THE MASS SPECTRA AND CORRELATIONS WITH STRUCTURE FOR SOME 1-(5-ETHYL-2-THIENYL)-1-THIAALKANES

A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE IN ANALYTICAL CHEMISTRY IN THE GRADUATE SCHOOL OF THE TEXAS WOMAN'S UNIVERSITY

COLLEGE OF ARTS AND SCIENCES

BY

PISAL CHANDRASURIN, DIP. P. H., B. A.

DENTON, TEXAS

AUGUST, 1975

Texas Woman's University

Denton, Texas

May 8, 19 75

We hereby recommend that the thesis prepared under our supervision by Pisal Chandrasurin entitled The Mass Spectra and Correlations with Structure for some 1-(5-ethyl-2-thienyl)-1-thiaalkanes

be accepted as fulfilling this part of the requirements for the Degree of Master of Science

Committee:

Norman G. Foster
Chairman
Everett C. Hurdis
George H. Stewart

Accepted:

Mary Evelyn Huey
Dean of Graduate Studies

ACKNOWLEDGEMENTS

The author wishes to express his sincere gratitude to Texas Woman's University for the Research Grant which made this investigation possible. He is especially deeply grateful to Dr. Norman G. Foster, who has directed his research work with encouragement, consideration and enthusiasm during the entire period of his graduate studies.

The author would like to show his special appreciation to Dr. George H. Stewart and Dr. Everett C. Hurdis for the suggestions and assistance in the preparation of this manuscript. Finally, he wishes to acknowledge his thankfulness to the late Dr. Robert W. Higgins whose synthesis work, supported by the Robert A. Welch Foundation of Houston, Texas, made the present studies possible.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

INTRODUCTION

Molecular structures of organic compounds are determined from mass spectra by comparing a spectrum with reference spectra or by relating molecular structure to fragmentation (1). The latter approach is the subject of this research. If several compounds contain the same strong directing functional group, differences in identity and quantity of ions and their spectra depend on the spatial relationships of the other atoms to the functional group. The differences can be correlated with molecular structure so that one can predict identities and approximate quantities of ions when reference spectra are not available.

The sulfur atom possesses two important features that can be helpful in studying mass spectrometric fragmentation. First is the presence of the sulfur-34 isotope which occurs naturally to about 4.4 percent abundance. Second is the availability of d-orbitals in the sulfur atom. These permit hybrid bond orbital formation of the *spd* variety among other (at relatively low energies) which may alter the types of fragment ions formed and certainly leads to unique species.

HISTORICAL BACKGROUND

Sulfur is one of the most plentiful elements in nature, ranking thirteenth in abundance in the earth's crust. It appears in the elemental state, combined with other elements as minerals and as a vital constituent in plant and animal tissue (2). Sulfur compounds are the most important non-hydrocarbons in petroleum, not only because they are present in the largest percentages, but also because of their corrosive nature and their deleterious effects on petroleum products. The mean sulfur content of U.S. crude oil production in 1966 was 0.67 percent and the Middle East crudes are known to be high in sulfur up to 4+ percent.

The sulfur-containing constituents of petroleum have been of interest and concern to the petroleum industry. However, it was not until the inception of the American Petroleum Institute (API) Research project 48 in 1948 that a systematic study was undertaken to isolate and identify the sulfur compounds present in the distillate fractions of several crude oils (3).

Much research was done before 1948 on the development of processes to remove sulfur compounds from petroleum products or to neutralize their effects, but up to

that time no thorough study to identify the types of sulfur compounds in petroleum or obtain physical properties of these compounds was done. Thus, the science of petroleum sulfur compounds dates back a little over 25 years.

Since 1948, organic sulfur chemistry has progressed extensively with the establishment of API-RP 48; however, the identification of individual sulfur compounds in petroleum becomes difficult because the number of isomers increases greatly with increasing molecular weight. During the course of these studies, much experience was obtained with the interpretation of mass spectra, and analytical correlations were developed for sub-classes, including some ideas concerning the relationship of structure to fragmentation. A summary up to 1959 for sulfur compounds was made by Cook and Foster (1). An important class of sulfur compounds in petroleum is the thiophenes. Some studies on a few alkylthiophenes were reported by Hochgesang (4) in Hartough's book on thiophenes. A large number of mass spectra of organosulfur compounds has been reported in various Bureau of Mines publications to be cited as needed.

In 1951, Kinney and Cook (6) first reported upon a group of alkylthiophenes with molecular weight range 84 to 140 and showed that fragmentation of the alkyl chain at a bond beta to the ring was favored. The base peak for the monoalkylthiophenes occurs at mass 97 by breaking a beta-bond

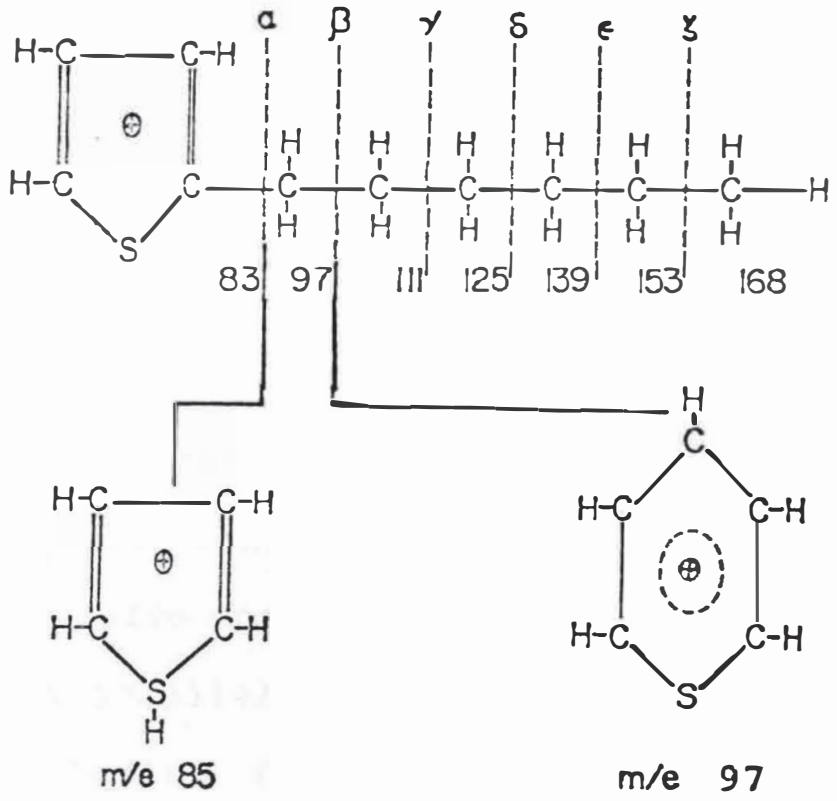


Fig. 1. Major Chain Fragmentation Possibilities of 1-(2-thienyl)hexane

They also showed that some alpha bond cleavage apparently occured to form the ions at mass 84 and 85. This requires the rearrangement of one and two hydrogen atoms respectively with origin and destination unknown. The extra hydrogen atoms are depicted as bound to the sulfur atom, but their location is not known.

Foster and co-worker (6, 7, 8) confirmed the correlations of Kinney and Cook in a series of work. Foster and Higgins (10) reported the mass spectrum of 1-(1-thienyl) hexane-1-^{13}C with a carbon - 13 label in the alpha position (1968). The principal fragmentation routes of the parent ion of monoalkylthiophenes are delineated. Many of the neutral particles lost in the formation of these fragment

ions are typical of those encountered in the alkylbenzenes or other aromatic ion systems. The processes are also thought to be similar with the ejection of a neutral sulfur atom being comparable to the ejection of a neutral C_2H_2 particle. Beta cleavage of the alkyl chain predominates, and in this cleavage the alpha carbon is carried with the ring moiety.

In 1959, Hanus and Cermák (10) using butyl and small alkyl substituted compounds proposed the ring expansion of the alkyl to parallel to the tropylium ion formation at m/e 91 proposed earlier for the alkyl benzenes by Rylander, Meyerson, and Grubb (11) in the mass spectrometer as shown in Figure 2.

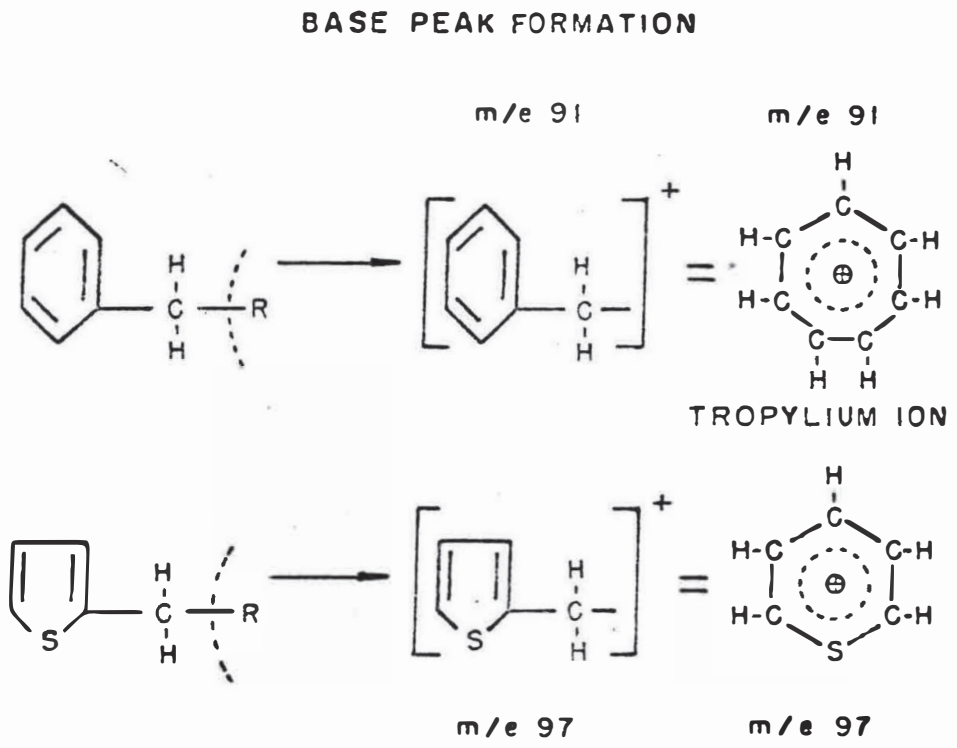
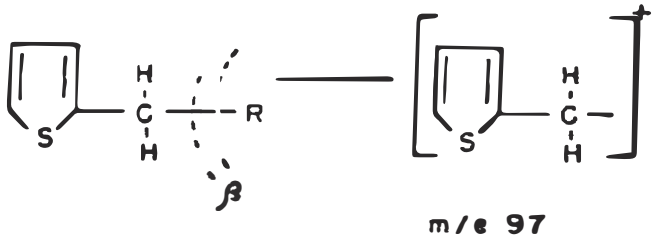


Fig. 2. The Tropylium Ion Mechanism--the Sulfur Analog

The cyclic expanded ring structure plus a hydrogen atom rearrangement to the ring was proposed by Cook and Foster, with the availability of higher molecular weight isomers and the use of low ionization voltage data. They reported the increase in rearrangement ion intensity at mass 98 with increasing chain length. At this time it was also proposed that the processes involved might be the parent ion producing the mass 98 ion, and it in turn producing the mass 97 ion. A metastable at mass 96 substantiating that the process of m/e 98 to yield 97 occurred has been reported (12).

The fragmentation of some alkylthiophenes was discussed (4) and the conclusions reached as follows:

1. Beta cleavage. The base peaks are formed in all cases by cleaving the beta bond as



m/e 97

It was also demonstrated that although a beta carbon bond does break for base peak formation of compounds that contain isopropyl or t-butyl groups, the resulting ion does not interfere with the correlations developed for the 2-alkyl and 2, 5-alkyl compounds.

2. Gamma cleavage. Cleavage at the gamma bond from the thiophene ring results in peaks 14 mass units higher than the base peak. As the alkyl substituent becomes larger and provided at least three carbon atoms are in the chain, the peak resulting from gamma cleavage becomes larger. However, even for C_{12} substitution, its intensity is only 11 percent, indicating that the gamma bond is still considerably stronger than the beta bond for the branched 2-alkylthiophenes, variations in intensity of ions produced by cleaving the gamma bond depend upon branching at the beta carbon atom or beyond.

3. Alpha cleavage. The m/e 84 and 85 peaks are assumed to come from alpha bond cleavage processes and the m/e 45 peak is assumed to come at least in part from further fragmentation of the 84 and 85 ring ions. Hence it appears that the bulk of spectra at lower m/e come from the further fragmentation of the base peak ion species (the C_5H_5S+ ion at mass 97).

Low ionization voltage studies of a pure compound are often enlightening as to the mechanism of base peak formation and may define fragmentation paths. Usually the base peak ion of a given compound appears at a low voltage shortly after the parent peak appears. The base peak then grows in relative size as the voltage is increased until it is the largest peak in the mass spectrum.

The usual order of appearance of strong peaks in spectra of the 2-alkylthiophenes is parent peak, m/e 98, and m/e 97. The m/e 98 appears in a detectable quantity at a lower voltage than the m/e 97 if alkyl group contains four or more carbons. The low voltage spectra support the suggestion that the m/e 97 is a product of a consecutive reaction in which

Molecular ion $\longrightarrow$ m/e 98 $\longrightarrow$ m/e 97.

The fragmentation mechanisms of 2, 5-di-n-alkylthiophenes have been discussed (6, 7). The base peak is formed by beta cleavage at the longer chain R_1 as shown in Figure 3.

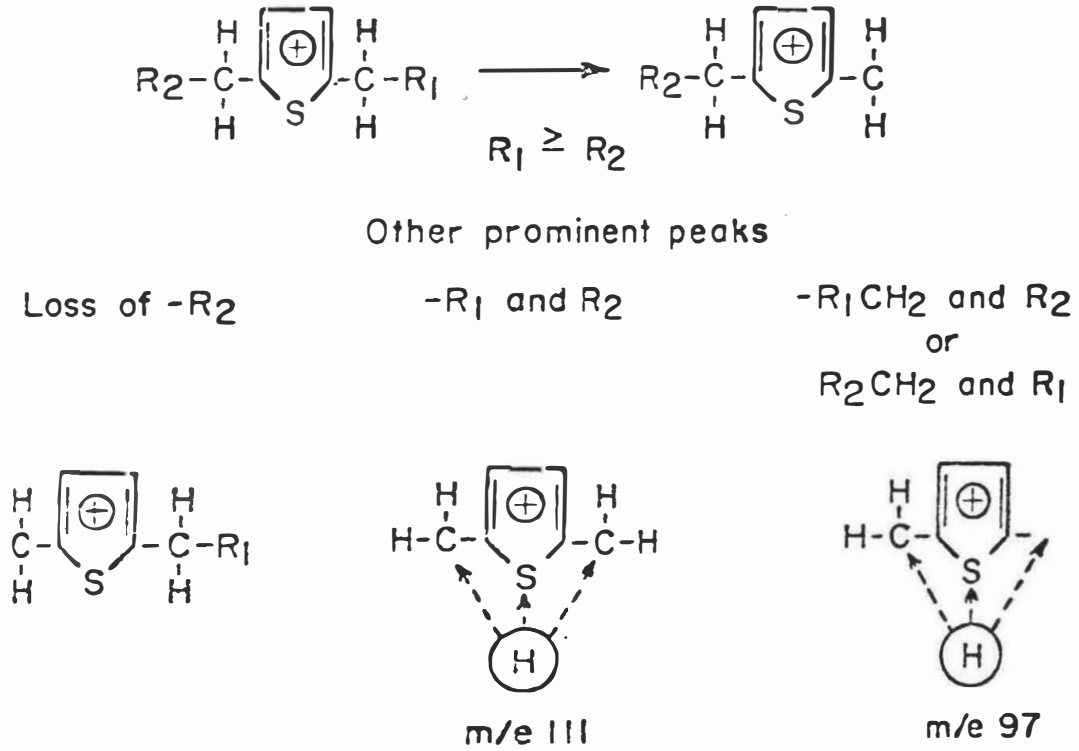


Fig. 3. Beta cleavage - 2,5-dialkylthiophenes

As R_1 increases in size, cleavage at the other alkyl group R_2 reaches a constant value. The intensities for the beta cleavage at R_2, when R_1-CH_2- is hexyl, heptyl, or octyl, are all approximately 5.4 percent. Apparently, when R_1-CH_2- is hexyl or larger, the inductive effect on the beta bond and hence, on beta cleavage of R_2 is constant. The peak at m/e 111 may result if both R_1 and R_2 are cleaved and a hydrogen atom is rearranged to the ring. The loss of one $R-CH_2-$ group and beta cleavage of the other R group, with hydrogen rearrangement, results in an ion of m/e 97. The m/e 111 has a constant ratio of intensity compared to that of the base peak for the hexyl, and heptyl, and octyl compounds. No correlation is apparent for the m/e 97 ion. The peak intensities illustrate the tendency for the longer alkyl group to be cleaved when there is a choice, and despite a possibly more complex mechanism, the shorter alkyl group, R_2, is more subject to beta cleavage (if R_1 is large) when R_2 increases in chain length.

