the reaction mixture was allowed to cool ambiently for four hrs with stirring. The solvent was removed on a rotary evaporator and the resulting oil solidified on dilution to 400 ml with ether. After overnight refrigeration, the golden yellow product was collected on a filter and air dried to give 0.7 g (86%), mp 214-6° dec. Recrystallization from boiling glacial acetic acid gave an analytical sample: mp 215-18° dec.; visible and uv max (1% perchloric acid in acetonitrile), 243 mμ (log $\varepsilon = 4.49$), 302 (4.18), 361 (3.64), 423 (3.74); nmr (CF_3CO_2D) δ 9.93-9.60 (m, 2, H-2 and H-4), and 9.13-7.75 (m, 5, H-2, H-5, 6, 7, 8) ppm.

Anal. Calcd for $C_{11}H_7ClO_4S_2$: C, 43.64; H, 2.33; S, 21.18. Found: C, 43.76; H, 2.59; S, 21.08.

3-Thienyl-n-butylsulfide (49)

To 6.94 g (1.0 g-atom) of lithium metal stirred under a helium atmosphere in 300 ml of dry ether (distilled from lithium aluminum hydride) was added 68.5 g (0.5 mol) of n-butyl bromide at -10 to 0° over twenty min. After stirring one hr at <0°, the slurry was cooled to -70° and 81.52 g (0.5 mol) of 3-bromothiophene was added at -67 to -70° over one hr. Then 16 g (0.5 g-atom) of sulfur was added slowly so that the temperature was -50° at the end of the addition. The mixture was allowed to warm to 10° and then was refluxed for five hrs. After the cautious addition of 100 ml of water, the layers were separated. The ether layer was washed with two 100 ml portions of water. The aqueous layers were acidified with concentrated hydrochloric acid and extracted with three 100 ml portions of benzene. The combined benzene layers were dried ($MgSO_4$), filtered and evaporated on a rotary evaporator to a smidgen of oil.

Evaporation of the ether layer and distillation gave 29.4 g of a product: bp 80-5° (0.25 mm), lit.[63] bp 137-150° (impure) (30 mm). Redistillation gave 24 g, bp 67° (0.50 mm) (48%, after correcting for unreacted 3-bromothiophene); ir (neat) 3100 medium (aromatic H), 2955, 2925, 2870 strong (methyl and methylene), and other bands at 1462, 1350, 1195, and 1100 medium and strong bands at 894, 852 and 775-755 cm^{-1}; nmr (CCl_4) δ 7.30-6.85 (m, 3, Ar-H), 2.77 (t, 2, J = 7.5, $SC\underline{H}_2$), 1.77-1.20 (m, 4, $C\underline{H}_2C\underline{H}_2$), and 1.03-0.67 (m, 3, $C\underline{H}_3$) ppm.

Anal. Calcd for $C_8H_{12}S_2$: C, 55.76; H, 7.02; S, 37.22. Found: C, 55.83; H, 7.29; S, 37.21.

6-Methyl-1,3,4,5-tetrahydrothiapyrano[4,3-b]indole (24)

A mixture of 31.7 g (0.22 mol) of *O*-tolylhydrazine hydrochloride, 23.2 g (0.20 mol) of tetrahydro-1,4-thiapyrone and 16.4 g (0.20 mol) of anhydrous sodium acetate in 50 ml of acetic acid was refluxed twelve hrs. The solution was poured into water to give an oil, which was extracted with benzene. The benzene solution was dried (K_2CO_3), filtered and evaporated to an oil which crystallized from ethyl acetate-petroleum ether to give 6.0 g of crude product, mp 135-148°. Recrystallization from ethanol-water and final sublimation at 130° (0.04 mm) yielded 3.7 g of 6-methyl-1,3,4,5-tetrahydrothiapyrano[4,3-b]indole as white crystals, mp 154-158°.

Anal. Calcd for $C_{12}H_{13}NS$: C, 70.89; H, 6.45; N, 6.89; S, 15.77. Found: C, 70.98; H, 6.22; N, 7.07; S, 15.80.

6-Methylthiapyrano[4,3-b]indole (20)

A mixture of 2.03 g (0.01 mol) of 6-methyl-1,3,4,5-tetrahydrothiapyrano[4,3-b]indole and 4.92 g (0.02 mol) of chloranil in 150 ml of xylene was refluxed for four hrs. The resulting solid complex was filtered while hot, dried and stirred with 200 ml of 10% aqueous sodium hydroxide overnight. The alkali-insoluble residue was collected on a filter, washed thoroughly with water and air dried to give a crude product which was sublimed at 160° (0.09 mm) to yield 0.06 g (3%) of 6-methylthiapyrano[4,3-b]indole as yellow crystals, mp 162.5-165°; visible and uv max (95% ethanol) 228 mμ (log $\varepsilon = 4.23$), 275 (4.59), 300 (4.14), 359 (3.47) sh, 413 (3.48); nmr ($CDCl_3$) δ 8.76 (d, 1, $J_{14} = 3.0$ Hz, H-1), 8.27 (d, 1, $J_{34} = 9.5$ Hz, H-4), 8.00-7.20 (m, 4, H-3, 7, 8, 9) and 2.82 (s, 3, $C\underline{H}_3$) ppm.