The low voltage data of selected members of 2-Ethyl-5-n-alkyl series are presented in Figure 4. The intensity of the peak resulting from beta cleavage of the longest side chain exceeds the corresponding peaks at m/e 153,181 and 195, respectively, from beta cleavage of the ethyl side chain. This shows that a fragmentation of an alkyl chain to form a neutral metyl group is not favored over cleavage to form any other size alkyl group. Beta cleavage of the

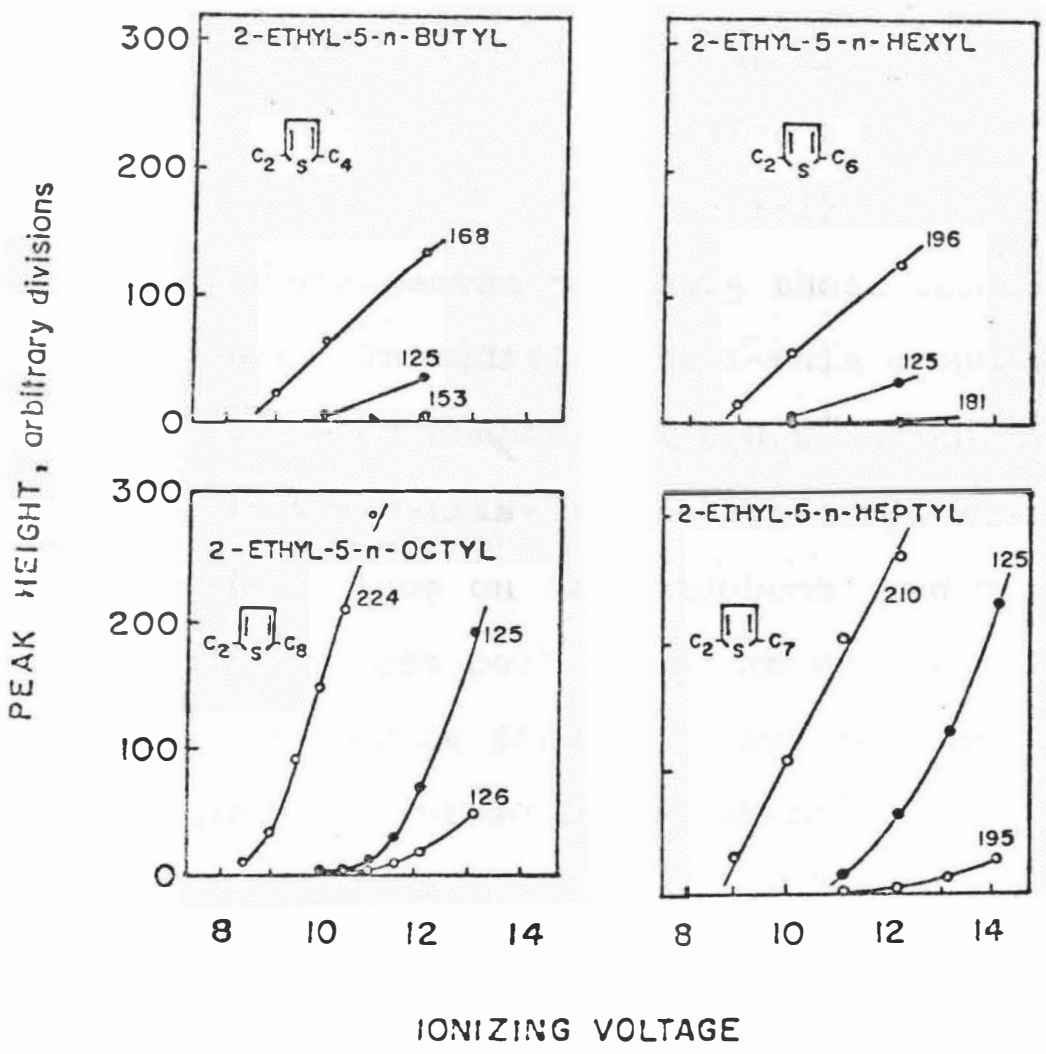


Fig. 4. Low Ionization Voltage Data for Disubstituted Alkyl Thiophenes

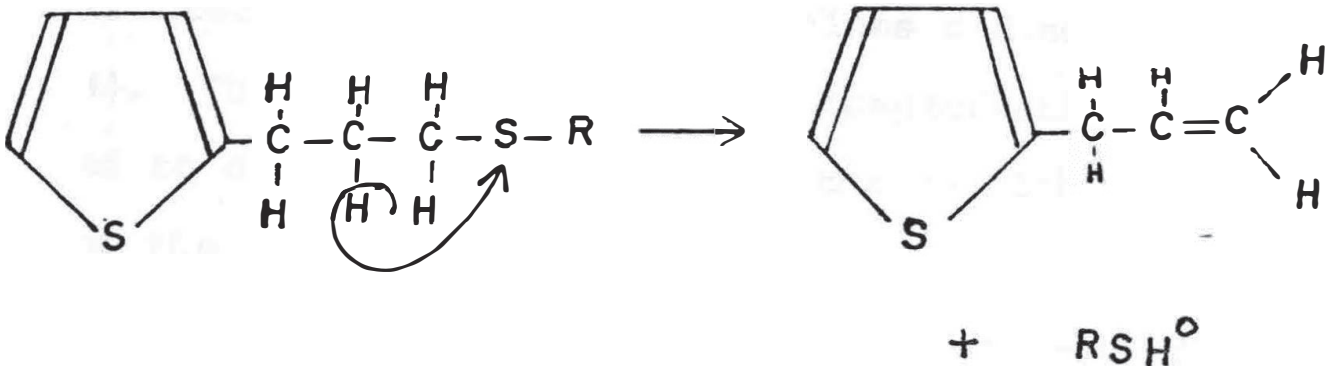
ethyl substitutent would require the formation of a neutral methyl group or methylene, CH_2.

The mass spectra and correlations for some (2-thienyl)-thiaalkanes of the 1-thia-, 3-thia-, and 4-thia-variety have been reported (13, 14). The differences in fragmentation caused by the location of the sulfur atom in the 1-, 3-, and 4- position from the thiophene ring have been described. The

unsubstituted 1-thiaalkanes all have an m/e 116 rearrangement base peak ion which is apparently formed by breaking a bond beta to the thiophene ring in the thiaalkyl chain. The m/e 116 ion is readily identified as $C_4H_4S_2$ in composition because of the S^{34} isotope contribution to the m/e 118 peak. This rearrangement parallels those observed for the alkylthiophenes. In addition the 1-thia compounds produce strong m/e 71 ion of composition $C_3H_3S^+$ which do not appear in quantity in the 3-thia- and 4-thia-compounds. Substitution of an alkyl group on the thiophene ring produces a rearrangement ion base peak having an m/e of 116 plus R less H. An ion at m/e 82 is diagnostic for the unsubstituted compounds, possibly formed by the abstraction of an hydrogen atom from the ring to produce the ion with the ejection of the neutral RSH group. The m/e 82 ion is $C_4H_2S^+$ and may be called thiaphyne. The structure for this ion is unknown.

The 1-(2-thienyl)-3-thialkanes exhibits base peak at a variety of m/e's, in contrast to the 1-thia compounds, which can also exhibit some direct beta cleavage (from the ring) to produce the ion at m/e 97 of the composition $C_5H_5S^+$. This ion is considered to be a very stable Hückel ion and also is characteristic of alkyl thiophenes. No excess m/e 98 peak above expected isotopic amounts is observed. In addition to have RSC^+ ions the m/e 61 ion, alkyl, and even alkenyl ion as base peaks these molecules do produce rearrangement ions at m/e 110.

The 1-(2-thienyl)-4-thiaalkanes exhibit a rearrangement base peak at m/e 124 ($C_7H_8S^+$) in all spectra examined. The appearance of metastable peak for the process: $124^+ \longrightarrow 123^+ + H^o$ m* = 122.04 coupled with the low ionization voltage data suggests that the m/e 124 base peak ion forms with a hydrogen shift away from the alkyl group adjacent to the ring and toward the alkylsulfide moiety:



The m/e 91 (C_7H_7) ion is observed in the spectrum of every isomer examined and does not appear in the spectra of other subclasses. Both the m/e 98 rearrangement ion and its daughter, the m/e 97 ion, appear for these compounds since now hydrogen atoms are again available from the chain.

Structure fragmentation correlations of benzothienyl thiaalkanes have been made and discussed (15). The base peak is a rearrangement ion at m/e 166 (up the expected 50 mass units from 116) which is formed by breaking a C-S bond beta to the ring accompanied by a hydrogen atom shifting to the charged moiety. This shows that the mechanism proposed

for the 1-(2-thienyl)-1-thiaalkanes can be extended when there is a benzo group fused on one side of the thiophene ring.

During the examination of the class of 1-(2-thienyl)-thiaalkanes, two compounds of the 1-(5-Ethyl-2-thienyl)-1-thiaalkanes were surveyed. These were utilized to establish that interference with the correlations for the unsubstituted thienyl-1-thiaalkanes class did not occur (13, 14). The ions observed and the fragmentation routes appeared to differ considerably from the alkylthiophenes and from the 1-(2-thienyl)-thiaalkanes. Thus an in depth study of seventeen samples of the 1-(5-Ethyl-2-thienyl)-1-thiaalkanes was warranted.

The series of compounds reported in this work were synthesized by Maria Chyang Young, working under the direction of Dr. Robert W. Higgins (16).

EXPERIMENTAL

A. Primary Survey of Compounds

Seventeen of the compounds prepared by Dr. R. W. Higgins and his students were examined. Survey conditions of 70, 15, 14 and down in 1 volt decrement to 7 ev ionizing voltage were used, in order to ascertain the purities of the compounds and to define the general direction the research was to take. After the survey, three mislabelled sample bottles were discovered, causing two duplications.

B. Purification by Chromatography

Most of the samples were dark-colored liquids and were impure as shown by the mass spectrometric survey of the compounds. Therefore, purification by chromatography was required.

1. Gas-liquid chromatography

An Aerograph A-700 "Autoprep" automatic preparative gas-liquid chromatograph (gc or glc) was used for purification and separation. A column of 3/8" l.d. x 20', packed with 30 percent SE 30 Silicone rubber on 30-60 mesh Chromosorb P., was utilized with helium having a flow rate of 100 and 150 ml/min as a carrier gas. The operating conditions used were varied. These included: column

temperature, 220-260°C; collector temperature 225-228°C; detector temperature 300-360°C; and injector temperature 282-325°C. The operating conditions and retention times of the individual compounds are recorded in Table 1. The operating temperatures might have been a little too high considering thermal decomposition hazardous for sulfur compounds. In addition as the temperature was raised higher the column started "bleeding." Impurities from this showed in the mass spectrum of compounds with alkyl groups of C_3 or larger. Characteristically they showed a peak at m/e 207, which had never appeared prior to this time for these samples of this gas chromatograph column.

2. Column chromatography

Column chromatography was therefore performed. Silica gel Bio Sil A 100-200 mesh size was employed with heptane and benzene as eluent. The m/e 207 peak disappeared from the mass spectra of some of the compounds.

C. Mass Spectrometer Operations

1. Instrumental Conditions

The mass spectra of this class of compounds were obtained by using a Consolidated Electrodynamics Corporation (CEC) single-focusing mass spectrometer, model 21-104. The instrument was equipped with a CEC heated inlet system operated at an oven temperature of 172-180°C, and the ionization chamber was controlled automatically at 250°C.

TABLE 1

COMPOUNDS STUDIED AND GAS-LIQUID CHROMATOGRAPHY DATA

Using "Autoprep," Column 3/8" x 20', packed with 30% SE 30 Silicone Rubber on 30-60 Mesh Chromosorb P.

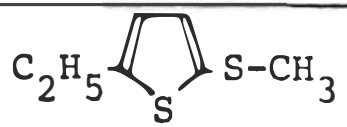
	COMPOUND	Molecular Weight	Temperature, °C				Rate of Carrier Gas ml/min.	Number of Peaks	Retention Time (min.)
			Column	Collector	Detector	Indicator			
1.		158	225	240	315	300	100		21.0
2.	$-CH_2-CH_2$	172	220	240	310	300	100		31.5
3.	$-CH_2-CH_2-CH_3$	186	232	240	320	285	100		32.0
4.	$-CH(CH_3)-CH_3$	186	225	225	300	282	100		33.0
5.	$-CH_2-CH_2-CH_2-CH_2$	200	225	230	305	285	100		75.0
6.	$-CH_2-CH(CH_3)-CH_3$	200	225	230	305	285	100		74.5

TABLE 1--Continued

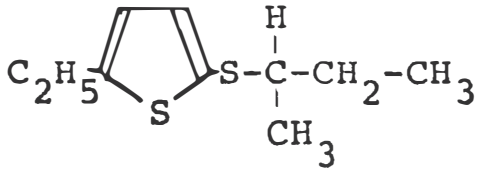
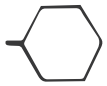
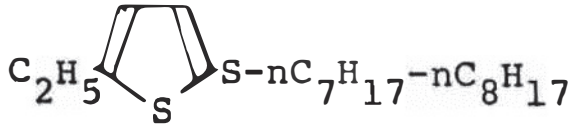
	COMPOUND	Molecular Weight	Temperature, °C: Column	Collector	Detector	Indicator	Rate of Carrier Gas ml/min.	Number of Peaks	Retention Time (min.)
7.		200	242	245	320	318	150		19.00
8.	$-nC_5H_{13}$	214	252	280	300	315	150		23.0
9.	$-CH_2-CH_2-CH(CH_3)-CH_3$	214	260	275	350	320	150		18.5
10.		226	255	255	305	310	150		40.0
11.	$-CH_2-CH(CH_2-CH_3)-CH_3$	228	255	260	312	312	150		58.0
12.	$-nC_7H_{15}$	242	250	250	325	315	150		46.5

TABLE 1--Continued

	COMPOUND	Molecular Weight	Temperature, °C: Column	Collector	Detector	Indicator	Rate of Carrier Gas ml/min.	Number of Peaks	Retention Time (min.)
13.		256	255	255	305	310	150		49.0
14.	$-nC_9H_{19}$	270	255	255	330	325	150		58.0
15.	$-nC_{10}H_{21}$	286	Compound not run through GC. Reported neat.						

Ionization was accomplished with 70 volt electron. An ionizing current of 10 microamperes was used for all spectra. Repeller settings were (1) 4.2 and (2) 5.8. Magnet current was 7.3 amperes to scan from m/e 37 upwards, and the initial accelerating voltage of about 3450-3500 volts was employed. The slit width was 4 mils, and an electrostatic scanning rate of 9 with a recording chart rate of 1/4" per second was used. For each compound, 2 or 3 microliters of liquid sample were injected to the mass spectrometer depending upon volatility of the compound. The electron multiplier detector was used at 160 volts per stage.

2. Low ionization voltage data

Low ionization voltage data were obtained in support of the suggested mechanisms of fragmentation. Data was taken at one volt intervals from 15 usually down to 5 volts (meter). Calibration was achieved against a concurrently introduced sample of benzene which produced a molecular ion at similar potentials. The appearance potential values reported in figures were obtained by the method of Lossing et al (17) and checked by the extrapolated voltage difference method of Warren (18). For a synopsis of details see (19).

DATA

A total of seventeen samples of the 1-(5-Ethyl-2-thienyl)-1-thiaalkanes class were examined by survey mass spectrometry. A mislabeling of bottles, previously undetected, had occurred, and despite all efforts, no sample of the n-hexyl substituted variety could be found. Hence, this work reports on only fifteen high purity compounds. The compounds and their purities are reported in Table 2, to be found in the discussion section. The entire set of reference quality mass spectral data are given in Appendix I. A secondary reference spectrum of n-hexadecane is to be found as Appendix II. Low ionization voltage data is not presented in a raw, or tabulated form, but rather is shown in a series of figures to be found in the discussion of low ionization voltage results. Similarly, appearance potential data for selected ions appears in those figures. It should be noted that the n-decyl species of compound is reported as neat, purification by GC being considered infeasible because of the high temperatures involved.

DISCUSSION

The purpose of this thesis is to develop useful mass spectral correlations with molecular structure for the class of compounds 1-(5-ethyl-2-thienyl)-1-thiaalkanes. In utilizing Table 2 with purities and total ion intensity data for the compounds studied, the reader should note that only four significant figures have been used to allow a compact presentation. Data are supplied to five significant figures in Appendix I.

A. Molecular Ion Intensities (M)

The intensities of the molecular ion peaks of this class of compounds, 1-(5-ethyl-2-thienyl)-thiaalkanes are fairly strong, ranging from about 0.5 percent (for the S-C_{10} isomer) to about 7.2 percent (for the S-C_2 isomer) of the total ion intensity. They have more intense molecular ions than the corresponding alkanes or thiaalkanes, but less than the corresponding thiophenes. These intensities generally decrease as the number of carbon atoms in the alkyl side chain increases. This class of compounds has slightly lower molecular ion intensities than the corresponding (2-thienyl)-thiaalkanes of the 1-thia-, 3-thia-, and 4-thia- variety.

TABLE 2

PARTIAL MASS SPECTRAL DATA OF 1-(5-ETHYL-2-THIENYL)-1-THIAALKANES

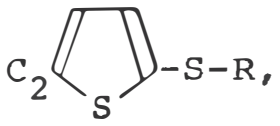
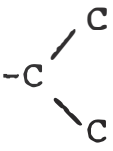
 R=	$-C_1$	$-C_2$	$-nC_3$		$-nC_4$
Purity	99.969%	99.83%	98.85%	98.59%	99.28%
M.W. / m/e	158	172	186	186	200
M	6.12	7.17	4.42	2.28	4.04
M-15	12.47	9.20	2.15	0.07	1.14
157	0.25	-	0.02	0.01	0.29
144	0.99	0.56	4.17	4.57	7.99
129	0.14	6.01	10.30	9.28	11.86
116	0.06	0.19	0.27	0.23	0.34
112	0.13	0.20	0.35	0.11	0.73
111	1.01	1.18	1.02	0.85	1.17
99	2.83	4.71	2.11	1.18	2.31
97	1.48	1.48	1.11	0.63	1.51
71	2.74	3.02	2.15	1.76	2.27
69	4.49	0.01	2.25	1.87	2.19
67	1.65	1.58	0.96	0.83	1.09
65	2.40	2.58	-	1.56	2.06
59	3.93	5.86	2.85	2.71	3.78
57	1.32	0.67	0.36	0.33	0.38
55.0	0.26	0.40	0.30	0.93	1.31
45	9.65	8.44	6.37	5.29	6.85
43.1	0.15	0.03	4.73	13.30	0.35
41.1	2.71	2.83	6.36	10.04	9.67
39	6.59	5.23	6.29	6.27	5.84
Σ R's	3.39	7.54	14.93	30.82	18.05

TABLE 2--Continued

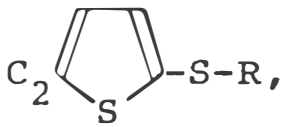
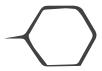
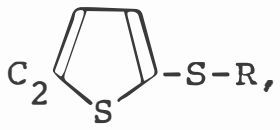
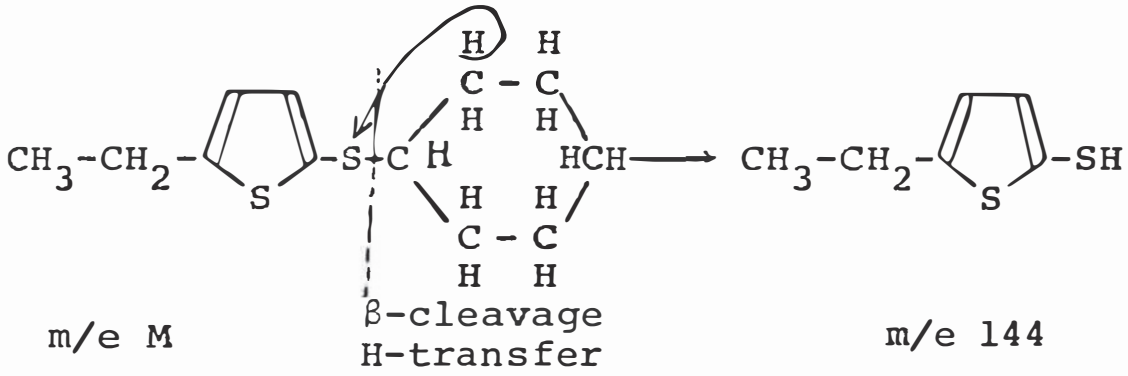
 R =	-C-C-C (C)	-C-C-C (C)	-nC$_5$	-C-C-C-C (C)	
Purity	99.77%	99.99%	99.99%	99.99%	99.99%
m/e \ M.W.	200	200	214	214	226
M	3.61	3.41	3.61	2.84	2.47
M-15	0.19	0.070	0.79	0.45	-
157	0.30	0.01	0.32	0.27	0.02
144	9.75	11.57	9.40	8.13	16.34
129	10.50	13.43	10.56	7.11	8.91
116	0.26	0.31	0.27	0.19	0.21
112	0.48	0.18	0.76	1.11	0.13
111	0.93	1.12	1.00	0.77	0.73
99	1.65	1.67	2.14	1.70	1.42
97	1.13	0.91	1.43	1.26	0.63
71	1.93	2.24	1.87	1.61	1.47
69	1.89	2.09	1.60	1.46	1.08
67	0.88	1.07	1.05	0.84	1.42
65	1.81	1.94	1.74	1.52	1.38
59	2.98	3.98	3.34	3.02	2.51
57	0.33	0.32	0.24	0.22	0.16
55.0	0.87	1.24	1.96	-	-
45	6.65	11.02	5.26	4.84	3.31
43.1	0.60	0.09	14.25	20.91	0.88
41.1	11.60	11.02	1.84	8.46	12.99
39	6.32	6.24	4.41	4.78	5.09
Σ R's	23.53	22.23	18.46	35.21	30.32

TABLE 2--Continued

 R =	-C-C-C-C (C branch)	$-nC_7$	$-nC_8$	$-nC_9$	$-nC_{10}$
Purity	99.40%	99.99%	99.99%	99.99%	99.99%
M.W. / m/e	228	232	256	270	284
M	2.16	2.25	1.97	1.74	0.56
M-15	0.03	0.34	0.23	0.21	0.05
157	0.25	0.27	0.23	0.22	0.15
144	11.77	9.44	7.51	6.95	2.33
129	6.45	6.71	5.05	3.64	1.66
116	0.17	0.19	0.16	0.14	0.33
112	0.37	0.64	0.53	0.47	0.28
111	0.63	0.71	0.60	0.50	0.49
99	1.89	2.09	1.97	1.39	0.61
97	0.97	0.98	0.84	0.70	1.17
71	1.33	1.18	1.28	0.82	0.60
69	1.18	0.96	0.83	0.70	0.47
67	0.92	1.03	1.23	0.88	0.75
65	1.38	1.40	1.23	0.78	0.47
59	2.82	3.17	2.98	1.84	5.91
57	0.16	-	-	-	-
55.0	-	-	-	-	0.005
45.	4.06	4.45	4.00	2.28	1.97
43.1	24.31	9.44	13.69	16.68	12.93
41.1	7.68	11.80	13.69	11.26	12.168
39	3.46	4.24	3.93	2.42	3.67
Σ R's	39.68	37.88	44.32	51.26	42.06

B. The Rearrangement Ion at m/e 144

The m/e 144 ion is prominent in the spectra of all the compounds examined except for the S-CH_3 and S-C_2H_5 which must be considered separately. The base peak (ion of largest intensity) of the 1-(5-Ethyl-2-thienyl)-cyclohexyl sulfide is formed at m/e 144 by breaking of β bond to the thiophene ring in the thiaalkyl chain with a concurrent hydrogen transfer from somewhere on the cyclohexyl rings as shown below. Four hydrogen atoms located β to the sulfur



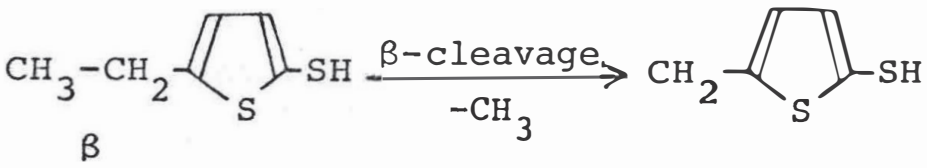
m/e M m/e 144

atom are readily available for this generally recognized type of rearrangement.

Intensity of the m/e 144 ion starts to climb noticeably from the S-nC_3 compound until it reaches a maximum with about six carbon atoms attached to the thiaalkyl sulfur atom. From this point on the intensity drop down with increasing carbon numbers in the chain. This is parallel to the behavior of the molecular ion. In part this decrease in m/e 144 may be attributable to the more "paraffinic" behavior to be expected as the chain gets longer. This will be discussed in more detail in a later section.

C. The Ion at m/e 129

The ion at m/e 129 is the base peak for 1-(5-Ethyl-2-thienyl) of -1-thiabutane, -1-thiapentane and -2-methyl-1-thiabutane. It is possibly a further rearrangment from m/e 144 by a β bond cleavage on the ethyl side chain. To lose this methyl group should require a higher energy process.



m/e 144 m/e 129

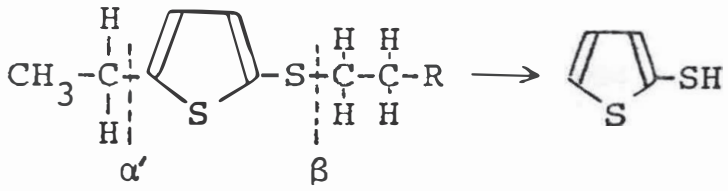
The m/e 129 ion does not appear in any quantity of the spectrum of the S-CH_3 compound but is a strong peak (in excess of 10% of Σi), until a branched C_5 chain is reached. Thereafter it decreased in a regular fashion parallel to the m/e 144 ion with the increasing molecular weight.

D. Other Diagnostically Useful Ions

1. m/e 116

Since the m/e 116 ion is the base (and rearrangement) peak for all of the 1-(2-thienyl)-thiaalkanes previously studied (15) its presence in these spectra must be explained and any interference considered. Fortunately the ions are of low intensity, but for that very reason they might suggest impurities to some mass spectroscopists. The m/e ion is possibly formed by two cleavages of the bonds at the position β and α prime to the thiophene ring as

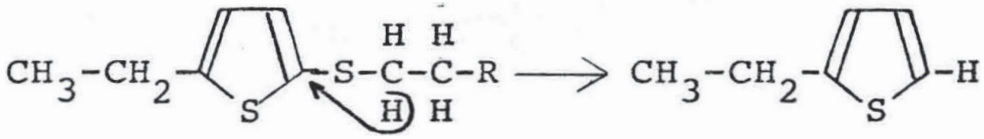
shown below. A hydrogen transfer is required in each case. Two hydrogen atoms, β to the sulfur, and either of two hydrogens β′ to the ring are readily available for the necessary rearrangements.



molecular Ion m/e 116

2. m/e 112

The m/e 112 ion is possibly formed by direct α cleavage in the molecular ion and hydrogen transfer from the β position to the ring.

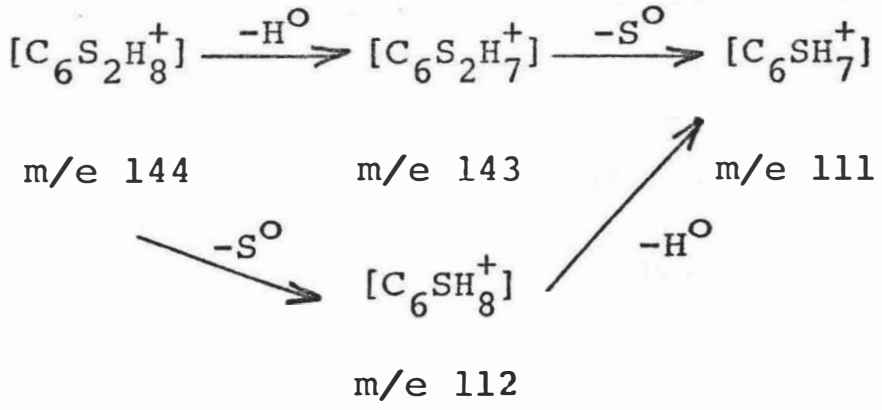


m/e 112

The m/e 112 ion may also be formed as a daughter ion from the m/e 144 rearrangement ion by a similar process. It should be noted that these processes occur for the 1-(2-thienyl) thiaalkanes to form the m/e 84 peak. Similarly the alkylthiophenes exhibit an m/e 84 peak formed much the same. In the case of these latter two classes of compounds a second hydrogen atom is often transferred, and in the present compounds a small but definite m/e 113 ion (above expected isotopic quantities) is observed.

3. m/e 111

The m/e 111 ion intensities slightly increase for the short chain or branched alkyl group of the thiaalkane chain, and then decrease slowly with increasing molecular weight. There are at least three routes for formation of this ion. In addition to direct cleavage from the molecular ion two routes from the rearrangement ion at m/e 114, or the M^+ ion via the 113 ion pathway discussed above:



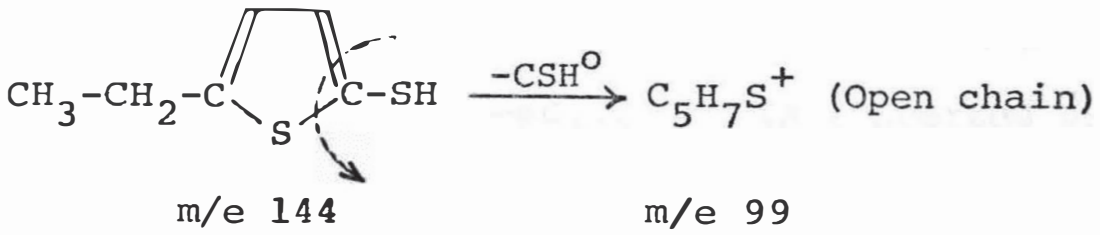
4. m/e 85 and 84

The m/e 85 and 84 ions are not diagnostically useful for this kind of compound, nor is the m/e 82 ion found to be significant as was the case for unsubstituted 1-(2-thienyl)-2-thiaalkanes. For the class of 1-(5-Ethyl-2-thienyl)-1-thiaalkanes, the m/e 113 and 112 ions can be considered to have been substituted for these ions.

E. Ring Fragment Ions

1. The m/e 99 ion

The m/e 99 ion shows high intensities in this class of compounds, unlike and of the other sulfur classes discussed. It was unexpected but might be formed by the process shown below. Note that this is in reality a ring rupture

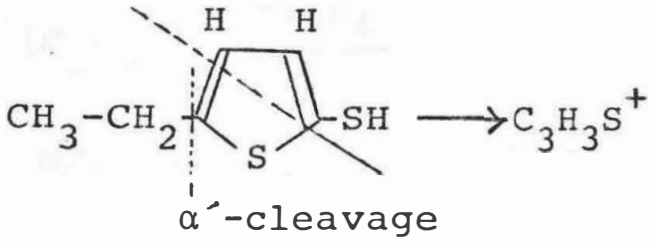


process. The intensity of the m/e 99 ion is 4.96% for the S-C_2 isomer and drops regularly as the chain length increases to 0.61% for the S-nC_{10} isomer. The ion intensity also decreases with chain branching. The m/e 99 ion should have been anticipated because of the work of Miss Shiu with the 1-(2-thienyl)-thiaalkanes which showed quite sizable m/e 71 ions which were correctly recognized as ring fragment ions (15). In the present case, the ethyl substitution for a hydrogen in the 5 position raises the net m/e by 28. Seventy-one plus 28 gives us the 99. It should be noted that any of the rearrangement ions of m/e 144 can release a neutral CSH fragment to produce the observed 71.0 ions of small but detectable size in this class of compounds. Other fragmentation routes could also lead to both of these species

for this class of compounds, but m/e 99 could not be formed by the unsubstituted 1-thia variety.