Anal. Calcd for $C_{12}H_9NS$: C, 72.32; H, 4.55; N, 7.03; S, 16.09. Found: C, 72.25; H, 4.53; N, 7.19; S, 16.03.

8-Chlorothiapyrano[4,3-b]indole (21)

A mixture of 2.24 g (0.01 mol) of 8-chloro-1,3,4,5-tetrahydrothiapyrano[4,3-b]indole and 4.92 g (0.02 mol) of chloranil in 150 ml of xylene was refluxed for twelve hrs. The resulting brown solid complex was filtered while hot, dried and stirred with 150 ml of 10% aqueous sodium hydroxide overnight. The alkali-insoluble residue was collected on a filter, washed thoroughly with water and dried to yield 0.60 g (27.2%) of crude 8-chlorothiapyrano[4,3-b]indole, mp 192-196° dec. Two sublimations, the last at 130° (0.10 mm), gave orange-yellow crystals, mp 194-196.5° dec.; visible and uv max (95% ethanol) 229 mμ (log $\varepsilon = 4.41$), 278 (4.49), 284 (4.61), 303 (4.40), 356 (3.59), 410 (3.44); nmr ($CDCl_3$) δ 8.80 (d, 1, $J_{13} = 3.0$ Hz, H-1), 8.18 (d, 1, $J_{34} = 10.0$ Hz, H-4), 8.00-7.50 (m, 4, H-3, 6, 7, 9) ppm.

Anal. Calcd for $C_{11}H_6ClNS$; C, 60.13; H, 2.75; Cl, 16.14; N, 6.38; S, 14.60. Found: C, 60.16; H, 2.77; Cl, 16.34; N, 6.35; S, 14.55.

8-Methoxythiapyrano[4,3-b]indole (22)

A mixture of 2.17 g (0.01 mol) of 8-methoxy-1,3,4,5-tetrahydrothiapyrano[4,3-b]indole and 4.56 g (0.02 mol) of DDQ in 150 ml of xylene was refluxed for five hrs. The resulting brown, solid complex was filtered while hot, dried and stirred with 200 ml of 10% aqueous sodium hydroxide overnight. The alkali-insoluble residue was collected on a filter and thoroughly washed with water to give a gummy solid which was dried *in vacuo* over potassium hydroxide and then sublimed at 142° (0.08 mm) to yield 0.040 g (2%) of orange-red crystals, mp 135-6°, and resolidified and remelted at 148-9°; visible and uv max (95% ethanol) 226 mμ (log $\varepsilon = 4.28$), 286 (4.60), 2.95 (4.55) sh, 367 (3.51) sh, 426 (3.24); nmr ($CDCl_3$) δ 8.75 (d, 1, $J_{13} = 3.0$ Hz, H-1), 8.15 (d, 1, $J_{34} = 9.5$ Hz, H-4), and 7.96-7.16 (m, 4, H-3, 6, 7, 9) and 3.93 (s, 3, $C\underline{H}_3$) ppm.

Anal. Calcd for $C_{12}H_9NOS$: C, 66.95; H, 4.21; N, 6.51; S, 14.90. Found: C, 66.92; H, 4.09; N, 6.42; S, 14.77.

8-Nitrothiapyrano[4,3-b]indole (23)

A mixture of 2.35 g (0.01 mol) of 8-nitro-1,3,4,5-tetrahydrothiapyrano[4,3-b]indole and 4.56 g (0.02 mol) of DDQ in 200 ml of xylene was refluxed for three hrs. The dark, insoluble complex was filtered while hot, dried and stirred for 24 hrs with 200 ml of 10% aqueous sodium hydroxide. The alkali-insoluble residue was collected on a filter and thoroughly washed with water to give 0.5 g of crude product. Sublimation at 220° (0.06 mm) gave 0.35 g (15%) of 8-nitrothiapyrano[4,3-b]indole as yellow crystals, mp 272-3°; visible and uv max (95% ethanol) 273 mμ (log ε = 4.48), 320 (3.89), 398 (3.55).

Anal. Calcd for $C_{11}H_6N_2O_2S$: C, 57.38; H, 2.63; N, 12.17; S, 13.93. Found: C, 57.52; H, 2.74; N, 11.82; S, 13.72.

Trityl perchlorate

This compound was prepared according to the procedure of Hofmann and Kirmreuther.[64]

To a stirred, cooled to <10° (prewarmed for solution, but crystallization always occurs on cooling) solution of 7.8 g (0.03 mol) of triphenylcarbinol in 78 ml of acetic anhydride was added 3.12 ml of 70% perchloric acid at T <40°. The yellow slurry was cooled to 10° after the addition was complete. The product was collected on a filter, washed with 50 ml of ether, and dried in vacuo over sulfuric acid to yield 9.2 g (90%) of yellow crystals, mp 130-2°; lit.[64] mp 143-4°.

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