2. The m/e 71 ion

The m/e 71 ion could possibly be formed through the process described above. Also, α´ cleavage could occur simultaneously as shown:



$\longrightarrow C_3H_3S^+$ (a concerted process)

m/e 144 m/e 71

The intensity of the m/e 71 ion parallels the behavior of the 99 ion. It could also be formed by the process shown below: (A multi-step process).

$$[C_6H_8S_2^+] \xrightarrow{-CH_3^o} [C_5H_5S_2^+] \xrightarrow{-S^o} [C_5H_5S^+] \xrightarrow{-C_2H_2^o} [C_3H_3S^+]$$

m/e 144 m/e 129 m/e 97 m/e 71

3. The m/e 69.0 ion

The m/e 69.0 ion intensities are high for short chain and normal alkyl groups except for the S-C_2H_5 compound, and decrease regularly with increasing molecular weight. For example, the intensity for the S-C_1 is 4.49 percent while only 0.47 percent of the total ionization for the S-nC_{10} compound. It varies similar to both the 99 and 71

ions. It is likely that the ion is formed directly from either of these two ions. Ions at m/e 69.1 are resolved from the 69.0 ion which is a sulfur containing ion. All ions at .1 mass values are attributed to purely hydrocarbon species. The ions arising from the alkyl chains are discussed in a later section.

$$[C_5H_7S^+] \xrightarrow{-C_2H_4^{\circ}} [C_3H_3S^+] \xrightarrow{-2H^{\circ}} [C_3HS^+]$$

m/e 99 m/e 71 m/e 69.0

Staley (20) has observed this kind of stripping of hydrogen from an ion, which resulted in species that always retained one hydrogen atom as an apparently stable end product of fragmentation. This m/e 69.0 ion could fit into this theory. Alternatively it could be formed from the m/e 97 ion as follows:

$$[C_5H_5S^+] \xrightarrow{-C_2H_4^{\circ}} C_3HS^+$$

m/e 97 m/e 69.0

4. The m/e 67 ion

The m/e 67 ion could be formed from the m/e 99 ion by the ejection of a neutral sulfur atom:

$$[C_5H_7S^+] \xrightarrow{-S^{\circ}} [C_5H_7^+]$$

m/e 99 m/e 67

This open chain hydrocarbon species ion persists in the low ionization spectra.

5. The m/e 97 ion

The m/e 97 ion is possibly formed from cleavage of the m/e 144 rearrangement ion through a two step process.

$$[C_6H_8S_2]^+ \xrightarrow{-CH_3^o} [C_5H_5S_2^+] \xrightarrow{-S^o} [C_5H_5S^+]$$

m/e 144 m/e 129 m/e 97

If the m/e 129 ion is formed directly from the molecular ion (a process for which no evidence could be obtained) then only the second step given above need occur. The peak intensity of this ion behaves the same way as the m/e 99 except for the methyl and ethyl isomers and the S-nC_{10}. The m/e 97 ion could also form from the m/e 99 ion, although this is considered a highly improbable process:

$$[C_5H_7S^+] \xrightarrow{-2H^o} [C_5H_5S^+]$$

m/e 99 m/e 97

6. The m/e 65 ion

The m/e 65 ion could be formed by the ejection of a neutral sulfur atom from the m/e 97 ion, a recognized process. The ion intensity varies with the 97 ion.

$$[C_5H_5S^+] \xrightarrow{-S^o} [C_5H_5^+]$$

m/e 97 m/e 65

7. The m/e 45 ion

The m/e 45 ion intensities are quite high, ranging from 1.97 percent for the S-nC_{10} compound to 11.02 percent of the total ionization for the S-C(-C)-C-C compound. One fragmentation route from the m/e 71 ion is expected:

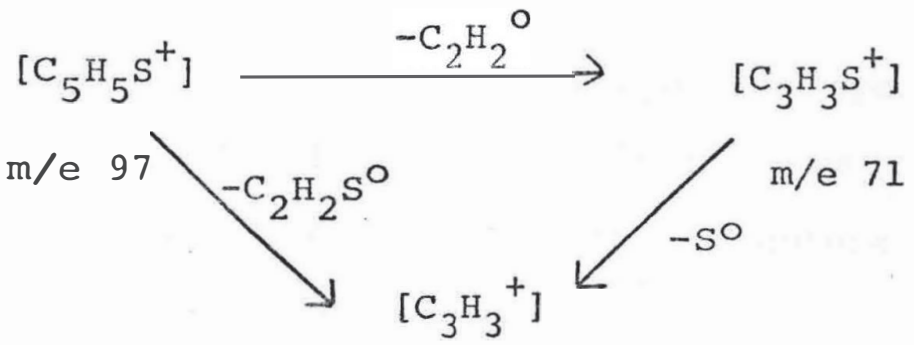
$$[C_3H_3S^+] \xrightarrow{-C_2H_2^o} [CHS^+]$$

m/e 71 m/e 45

Also, ring fragmentation of either the m/e 84 or 97 ions can occur as reported for the alkylthiophenes (6, 7) to produce this ion.

8. The m/e 39 ion

Another ring fragment ion is the m/e 39 ion whose intensity is rather high for all the compounds. It ranges from 2.42 percent for the S-nC_{10} isomer to 6.59 percent for the S-C_1 compound. The formation of this ion is expected as follows:

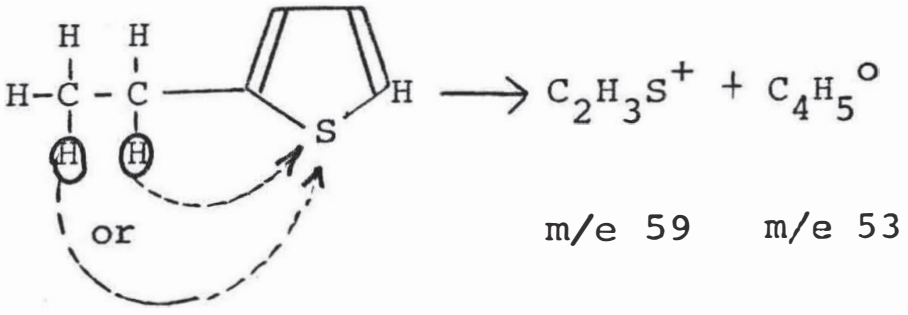


Again, cleavage of the thiophene ring also leads to this ion, just as it produces the m/e 45 ion.

F. Fragment Ions from Other Processes

1.

Additional fragment ions at m/e 59 ($C_2H_3S^+$) and m/e 53 ($C_4H_5^+$) are observed ranging from about 2-6 percent for the former ion and from about 1-2 percent for the m/e 53 ion. Both of these ions may form from cleavage of the m/e 112 species as shown:

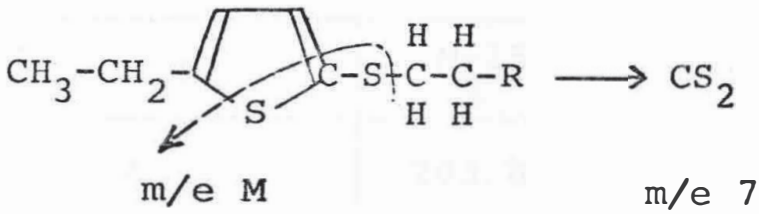


m/e 112

With charge competition being won by the sulfur containing moiety, the 59 ion is greater in intensity than the m/e 53 ion.

2.

The m/e 76 ion exists in all of the spectra for these compounds. It also persists in the low voltage data. The ion may be formed by breaking the thiophene ring including the sulfur atom from the thiaalkyl chain:



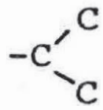
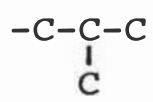
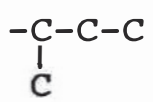
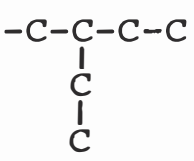
Many additional routes can be offered to this ion, all without proof by means of a metastable ion. It indicates the presence of two sulfur atoms in the molecule.

3.

The alkyl fragmentations and their daughter ions are prominent in these spectra. As the chain lengthens the sum of the intensity of the ions (41, 43, 55, 57, 69, 71, 83, 85) increases markedly. Almost half of all ions formed are of this origin for the molecules with C_8-C_{10} side chain. For a chain branched versus the normal isomer an appreciable enhancement occurs. If a novice mass spectroscopist were to examine these spectra, a first interpretation would suggest a mixture of thiophenes, alkanes and thiaalkanes. The only way to avoid this is through known correlations or reference spectra.

4.

The molecular minus fifteen mass units ion (M-15) is possibly formed by competition for charge in the ion moiety between the ethyl side and the thiaalkyl side chain of thiophene ring. The ratio of the molecular ion to the M-15 ion is shown as follows:

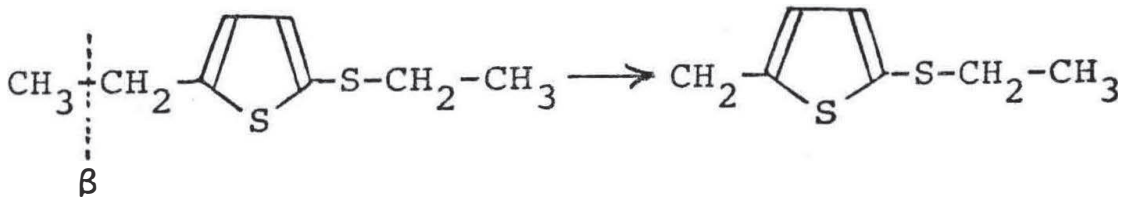
R	$\frac{M-15}{M}$
C_1	203.86
C_2	128.17
nC_3	48.73
	2.85
$-nC_4$	28.12
	5.12
	.62
$-nC_5$	21.98
	None
	1.53
$-nC_7$	15.00
$-nC_8$	11.60
$-nC_9$	11.07
$-nC_{10}$	8.68

For the n-alkyl group of the thiaalkanes, S-nC_3 has the highest M-15 to M^+ ratio (about 48.73%) and S-nC_{10} has the lowest at 8.68 percent. Thus, the ratio is decreasing with increasing chain length. It is obvious that the longer the chain length of alkyl group, the more excess energy is absorbed by the thiaalkyl chain. Hence, the ejection of less CH_3group on the ethyl side chain will result in less M-15 ion due to the lack of energy.

G. Compounds Exhibiting Exceptions to the Correlations

1.

The 1-thiapropyl derivative is the only compound producing a substantial m/e 157 ion. The base peak at mass M-15 occurred for 1-thiaethane (at m/e 143) and 1-thiapropane (at m/e 157). As suggested above these ion peaks are possibly formed by breaking of a β bond in the ethyl side chain instead of the thiaalkyl side with no hydrogen transfer.

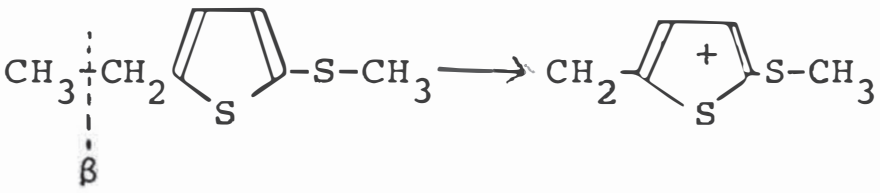


m/e 172 m/e 157

These compounds are exceptions in other ways, i.e. the thiapropyl compound shows a negligible m/e 69 ion.

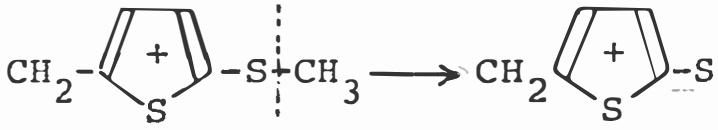
2.

The most striking exception, however, is for the 1-thiaethane compound. It shows an appreciable m/e 128 ion, either a rearrangement of unusual nature or an unusual cleavage:



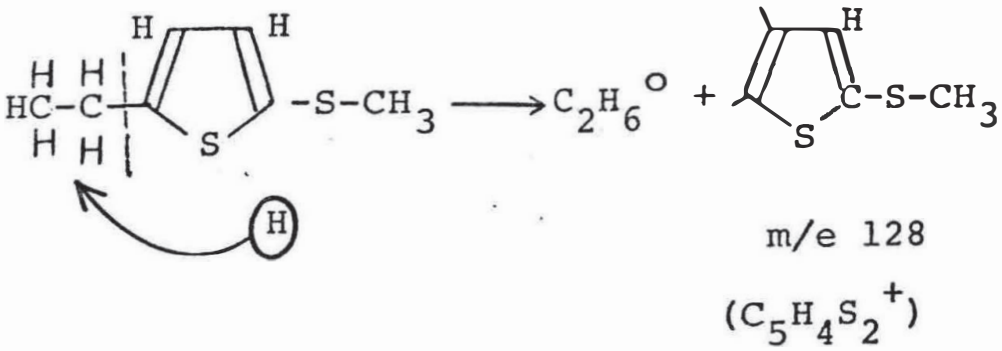
m/e 158 m/e 143

Now, the m/e 143 can cleave as shown:



m/e 143 m/e 128

Alternatively one may suggest the molecular ion losing the equivalent CH_3-CH_3 by some hydrogen abstraction process to give m/e 128:



m/e 128

$(C_5H_4S_2^+)$

H. General Fragmentation Pathways

In synopsis of what has been learned, a general fragmentation scheme is presented applicable to all of the compounds given above. This is presented in Figure 5.

I. Low ionization voltage results.

In Figure 6 the low ionization voltage data are presented for four compounds of the S-C_4 and the S-nC_5 variety. As expected, the curves for the M^+ ions are essentially superimposable. Other prominant ions at m/e 144, 57, 112, and 129 appear for all three of the C_4 isomers. For the nC_5 compound the m/e 71 (alkyl) ion and the 43 ion replace the 57 and 41 ions. For the S-C_4 isomers, the m/e 57 ion can arise by direct cleavage β to the ring on the thiaalkyl side. If this simple cleavage occurs to produce this ion it is quite in contrast to the formation of the rearrangement m/e 144 ion which abstracts a hydrogen atom from the alkyl chain and allows a neutral olefinic species to be ejected. Increasing the side chain to pentyl does show ions at m/e 71 and 55, up one carbon number from the 57 and 41. A striking difference is the ion at m/e 43 which is quite large. Based upon its growth curve and appearance potential suggests either an unusual cleavage δ from the ring or a cyclization of the alkyl ring before fragmentation. Additional ions at m/e 112, 129, M-15, 97 and 76 are shown to give some idea of their relative importance, and to aid

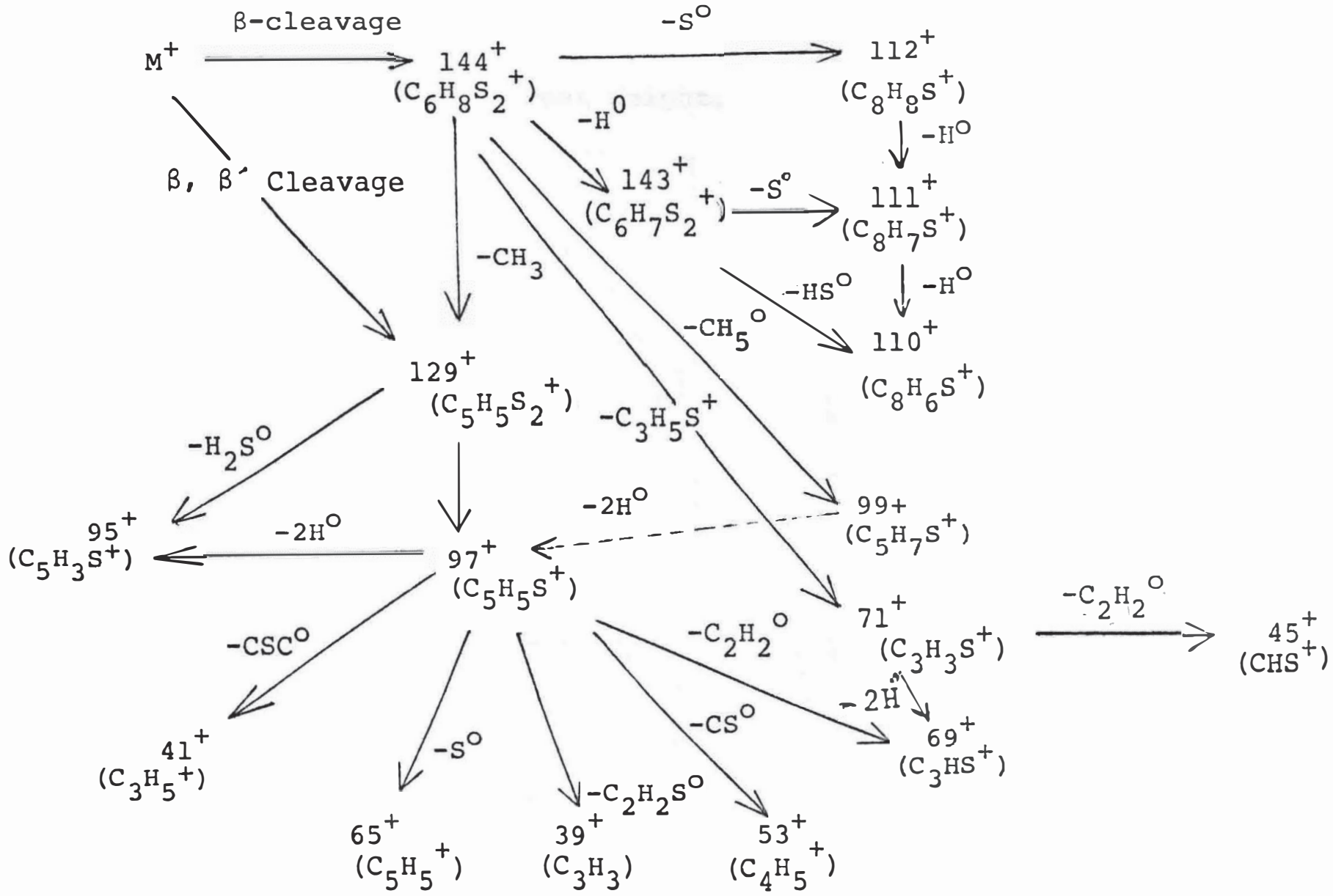


Fig. 5. Some Fragmentation Paths of the 1-(5-ethyl-2-thienyl)-1-thiaalkanes.

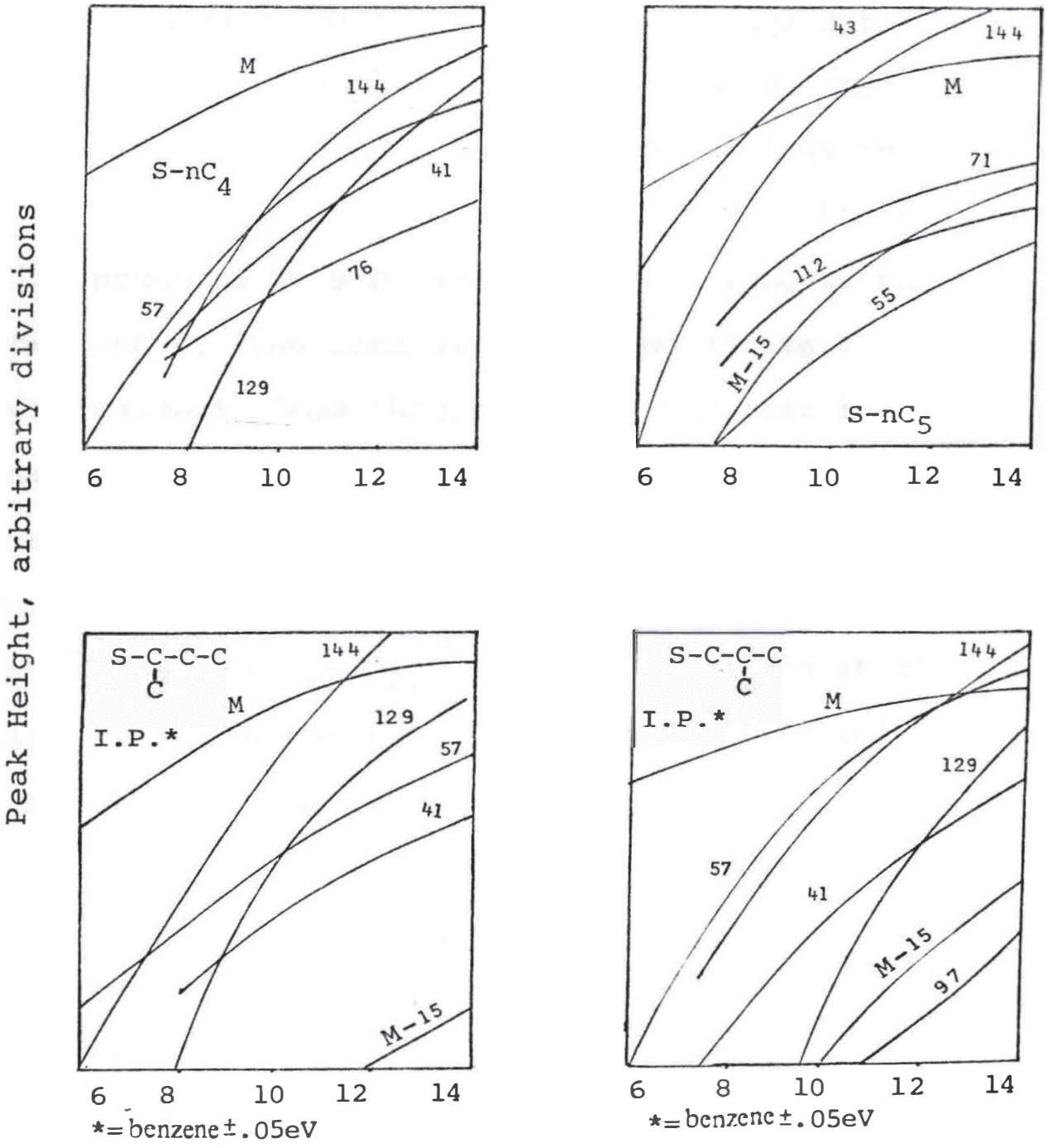


Figure 6. Low Ionization Voltage Data for $S\text{-}C_4$ and $S\text{-}nC_5$

in the discussion of other compounds below.

In Figure 7 the low ionization voltage data for four higher molecular weight isomers are presented. The cyclohexyl derivative presents expected fragment ions in the anticipated order. That is, the m/e 83 ion is the cyclohexyl ion produced by β cleavage from the ring in the manner described above. The ions at m/e 55 and 41 are the expected daughter fragments from this species. The most important fact derivable from the data is that the m/e 129 ion appears in the same relative strength and position as the 129 ions in the spectra of the other compounds. This is interpreted as further proof of cleavage of the m/e 144 ion at the remaining bond β to the ring to produce the m/e 129 ion and a neutral methyl group.

The S-nC_8 compound shows a modest production of the M-15 ion (at m/e 241), once again indicating that this relatively high energy process is occurring to an appreciable extent. The rearrangement ion at m/e 144 and the m/e 129 ion for all compounds shown are in approximately the same strength and order.

The production of alkyl ions from these compounds (excluding the cyclohexyl derivative) is worthy of further consideration. For the branched chain 1-thia-2-ethylbutyl isomer, the m/e 85 ion does appear in strength, supporting the indications obtained that branch chain isomers will undergo direct β cleavage to produce the charged alkyl

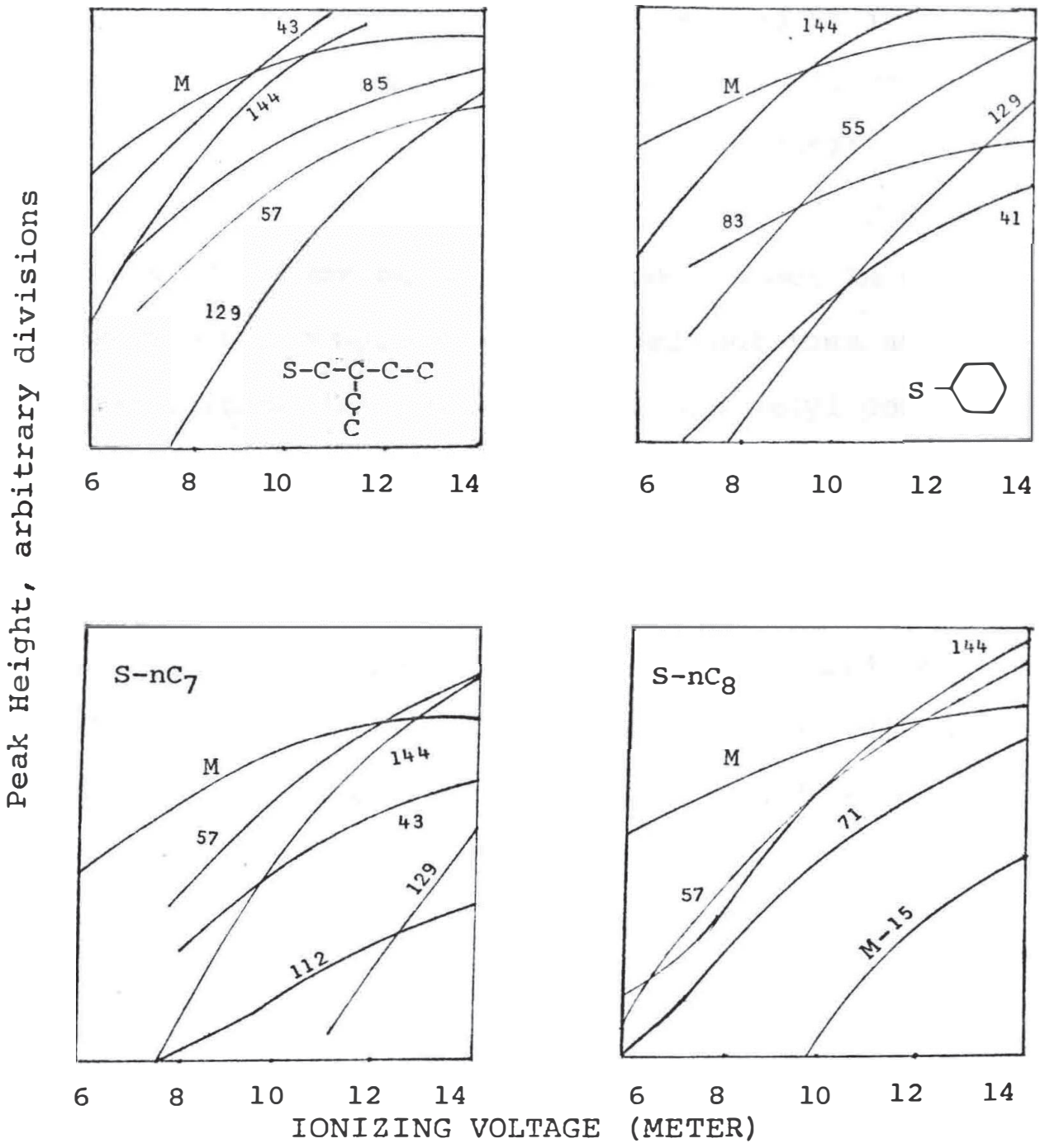


Figure 7. Low Ionization Voltage Data for S-C_6 and Higher

moiety in competition with the rearrangement ion at m/e 144. Strong production is shown for the m/e 43 and 57 ions while the m/e 71 (not shown) is produced, but in small quantity. Somewhat surprising is the behavior of the heptyl compound which produces very little 71 ion, but does have prominent ions at 57 and 43. Moving up one carbon number in chain length, the n-octyl compound shows prominent ions at 43, 57 and 71. Low voltage data on the nonyl and decyl compounds was not obtained, but the high voltage (70 ev) data suggest that this problem remains unsolved. The nonyl isomer shows small ion intensities for the continuation of the alkyl fragment series, i.e., m/e 83, 85, 97, 99, 11, 113, etc. Of these the largest (only 2.0% of Σi) occur for m/e 97 and 97, corresponding to the heptyl ion and its daughter. Meanwhile, the C_3 to C_5 alkyl fragments are quite intense (about 45% of the total ions). For the n-decyl compound, one might expect the octyl ion fragments (m/e 113, 111) to be somewhat larger than those up or down one carbon number. Such is not the case; the ions are small and not out of magnitude order with respect to the other alkyl ions.

From all of the data obtained it is quite apparent that the production of alkyl ions, at least from the longer chain compounds, is enigmatic and that a plethora of possible scramblings of the chain carbon atoms, as well as simple cleavages must be occurring.

The data for the 1-thiaethane compound shows that the largest ion is the m/e 143 ion, and the m/e 144 is present only as an isotope. Hence an obvious conclusion is reached, viz., the molecular ion has lost a methyl group (not ordinarily favored) primarily because No other processes are available for fragmentation. Some α cleavage of the $S-C_1$ group must occur directly to produce the m/e 111. The ions at m/e 59, 99, 67 and 41 all must come from ring fragmentation. The ion at m/e 128 implies that the m/e 143 ion now releases a second methyl group. The exact sequence of events could only be delineated by additional study involving metastable ions and isotopic labeling. The low ionization voltage data for 1-(5-ethyl-2-thienyl)-1-thiaethane is shown in Figure 8.

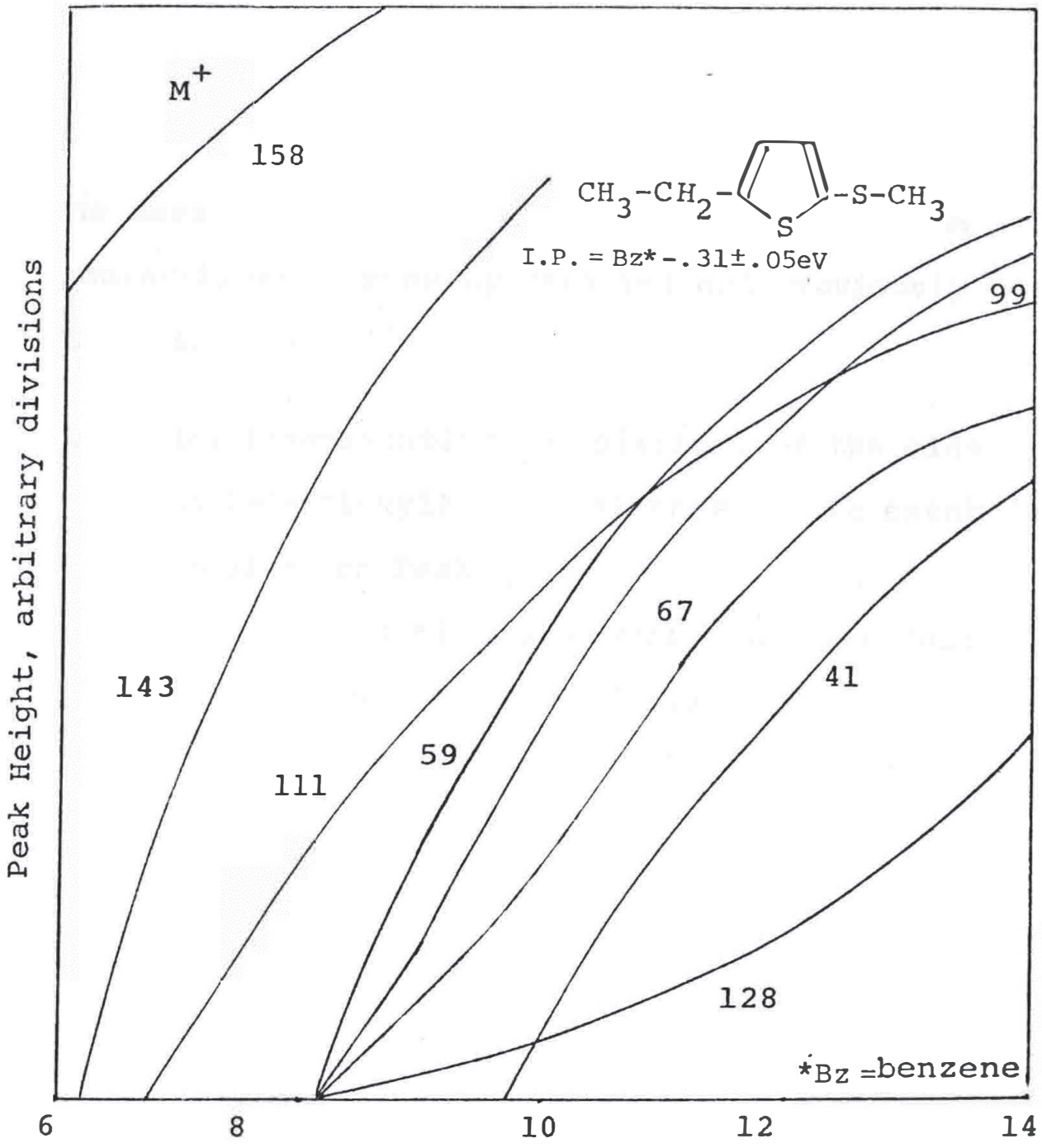


Figure 8. Low Ionization Voltage Data for 1-(5-ethyl-2-thienyl)-1-thiaethane

CONCLUSIONS

From this study, the following general conclusions can be made:

A. The mass spectra have been obtained for fifteen sulfur compounds whose mass spectra had not previously been studied.

B. Structure-fragmentation correlations of the class 1-(5-ethyl-2-thienyl)-1-thiaalkanes can be established:

1. Molecular Ion Peak

   a. The intensities of parent peaks are fairly strong (0.5 to 7.2% of Σi).

   b. These intensities generally decrease as the number of the alkyl side chain carbon atom increases.

2. The Rearrangement Ion at m/e 144

   a. The ion is prominent in the spectra of all the compounds examined except for the $S-CH_3$ and $S-C_2H_5$.

   b. The ion is apparently formed by breaking of a β bond to the thiophene ring in the thiaalkyl chain with a concurrent hydrogen transfer.

c. The ion intensity behaves very similar to that of molecular ion with respect to increasing chain length.

3. Base Peak

The mass spectroscopist usually expects the series of compounds to yield one, two or possibly three different base peaks. The fifteen compounds produce six different m/e base peaks: 157 (1), 144 (1), 143 (1), 129 (3), 43 (7) and 41(2). Since the latter two are typical of alkanes, nine out of fifteen suggests that these molecules are quite unusual.

4. Other Diagnostically Useful Ions

a. The m/e 116 is possibly formed by two cleavages, one at the bond at the position β on the thiaalkyl side and the other α on the ethyl side to the thiophene ring with a hydrogen transfer in each case.

b. The m/e 112 is possibly formed by direct α cleavage on the thiaalkyl side chain in the molecular ion and hydrogen transfer from the β position to the ring.

c. The m/e 111 might be formed by at least three routes: from the rearrangement ion at m/e 144, or the M^+ ion via m/e 122 pathway.

5. Ring Fragment Ions Characteristic of this Species

a. The m/e 99 ion shows high intensities in this class of compounds. The ion intensity, range from 0.61 to 4.96 percent of total intensity, decreases as the chain length increases and with the chain branching. This ion is considered to be of the composition, C_2H_5-$[C_3H_2S]^+$, a fragment from either the rearrangement ion or possibly the 112 ion species.

b. The m/e 71 ion was recognized as ring fragment ion in previous work and formed by a concerted process. The m/e 99 ion intensity parallels the behavior of the 71 ion.

c. The m/e 69.0 ion intensities are high for short chain and normal alkyl group except for S-C_2H_5 compound, and decrease with increasing molecular weight.

d. The m/e 67.1 may be formed from the m/e 99 ion by the ejection of a neutral sulfur atom.

e. The m/e 97 ion is possibly formed from cleavage of the m/e 144 rearrangement ion through a two step process.

f. The m/e 65 ion could be formed by the ejection of a neutral sulfur atom from the m/e 97 ion. The ion intensity varies with the 97 ion.

g. The m/e 45 ion intensities are quite high (1.97 to 11.02% of Σi). The m/e 45 and m/e 97 ions, which are fragment peaks typical of the alkylthiophenes, have decreasing intensities as the number of carbon atoms on the thiaalkyl side chain increases.

h. The m/e 39 ion intensity is high for all compounds and parallels the m/e 45 ion behavior.

6. Fragment Ions from other Process

a. The m/e 59 and m/e 53 may be formed from the cleavage of the m/e 112 species. With charge competition being won by the sulfur containing moiety, the m/e 59 ion intensity is greater than that of m/e 53.

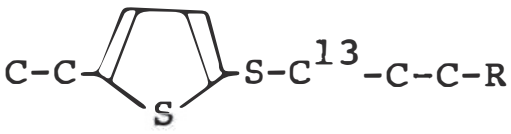
b. The m/e 76 may be formed by extensive fragmentation of the thiophene ring to the sulfur atom from the thiaalkyl chain as well as the carbon and sulfur atoms from the ring.

7. The hydrocarbon fragment ions (Σ 41-43 etc.) are formed ranging from 3.39 percent for $S\text{-}CH_3$ to 51.26 percent for $S\text{-}nC_9$ of the total ion intensity. Thus, the mass spectroscopist may be confused by these compounds and believe he has a mixture. The mechanisms of fragmentation to produce the various alkyl ions is not necessarily simple and straightforward.

8. The low ionization voltage studies support most of the mechanism suggested in this work. They also verify that fragmentations involving high energy requirements occur as suggested at various points. A further benefit is the proof of mechanism for those compounds which are notable exceptions to the correlations developed.

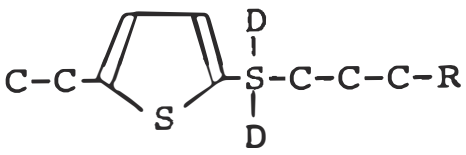
C. Suggestions for Further Studies

Labeled molecules should be made and their mass spectra should be studied to obtain a clearer picture of the rearrangement, correlations with the structure, and the mechanisms. The following labeled molecule should be considered.

1. 

The mass spectrum of this molecule would help to understand the expansion mechanism of the m/e 144 ion and it, no doubt, would disclose the further fragmentation routes of the alkyl groups.

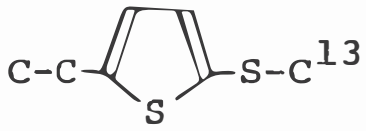
2. Deuteration on alkyl hydrogens



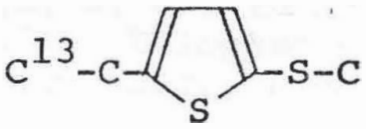
A molecule with two deuterium atoms on a carbon atom α, or β, γ, etc., to the chain sulfur atom

at a time, would show where the rearranged hydrogen atom or atoms come from.

3. As the special case of C-1 for the further 1-(5-ethyl-2-thienyl)-1-thiaethane study, labeled C^{13} should be on β position to the thiophene on either the thiaalkyl or ethyl side chain.

a. 

and

b. 

Pathways of principal fragmentation routes for all fifteen compounds have been proposed and discussed. This work extends knowledge of fragmentation studies on alkyl thiophenes and thienyl thiaalkanes to ethyl derivatives of these classes.

Some isotopically labeled compounds are suggested. Their mass spectra, if obtained and studied, will permit removal of the uncertainties of some of the mechanisms and fragmentation pathways discussed here.

This study illustrates the gross errors and misleading information that can be obtained if an investigator only considers short chain isomers such as methyl, ethyl, and even propyl in proposed research.

REFERENCES

1. Cook, G. L., and N. G. Foster, Proc. Am. Petrol. Inst., 41, III, pp. 199-214 (1961).

2. Rall, H. T. Sulfur Compounds in Crude Oil. Bulletin 659. (Washington), U.S. Dept. of Interior, Bureau of Mines (1972).

3. Thompson, C. J., H. J. Coleman, R. L. Hopkins, and H. T. Rall, "Sulfur Compounds in Petroleum," Authorized Reprint from the Copyrighted Hydrocarbon Analysis, Special Technical Publication No. 389, Published by the American Society for Testing and Materials (1965).

4. Hartough, H. D., editor, The Chemistry of Heterocyclic Compounds. Thiophene and Its Derivatives. Interscience Publishers, Inc., New York, 1952, pp. 132-141.

5. Kinney, I. W., Jr., and G. L. Cook, Anal. Chem. 24, pp. 1391-6.

6. Foster, N. G., D. E. Hirsch, R. F. Kendall, and B. H. Eccleston, U.S. Department of Interior, Bureau of Mines Report of Investigations #6433, 1964.

7. Foster, N. G., D. E. Hirsch, R. F. Kendall, and B. H. Eccleston, U.S. Department of Interior, Bureau of Mines Report of Investigations #6671, 1965.

8. Foster, N. G., U. S. Department of Interior, Bureau of Mines Report of Investigations #6741, 1966.

9. Foster, N. G., and R. W. Higgins, Org. Mass. Spec., 1, 1968, pp. 191-198.

10. Hanus, V., and V. Cermák, Coll. Czech. Commun., 24, pp. 1602-1607 (1959).

11. Rylander, P. N., S. Meyerson, and H. M. Grubb, J. Am. Chem. Soc., 79, pp. 842-846 (1957).

12. Catalog of Mass Spectral Data, Serial No. 1876, American Petroleum Institute Research Project 44, Chemical Thermodynamic Property Center, Texas A and M University, College Station, Texas (Looseleaf data sheets, extant, 1966).

13. Foster, N. G., D. W-K. Shiu, and R. W. Higgins, Biomed. Mass Spec. 1, #5, October 1974, pp. 297-304.

14. Shire, Diana, M.S. Thesis, Texas Woman's University, Denton, Texas, 1968.

15. Liao, Julie Pei-Min, M.S. Thesis, Texas Woman's University, Denton, Texas, 1969.

16. Young, M. C., M.S. Thesis, Texas Woman's University, Denton, Texas, 1962.

17. Lossing, F. P., A. W. Tickner, and W. A. Bryce, J. Chem. Soc., 9, 1951, p. 1254.

18. Warren, J. W., Nature, 165, (1950), p. 810.

19. Hamming, M. C. and N. G. Foster, Interpretation of Mass Spectra of Organic Compounds," Academic Press, New York and London, 1972.

20. Staley, S., and Reichard, D. W., (1968) J. Amer. Chem. Soc. 90, p. 816.

APPENDIX I

POLYISOTOPIC MASS SPECTRAL DATA

1-(5-ETHYL-2-THIENYL)-1-THIAALKANES

General Operating Conditions

See the Experimental

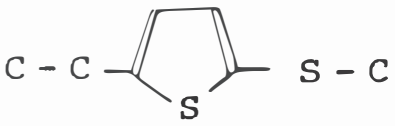
Key to Spectral Peaks

M: Molecular ion
m*: Metastable peak
d: Doubly charged ion

$$\text{Percent Total Ionization (Percent Total Ion Intensity)} = \frac{\text{individual peak}}{\text{sum of peaks}} \times 100$$

$$\text{Percent Relative Abundance (Percent Relative Intensity)} = \frac{\text{individual peak}}{\text{greatest peak}} \times 100$$

$C_7S_2H_{10}$ 1-(5-Ethyl-2-thienyl)-1-thiaethane



Purity: GLC Frac. 99.969%

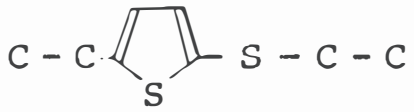
M.W: 158.002239 Date: 11/14/74

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
35.0	0.054	0.43	59.0	3.930	31.51
36.0	0.035	0.28	60.0	0.198	1.58
37.0	0.544	4.36	61.0	0.584	4.68
38.0	1.530	12.26	61.5	0.002	0.02
39.0	6.589	52.83	62.0	0.456	3.65
40.1	0.560	4.49	62.5	0.007	0.06
41.0	2.706	21.70	63.0	0.988	7.92
42.0	0.111	0.89	63.5	0.026	0.21
43.0	0.151	1.21	64.0	0.179	1.43
44.0	0.264	2.11	64.1	0.186	1.49
44.1	0.007	0.06	64.5	0.016	0.13
45.0	9.648	77.36	65.0	2.400	19.25
46.0	0.777	6.23	65.5	0.007	0.06
46.5	0.012	0.09	66.0	0.875	7.02
47.0	0.965	7.74	67.0	1.647	13.21
47.5	0.005	0.04	68.0	0.144	1.15
48.0	0.106	0.85	68.1	0.092	0.74
49.0	0.191	1.53	68.5	0.002	0.02
50.0	1.341	10.75	69.0	4.494	36.04
51.0	2.588	20.75	69.5	0.002	0.02
52.0	0.918	7.36	70.0	1.953	15.66
52.5	0.016	0.13	70.5	0.016	0.13
53.0	1.365	10.94	71.0	2.739	21.96
53.5	0.007	0.06	71.1	0.132	1.05
54.0	0.056	0.45	71.5	0.377	3.02
54.1	0.092	0.74	72.0	0.334	2.68
54.5	0.019	0.15	72.5	0.035	0.28
55.1	0.261	2.09	73.0	0.353	2.82
55.5	0.005	0.04	74.0	0.151	1.21
56.0	0.062	0.49	75.0	0.073	0.58
56.1	0.040	0.32	76.0	0.301	2.42
56.5	0.009	0.08	76.1	0.954	0.43
57.0	1.318	10.57	77.0	0.165	1.32
57.1	0.151	1.21	77.1	1.294	10.38
57.5	0.016	0.13	77.5	0.007	0.06
58.0	1.624	13.02	78.0	1.177	9.43
58.5	0.007	0.06			

1-(5-Ethyl-2-thienyl)-1-thiaethane

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
78.5	0.033	0.26	116.0	0.059	0.47
79.0	0.325	2.60	117.0	0.031	0.25
79.5	0.024	0.19	118.0	0.007	0.06
80.0	0.045	0.36	119.0	0.007	0.06
80.5	0.005	0.04	121.0	0.007	0.06
81.0	0.334	2.68	122.0	0.007	0.06
82.0	0.598	4.79	123.0	0.031	0.25
83.0	0.344	2.75	124.0	0.049	0.40
84.0	1.624	13.02	125.0	0.035	0.28
85.0	0.753	6.04	126.0	0.010	0.08
86.0	0.101	0.81	127.0	0.212	1.70
87.0	0.035	0.28	128.0	1.530	12.26
88.0	0.195	1.57	129.0	0.139	1.11
89.0	0.172	1.38	130.0	0.158	1.26
90.0	0.045	0.36	131.0	0.019	0.15
91.0	0.374	3.00	132.0	0.002	0.09
91.1	0.089	0.72	139.0	0.002	0.09
92.0	0.045	0.36	140.0	0.026	0.21
92.5	0.026	0.21	141.0	0.165	1.32
93.0	0.264	2.11	142.0	0.155	1.25
94.0	0.054	0.43	143.0	12.472	100.00
95.0	1.059	8.49	144.0	0.988	7.92
96.0	0.322	2.58	145.0	1.106	8.87
97.0	1.482	11.89	146.0	0.073	0.59
98.0	0.195	1.57	147.0	0.028	0.23
99.0	2.833	22.72	148.0	0.005	0.04
100.0	0.169	1.36	153.0	0.002	0.02
101.0	0.148	1.18	154.0	0.005	0.04
102.0	0.031	0.25	155.0	0.005	0.04
103.0	0.073	0.58	156.0	0.033	0.26
104.0	0.031	0.25	157.0	0.245	1.96
105.0	0.026	0.21	158.0M	6.118	49.06
106.0	0.026	0.21	159.0	0.569	4.57
107.0	0.032	0.26	160.0	0.527	4.23
108.0	0.256	2.06	161.0	0.049	0.40
109.0	0.534	4.28	162.0	0.016	0.13
110.0	1.200	9.62			
111.0	1.012	8.11			
112.0	0.125	1.00			
113.0	0.136	1.09			
114.0	0.296	2.38			
115.0	0.207	1.66			

$C_8S_2H_{12}$



1-(5-Ethyl-2-thienyl)-1-thiapropane

Purity: GLC Frac. 99.825%

M.W: 172.03804

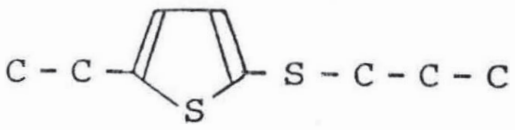
Date: 11/21/74

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
37.0	0.227	2.47	65.0	2.582	28.08
38.0	0.019	0.21	66.0	0.025	0.27
38.1	0.794	8.63	66.1	0.850	9.25
39.0	5.227	56.85	67.0	1.581	17.19
40.1	0.542	5.89	68.0	0.063	0.68
41.1	2.834	30.82	68.1	0.107	1.16
42.0	0.126	1.37	69.0	0.013	39.73
43.1	0.031	0.34	70.0	1.436	15.62
44.0	0.258	2.81	71.1	3.023	32.88
45.0	8.439	91.78	71.5	0.010	0.11
46.0	0.365	3.97	72.0	0.239	2.60
46.5	0.006	0.07	73.0	0.409	4.45
47.0	0.592	6.44	74.0	0.082	0.89
48.0	0.004	0.48	75.0	0.063	0.68
49.0	0.069	0.75	76.0	0.441	4.79
50.0	0.731	7.95	77.0	0.365	3.97
51.0	1.688	18.36	77.1	0.882	9.59
52.0	0.642	6.99	78.0	0.044	0.48
53.0	2.141	23.29	78.1	0.422	4.59
54.0	0.126	1.37	78.5	0.010	0.11
54.5	0.010	0.11	79.0	0.013	0.41
55.1	0.403	4.38	79.1	0.233	2.53
56.0	0.025	0.27	80.0	0.019	0.21
56.1	0.031	0.34	80.1	0.031	0.34
57.0	0.674	7.33	81.0	0.214	2.33
57.1	0.038	0.41	81.1	0.038	0.41
57.5	0.013	0.14	82.0	0.472	5.14
58.0	1.329	14.45	83.0	0.346	3.77
59.0	5.857	63.70	84.0	1.234	13.42
60.0	0.277	3.01	85.1	1.260	13.70
61.0	0.422	4.59	86.0	0.139	1.51
62.0	0.277	3.01	87.0	0.063	0.68
63.0	0.649	7.05	88.0	0.195	2.12
64.0	0.107	1.16	89.0	0.132	1.44
64.1	0.145	1.58	90.0	0.094	1.03

1-(5-Ethyl-2-thienyl)-1-thiapropane

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
91.0	0.025	0.27	130.0	0.403	4.38
91.1	0.069	0.75	131.0	0.491	5.34
92.0	0.019	0.21	132.0	0.031	0.34
92.1	0.019	0.21	133.0	0.013	0.14
93.0	0.170	1.85	134.0	0.006	0.07
94.0	0.038	0.41	135.0	0.006	0.07
95.0	0.568	6.16	136.0	0.006	0.07
96.0	0.258	2.81	137.0	0.013	0.14
97.0	1.329	14.45	138.0	0.019	0.21
98.0	0.157	1.71	139.0	0.057	0.62
99.0	4.912	53.42	140.0	0.031	0.34
100.0	0.283	3.08	141.0	0.170	1.85
101.0	0.239	2.60	142.0	0.120	1.30
102.0	0.038	0.41	143.0	2.645	28.77
103.0	0.076	0.82	144.0	0.560	6.10
104.0	0.010	0.11	145.0	0.249	2.71
105.0	0.031	0.34	146.0	0.050	0.55
105.1	0.019	0.21	147.0	0.013	0.14
106.0	0.019	0.21	148.0	0.006	0.07
107.0	0.025	0.27	155.0	0.038	0.41
108.0	0.220	2.40	156.0	0.019	0.21
109.0	0.548	5.96	157.0	9.195	100.00
110.0	1.385	15.07	158.0	0.756	8.22
111.0	1.178	12.81	159.0	0.756	8.22
112.0	0.202	2.19	160.0	0.063	0.68
113.0	0.183	1.99	161.0	0.025	0.27
114.0	0.397	4.32	170.0	0.044	0.48
115.0	0.239	2.60	171.0	0.164	1.78
116.0	0.189	2.05	172.0M	7.179	78.08
117.0	0.038	0.41	173.0	0.674	7.33
118.0	0.019	0.21	174.0	0.598	6.51
119.0	0.006	0.07	175.0	0.063	0.68
121.0	0.019	0.21	178.0	0.019	0.21
122.0	0.019	0.21			
123.0	0.069	0.75			
124.0	0.076	0.82			
125.0	0.038	0.41			
126.0	0.013	0.14			
127.0	0.183	1.99			
128.0	0.195	2.12			
129.0	6.046	65.75			

$C_9S_2H_{14}$



1-(5-Ethyl-2-thienyl)-1-thiabutane

Purity: GLC Frac. 98.848%

M.W: 186.05369

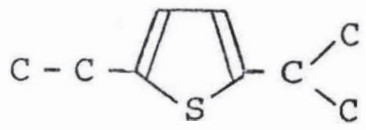
Date: 11/22/74

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
37.0	0.398	3.86	64.0	0.061	0.59
37.5	0.061	0.59	64.1	0.103	1.00
38.0	0.019	0.18	65.1	0.183	17.73
38.1	0.886	8.60	66.0	0.019	0.18
38.5	0.019	0.18	66.1	0.632	6.14
39.0	6.290	61.09	67.0	0.960	9.32
39.3m*	0.014	0.136	68.0	0.037	0.36
39.5	0.019	0.18	68.1	0.084	0.82
40.1	0.595	5.77	69.1	2.248	21.82
41.1	6.361	61.81	70.0	0.918	8.91
42.0	0.379	3.68	70.5	0.005	0.045
43.1	4.730	45.91	71.0	2.154	20.91
44.0	0.159	1.54	71.5	0.005	0.045
44.1	0.155	1.50	72.0	0.183	1.77
45.0	6.369	61.81	73.0	0.454	4.41
46.0	0.318	3.09	74.0	0.351	3.41
47.0	0.539	5.23	75.0	0.161	1.56
48.0	0.066	0.64	76.0	0.234	2.27
49.0	0.253	2.45	76.1	0.253	2.45
50.0	1.873	18.18	76.2m*	0.028	0.28
51.0	2.810	27.27	77.0	0.197	1.91
52.0	2.061	20.00	77.1	1.686	16.36
53.0	1.639	15.91	77.5	0.005	0.045
54.0	0.098	0.95	78.0	0.084	0.82
55.1	0.304	2.95	78.1	6.837	66.36
56.0	0.014	0.136	78.5	0.005	0.045
56.1	0.028	0.28	79.0	0.033	0.32
57.0	0.361	3.50	79.1	0.543	5.27
57.1	0.066	0.64	80.0	0.037	0.36
58.0	0.806	7.82	81.0	0.124	1.20
59.0	2.847	30.91	81.1	0.028	0.27
60.0	0.150	1.45	82.0	0.295	2.86
61.0	0.253	2.45	83.1	0.234	2.27
62.0	0.178	1.73	84.0	0.834	8.09
63.0	0.576	5.59	85.1	0.988	9.59

1-(5-Ethyl-2-thienyl)-1-thiabutane

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
86.0	0.098	0.95	126.0	0.014	0.136
87.0	0.056	0.54	127.0	0.117	1.14
88.0	0.107	1.05	128.0	1.358	1.32
89.0	0.075	0.72	129.0	10.303	100.00
90.0	0.066	0.64	130.0	0.656	6.36
91.0	0.019	0.18	131.0	0.815	7.91
91.1	0.047	0.91	132.0	0.056	0.54
92.0	0.014	0.136	133.0	0.028	0.27
92.1	0.028	0.27	134.0	0.005	0.045
93.0	0.089	0.86	135.0	0.005	0.045
94.0	0.023	0.23	136.0	0.005	0.045
95.0	0.379	3.68	137.0	0.009	0.09
96.0	0.220	2.13	138.0	0.005	0.045
96.5	0.009	0.09	139.0	0.005	0.045
97.0	1.105	10.73	140.0	0.009	0.09
98.0	0.131	1.27	141.0	0.089	0.86
99.0	2.107	20.45	142.0	0.126	1.23
100.0	0.126	1.23	143.0	0.998	9.68
101.0	0.122	1.18	144.0	4.168	40.45
102.0	0.023	0.23	145.0	0.384	3.73
103.0	0.056	0.54	146.0	0.342	3.32
104.0	0.005	0.045	147.0	0.028	0.27
105.0	0.009	0.09	148.0	0.009	0.09
106.0	0.009	0.09	153.0	0.009	0.09
107.0	0.014	0.136	155.0	0.023	0.23
108.0	0.126	1.23	156.0	0.005	0.045
109.0	0.361	3.50	157.0	0.023	0.23
110.0	0.815	7.91	158.0	0.028	0.27
111.0	1.016	9.85	159.0	0.023	0.23
112.0	0.351	3.41	169.0	0.005	0.045
113.0	0.286	2.77	171.0	2.154	20.91
114.0	0.253	2.45	173.0	0.206	2.00
115.0	0.155	1.50	173.0	0.178	1.73
116.0	0.272	2.64	174.0	0.019	0.18
117.0	0.042	0.41	175.0	0.005	0.045
117.8m*	0.005	0.045	184.0	0.023	0.23
118.0	0.028	0.27	185.0	0.033	0.32
119.0	0.005	0.045	186.0M	4.420	42.91
121.0	0.014	0.136	187.0	0.464	4.50
122.0	0.009	0.09	188.0	0.370	3.59
123.0	0.061	0.59	189.0	0.042	0.41
124.0	0.098	0.95	190.0	0.014	0.136
125.0	0.066	0.64	191.0	0.005	0.045

$C_9S_2H_{14}$



1-(5-Ethyl-2-thienyl)-2-methyl -1-thiapropane

Purity: GLC Frac. 98.59%

M.W: 186.05369

Date: 10/10/74

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
37.0	0.201	1.509	63.0	0.314	2.358
37.3m	0.008	0.057	64.0	0.055	0.415
38.0	0.030	0.226	64.1	0.073	0.547
38.1	0.672	5.057	65.0	1.556	11.698
39.0	6.273	47.170	66.0	0.005	0.075
39.3m*	0.015	0.113	66.1	0.547	4.113
40.1	0.903	6.792	67.0	0.828	6.226
41.1	10.037	75.472	68.0	0.003	0.028
42.0	0.023	15.283	68.1	0.060	0.453
43.1	13.298	100.000	69.1	1.807	13.585
44.0	0.148	1.113	70.0	1.425	6.415
44.1	0.424	3.189	70.1	0.878	6.604
45.0	5.294	39.811	71.0	1.756	11.509
46.0	0.198	1.490	71.1	2.083	15.660
47.0	0.447	3.358	71.5	0.005	0.038
48.0	0.050	0.377	72.0	0.143	1.075
49.0	0.078	0.585	72.1	0.108	0.811
50.0	0.434	3.264	73.0	0.354	2.660
51.0	1.029	7.736	74.0	0.060	0.453
52.0	0.389	2.925	75.0	0.045	0.340
53.0	1.455	10.943	76.0	0.304	2.283
54.0	0.120	0.906	76.1	0.028	0.208
54.5	0.004	0.030	77.0	0.163	1.226
55.1	0.928	6.981	77.1	0.467	3.509
56.0	0.018	0.132	78.0	0.040	0.302
56.1	0.153	1.151	78.1	0.374	2.811
56.5	0.003	0.019	78.5	0.008	0.057
57.0	0.329	2.472	79.0	0.018	0.132
57.1	2.660	20.000	79.1	0.093	0.698
57.5	0.003	0.019	80.0	0.008	0.057
58.0	0.803	6.038	80.1	0.023	0.170
58.1	0.115	0.868	81.0	0.090	0.679
59.0	0.271	20.378	82.0	0.216	1.622
60.0	0.143	1.076	83.0	0.171	1.283
61.0	0.208	1.566	84.0	0.677	5.094
62.0	0.125	0.943	85.0	0.853	6.415

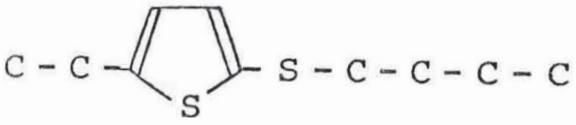
1-(5-Ethyl-2-thienyl)-2-methyl-1-thiapropane

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
85.1	0.080	0.604	119.0	0.010	0.075
85.5	0.005	0.038	120.0	0.003	0.019
86.0	0.075	0.566	121.0	0.005	0.057
87.0	0.038	0.283	122.0	0.005	0.057
88.0	0.095	0.717	123.0	0.020	0.151
89.0	0.060	0.453	124.0	0.010	0.075
90.0	0.053	0.396	125.0	0.013	0.094
91.0	0.013	0.094	126.0	0.005	0.038
91.1	0.030	0.226	127.0	0.078	0.585
92.0	0.010	0.075	128.0	0.105	0.792
92.1	0.008	0.057	129.0	9.284	69.810
93.0	0.063	0.472	130.0	0.607	4.566
94.0	0.015	0.113	131.0	8.280	62.264
95.0	0.246	1.849	132.0	0.050	0.377
96.0	0.146	1.094	133.0	0.003	0.028
96.5	0.005	0.038	134.0	0.003	0.019
97.0	0.630	4.736	135.0	0.003	0.019
98.0	0.073	0.547	136.0	0.003	0.019
99.0	1.179	8.868	137.0	0.023	0.170
100.0	0.354	2.660	138.0	0.018	0.132
101.0	0.088	0.660	139.0	0.008	0.057
101.1	0.033	0.245	140.0	0.008	0.057
102.0	0.018	0.132	141.0	0.048	0.358
103.0	0.038	0.283	142.0	0.065	0.491
104.0	0.005	0.038	143.0	0.419	3.150
105.0	0.008	0.057	144.0	4.567	34.340
105.1	0.005	0.038	145.0	0.376	2.830
106.0	0.005	0.038	146.0	0.369	2.774
107.0	0.008	0.057	147.0	0.030	0.226
108.0	0.078	0.585	148.0	0.013	0.094
109.0	0.236	1.774	149.0	0.004	0.030
110.0	0.532	4.000	151.0	0.004	0.030
111.0	0.853	6.415	152.0	0.005	0.057
112.0	0.110	0.830	153.0	0.005	0.057
113.0	0.048	0.358	154.0	0.003	0.019
114.0	0.166	1.245	155.0	0.010	0.075
115.0	0.100	0.755	156.0	0.003	0.019
116.0	0.228	1.717	157.0	0.005	0.057
117.0	0.038	0.283	158.0	0.003	0.019
117.8m*	0.008	0.057	160.0	0.005	0.038
118.0	0.030	0.226	170.0	0.004	0.030

1-(5-Ethyl-2-thienyl)-2-methyl-1-thiapropane

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
171.0	0.065	0.491	187.0	0.248	1.868
172.0	0.008	0.057	188.0	0.196	1.472
173.0	0.008	0.057	189.0	0.023	0.170
184.0	0.010	0.075	190.0	0.008	0.057
185.0	0.008	0.057	191.0	0.005	0.038
186.0M	2.283	17.170			

$C_{10}S_2H_{16}$



1-(5-Ethyl-2-thienyl)-1-thiapentane

Purity: GLC Frac. 99.276%

M.W: 200.06934

Date: 10/17/74

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
37.0	0.143	1.21	65.0	2.060	17.38
37.3m*	0.004	0.35	66.0	0.715	6.03
38.0	0.021	0.18	67.0	1.089	9.18
38.1	0.534	4.50	68.0	0.029	0.25
39.0	5.843	49.29	68.1	0.084	0.71
40.1	0.593	5.00	69.1	2.186	18.44
41.1	9.669	81.56	70.0	0.937	7.91
42.0	0.425	3.58	71.0	2.270	19.15
43.0	0.345	2.91	72.0	0.181	1.52
44.0	0.151	1.27	73.0	0.391	3.30
44.1	0.021	0.18	74.0	0.059	0.50
45.0	6.852	57.80	75.0	0.046	0.39
46.0	0.345	2.91	76.0	0.307	2.59
47.0	0.643	5.43	76.1	0.029	0.25
48.0	0.050	0.43	77.0	0.193	1.63
49.0	0.076	0.64	77.1	0.799	6.74
50.0	0.483	4.08	78.0	0.038	0.32
51.0	0.008	11.35	78.1	0.568	4.79
52.0	0.492	4.15	79.0	0.025	0.21
53.0	1.850	15.60	79.1	0.206	1.74
54.0	0.168	1.42	80.0	0.038	0.32
55.1	1.131	9.54	81.0	0.122	1.03
56.0	0.017	0.14	81.1	0.038	0.32
56.1	0.185	1.56	82.0	0.294	2.48
57.0	0.378	3.19	83.0	0.261	2.20
57.1	4.708	39.72	84.0	0.933	7.87
58.0	0.832	7.02	85.0	1.050	8.86
58.1	0.202	1.70	86.0	0.109	0.92
59.0	3.783	31.91	87.0	0.008	0.78
60.0	0.244	2.06	88.0	0.118	0.99
61.0	0.265	2.23	88.1	0.080	0.67
62.0	0.143	1.21	89.0	0.080	0.67
63.0	0.391	3.30	89.1	0.038	0.32
64.0	0.059	0.50	90.0	0.059	0.50
64.1	0.092	0.78	90.1	0.021	0.18

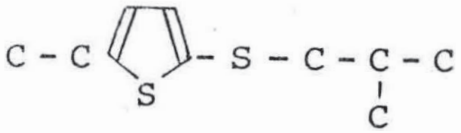
1-(5-Ethyl-2-thienyl)-1-thiapentane

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
91.0	0.017	0.14	128.0	0.168	1.42
91.1	0.114	0.96	129.0	11.855	100.00
92.0	0.008	0.07	130.0	0.765	6.45
92.1	0.034	0.28	131.0	0.942	7.94
93.0	0.084	0.71	132.0	0.063	0.53
94.0	0.025	0.21	133.0	0.029	0.25
95.0	0.391	3.30	134.0	0.008	0.07
96.0	0.210	1.77	135.0	0.013	0.11
97.0	1.513	12.77	136.0	0.008	0.07
98.0	0.151	1.28	137.0	0.017	0.14
99.0	2.312	19.50	138.0	0.013	0.11
100.0	0.097	0.82	139.0	0.105	0.89
101.0	0.097	0.82	140.0	0.029	0.25
102.0	0.025	0.21	141.0	0.101	0.85
103.0	0.059	0.50	142.0	0.177	1.49
104.0	0.008	0.07	143.0	1.068	9.00
104.1	0.008	0.07	144.0	7.987	67.38
105.0	0.008	0.07	145.0	0.681	5.74
105.1	0.008	0.07	146.0	0.647	5.46
106.0	0.008	0.07	147.0	0.059	0.50
107.0	0.017	0.14	148.0	0.021	0.18
108.0	0.135	1.13	151.0	0.008	0.07
109.0	0.404	3.40	153.0	0.017	0.14
110.0	0.925	7.80	155.0	0.042	0.35
111.0	1.156	9.75	156.0	0.008	0.07
112.0	0.731	6.17	157.0	0.290	2.45
113.0	0.362	3.05	158.0	0.034	0.28
114.0	0.282	2.38	159.0	0.021	0.18
115.0	0.177	1.49	167.0	0.008	0.07
116.0	0.341	2.89	169.0	0.008	0.07
117.0	0.055	0.46	171.0	0.029	0.25
117.8m*	0.025	0.21	172.0	0.021	0.18
118.0	0.042	0.35	173.0	0.008	0.07
119.0	0.008	0.07	184.0	tr	tr
121.0	0.017	0.14	185.0	1.133	9.57
122.0	0.017	0.14	186.0	0.164	1.38
123.0	0.076	0.64	187.0	0.122	1.03
124.0	0.109	0.92	188.0	0.017	0.14
125.0	0.097	0.82	189.0	tr	tr
126.0	0.017	0.14	198.0	0.025	0.21
127.0	0.135	1.13	199.0	0.029	0.25

1-(5-Ethyl-2-thienyl)-1-thiapentane

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
200.0M	4.036	34.04	203.0	0.042	0.35
201.0	0.475	4.01	204.0	0.017	0.14
204.0	0.353	2.98	228.0	tr	tr

$C_{10}S_2H_{16}$



1-(5-Ethyl-2-thienyl)-3-methyl-1-thiabutane

Purity: GLC Frac. 99.768%

M.W: 200.06934

Date: 11/21/74

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
37.0	0.126	1.09	67.0	0.882	7.61
38.0	0.489	4.22	68.0	0.024	0.20
39.0	6.319	54.49	68.1	0.067	0.58
40.1	0.639	5.51	69.0	1.891	16.30
41.1	11.597	100.00	70.0	0.832	7.17
42.0	0.588	5.07	70.1	0.017	0.14
43.1	0.595	5.13	71.0	1.933	16.67
44.0	0.113	0.98	71.1	0.038	0.33
44.1	0.025	0.22	71.5	0.004	0.04
45.0	6.655	57.39	72.0	0.164	1.41
46.0	0.304	2.62	72.1	0.004	0.04
47.0	0.534	4.61	73.0	0.357	3.08
48.0	0.050	0.43	73.1	tr	tr
49.0	0.059	0.51	74.0	0.050	0.43
50.0	0.391	3.37	75.0	0.042	0.36
51.0	1.076	9.28	76.0	0.248	2.14
52.0	0.437	3.77	76.1	0.025	0.22
53.0	1.723	14.86	77.0	0.160	1.38
54.0	0.130	1.12	77.1	0.634	5.47
55.1	0.874	7.54	78.0	0.025	0.22
56.0	0.008	0.07	78.1	0.479	4.13
56.1	0.181	1.56	79.0	0.021	0.18
57.0	0.328	2.83	79.1	0.202	1.74
57.1	10.420	89.86	80.1	0.029	0.25
58.0	0.697	6.01	81.0	0.097	0.83
58.1	0.416	3.59	81.1	0.029	0.25
59.0	2.983	25.72	82.0	0.252	2.17
60.0	0.092	0.80	83.0	0.214	1.85
61.0	0.206	1.78	84.0	0.773	6.67
62.0	0.105	0.91	85.0	0.958	8.26
63.0	0.378	3.26	86.0	0.008	0.80
64.0	0.050	0.43	87.0	0.067	0.58
64.1	0.084	0.72	88.0	0.008	0.80
65.1	1.807	15.58	88.1	0.021	0.18
66.1	0.615	5.30	89.0	0.067	0.58

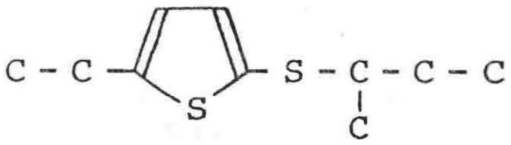
1-(5-Ethyl-2-thienyl)-3-methyl-1-thiabutane

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
89.1	0.017	0.14	127.0	0.109	0.94
90.0	0.050	0.43	128.0	0.143	1.23
90.1	0.013	0.11	129.0	10.504	90.58
91.0	0.025	0.22	130.0	0.655	5.65
91.1	0.130	1.12	131.0	0.815	7.03
92.0	0.038	0.33	132.0	0.059	0.51
93.0	0.071	0.62	133.0	0.029	0.25
94.0	0.017	0.14	134.0	0.008	0.07
95.0	0.348	3.00	135.0	0.008	0.07
96.0	0.193	1.67	136.0	0.007	0.06
97.0	1.126	9.71	137.0	0.008	0.07
98.0	0.130	1.12	139.0	0.008	0.07
99.0	1.647	14.20	140.0	0.010	0.09
100.0	0.097	0.83	141.0	0.080	0.69
101.0	0.109	0.94	142.0	0.160	1.38
102.0	0.025	0.22	143.0	0.828	7.14
103.0	0.050	0.43	144.0	9.748	84.06
104.0	0.010	0.09	145.0	0.765	6.59
105.0	0.010	0.09	146.0	0.761	6.56
106.0	0.010	0.09	147.0	0.063	0.54
107.0	0.013	0.11	148.0	0.025	0.22
108.0	0.105	0.91	149.0	0.007	0.06
109.0	0.172	2.93	151.0	0.004	0.04
110.0	0.735	6.34	153.0	0.007	0.06
111.0	0.933	8.04	155.0	0.013	0.11
112.0	0.475	4.09	156.0	0.007	0.06
113.0	0.420	3.62	157.0	0.298	2.57
114.0	0.227	1.96	158.0	0.378	3.26
115.0	0.139	1.20	159.0	0.029	0.25
116.0	0.261	2.25	160.0	0.004	0.04
117.0	0.042	0.36	167.0	0.004	0.04
117.8m*	0.017	0.14	169.0	0.013	0.11
118.0	0.038	0.33	170.0	0.004	0.04
119.0	0.007	0.06	171.0	0.008	0.07
120.0	0.004	0.04	172.0	0.004	0.04
121.0	0.013	0.11	185.0	0.185	1.59
122.0	0.013	0.11	186.0	0.025	0.22
123.0	0.084	0.72	187.0	0.021	0.18
124.0	0.139	1.20	198.0	0.021	0.18
125.0	0.084	0.72	199.0	0.017	0.14
126.0	0.013	0.11	200.0M	3.613	31.16

1-(5-Ethyl-2-thienyl)-3-methyl-1-thiabutane

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
201.0	0.412	3.55	204.0	0.013	0.11
202.0	0.311	2.68	205.0	0.004	0.04
203.0	0.042	0.36			

$C_{10}S_2H_{16}$



1-(5-Ethyl-2-thienyl)-2-methyl-1-thiabutane

Purity: GLC Frac. 99.99%

M.W: 200.06934

Date: 11/18/74

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
37.0	0.127	0.95	65.0	1.939	14.36
37.3m*	0.007	0.05	66.0	0.010	0.08
38.0	0.021	0.15	66.1	0.646	4.81
38.1	0.489	3.64	67.0	1.068	7.95
39.0	0.010	0.08	68.0	0.024	0.18
39.1	6.241	46.46	68.1	0.069	0.51
40.1	0.641	4.77	69.1	2.094	15.59
41.1	11.022	82.05	70.0	0.901	6.71
42.0	0.489	3.64	71.1	2.239	16.67
43.1	0.086	0.64	71.5	0.007	0.05
44.0	0.107	0.80	72.0	0.179	1.33
45.0	6.007	42.66	73.0	0.358	2.66
46.0	0.203	1.51	74.0	0.052	0.38
47.0	0.463	3.45	75.0	0.038	0.28
48.0	0.038	0.28	76.0	0.245	1.82
49.0	0.062	0.46	76.1	0.024	0.18
50.0	0.434	3.23	77.0	0.193	1.44
51.0	1.240	9.23	77.1	0.572	4.26
52.0	0.448	3.33	78.0	0.521	0.29
53.0	1.929	14.36	78.1	0.448	3.33
54.0	0.148	1.10	78.5	0.006	0.04
54.5	0.007	0.05	79.0	0.021	0.15
55.1	1.240	9.23	79.1	0.121	0.90
56.0	0.010	0.08	80.0	0.031	0.23
56.1	0.272	2.03	81.0	0.096	0.72
57.0	0.324	2.41	82.0	0.344	0.05
57.1	5.546	41.28	83.0	0.224	1.67
58.0	0.778	5.79	84.0	0.871	6.49
58.1	0.227	1.69	85.0	0.896	6.67
59.0	3.982	29.64	85.5	0.008	0.06
60.0	0.189	1.41	86.0	0.093	0.69
61.0	0.282	2.10	87.0	0.067	0.51
62.0	0.114	0.85	88.0	0.110	0.82
63.0	0.344	2.56	89.0	0.067	0.51
64.0	0.062	0.46	90.0	0.062	0.46
64.1	0.086	0.64	91.0	0.017	0.13

1-(5-Ethyl-2-thienyl)-2-methyl-1-thiabutane

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
91.1	0.052	0.39	129.0	13.433	100.00
92.0	0.014	0.10	130.0	0.840	6.26
92.1	0.014	0.10	131.0	1.710	8.72
93.0	0.067	0.51	132.0	0.069	0.51
94.0	0.017	0.13	133.0	0.034	0.26
95.0	0.338	2.51	134.0	tr	tr
96.0	0.179	1.33	135.0	0.007	0.05
97.0	0.909	6.77	136.0	tr	tr
98.0	0.110	0.82	137.0	0.021	0.15
99.0	1.665	12.56	138.0	0.034	0.26
100.0	0.107	0.79	139.0	0.021	0.15
101.0	0.118	0.88	140.0	0.017	0.13
102.0	0.024	0.18	141.0	0.083	0.62
103.0	0.052	0.39	142.0	0.152	1.13
104.0	0.007	0.05	143.0	0.751	5.59
104.1	0.007	0.05	144.0	11.573	86.15
105.0	0.010	0.08	145.0	1.033	7.70
105.1	0.010	0.08	146.0	1.033	7.70
106.0	0.007	0.05	147.0	0.069	0.51
107.0	0.014	0.10	148.0	0.024	0.18
108.0	0.110	0.82	149.0	0.006	0.04
109.0	0.348	2.59	150.0	0.003	0.03
110.0	0.803	5.98	151.0	0.007	0.05
111.0	1.119	8.92	153.0	0.003	0.03
112.0	0.175	1.30	155.0	0.021	0.15
113.0	0.069	0.51	156.0	0.007	0.05
114.0	0.248	1.85	157.0	0.014	0.10
115.0	0.145	1.08	158.0	0.006	0.04
116.0	0.307	2.28	159.0	0.003	0.03
117.0	0.551	0.41	160.0	0.003	0.03
117.8m*	0.017	0.13	161.0	0.003	0.03
118.0	0.044	0.33	166.0	0.003	0.03
119.0	0.014	0.10	167.0	0.006	0.04
121.0	0.007	0.05	169.0	0.010	0.08
122.0	0.007	0.05	170.0	0.003	0.03
123.0	0.048	0.36	171.0	0.067	0.51
124.0	0.014	0.10	172.0	0.014	0.10
125.0	0.021	0.15	173.0	0.014	0.10
126.0	0.007	0.05	174.0	0.003	0.03
127.0	0.117	0.87	185.0	0.021	0.15
128.0	0.165	1.23	186.0	0.003	0.03

1-(5-Ethyl-2-thienyl)-2-methyl-1-thiabutane

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
187.0	0.003	0.03	201.0	0.396	2.95
198.0	0.021	0.15	202.0	0.290	2.15
199.0	0.007	0.05	203.0	0.038	0.28
200.0M	3.410	25.38	204.0	0.007	0.05

$C_{11}S_2H_{18}$

1-(5-Ethyl-2-thienyl)-1-thiahexane

Purity: GLC Frac. 100.00%

M.W: 214.08499

Date: 10/14/74

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
37.0	0.076	0.53	68.0	0.018	0.06
38.0	0.597	2.31	68.1	0.125	0.88
39.0	4.409	30.94	69.0	1.603	11.25
39.3m*	tr	tr	69.1	0.356	2.50
40.1	0.548	3.84	70.0	0.739	5.19
41.1	1.839	55.00	70.1	0.089	0.63
42.0	0.757	5.31	71.0	1.871	13.13
43.1	14.253	100.00	71.1	0.833	5.84
44.0	0.049	0.34	71.5	0.004	0.03
44.1	0.445	3.13	72.0	0.147	1.03
45.0	5.256	36.88	72.1	0.053	0.38
46.0	0.249	1.75	73.0	0.365	2.52
47.0	0.477	3.34	74.0	0.098	0.69
48.0	0.036	0.25	75.0	0.036	0.25
49.0	0.045	0.31	76.0	0.145	1.47
50.0	0.303	2.13	76.1	0.027	0.19
51.0	0.882	6.19	77.0	0.111	0.78
52.0	0.374	2.63	77.1	0.632	4.44
53.0	1.559	10.94	78.0	0.031	0.22
54.0	0.125	0.88	78.1	0.526	3.69
55.0	1.960	13.75	79.0	0.027	0.19
56.0	0.009	0.06	79.1	0.205	1.44
56.1	0.116	0.81	80.0	0.031	0.22
57.0	0.241	1.69	81.0	0.085	0.59
57.1	0.045	0.31	81.1	0.036	0.25
58.0	0.610	4.28	82.0	0.232	1.63
59.0	3.341	23.44	83.1	0.205	1.44
60.0	0.187	1.31	84.0	0.806	5.66
61.0	0.241	1.69	84.5	0.004	0.03
62.0	0.098	0.69	85.0	0.922	6.49
63.0	0.298	2.09	86.0	0.098	0.69
64.0	0.045	0.31	87.0	0.223	1.56
64.1	0.076	0.53	88.0	0.089	0.63
65.0	1.737	12.19	89.0	0.067	0.47
66.0	0.615	4.31	90.0	0.049	0.34
67.0	1.051	7.38	91.0	0.120	0.84

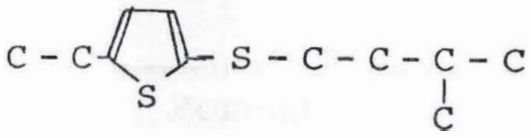
1-(5-Ethyl-2-thienyl)-1-thiahexane

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
92.0	0.009	0.06	127.0	0.125	0.88
92.1	0.036	0.25	128.0	0.160	1.13
93.0	0.067	0.47	129.0	10.560	71.25
94.0	0.018	0.13	130.0	0.659	2.94
95.0	0.334	2.34	131.0	0.828	5.81
96.0	0.187	1.31	132.0	0.053	0.38
97.0	1.425	10.00	133.0	0.027	0.19
98.0	0.143	1.00	134.0	0.009	0.06
99.0	2.138	15.00	135.0	0.013	0.09
100.0	0.134	0.94	136.0	0.009	0.06
101.0	0.143	1.00	137.0	0.013	0.09
102.0	0.085	0.59	138.0	0.013	0.09
103.0	0.058	0.41	139.0	0.080	0.56
104.0	0.018	0.13	140.0	0.018	0.13
104.1	0.018	0.13	141.0	0.107	0.75
105.0	0.018	0.13	142.0	0.200	1.41
105.1	0.018	0.13	143.0	1.011	7.09
106.0	0.013	0.09	144.0	9.398	65.94
106.50	0.004	0.03	145.0	0.793	5.56
107.0	0.018	0.13	146.0	0.779	5.47
107.5	0.004	0.03	147.0	0.067	0.47
108.0	0.116	0.81	148.0	0.027	0.19
109.0	0.365	2.56	149.0	0.009	0.06
110.0	0.846	5.94	151.0	0.013	0.09
111.0	1.007	7.06	152.0	0.009	0.06
112.0	0.757	5.31	153.0	0.058	0.41
113.0	0.387	2.72	154.0	0.013	0.09
114.0	0.245	1.72	155.0	0.053	0.38
115.0	0.160	1.13	156.0	0.013	0.09
116.0	2.665	1.88	157.0	0.321	2.25
117.0	0.062	0.44	158.0	0.036	0.25
117.8m*	0.013	0.09	159.0	0.031	0.22
118.0	0.036	0.25	160.0	0.007	0.05
119.0	0.009	0.06	167.0	0.009	0.06
120.0	0.004	0.03	168.0	0.004	0.03
121.0	0.018	0.13	169.0	0.009	0.06
122.0	0.018	0.13	170.0	0.009	0.06
123.0	0.089	0.63	171.0	0.013	0.09
124.0	0.116	0.81	172.0	0.004	0.03
125.0	0.116	0.81	181.0	0.009	0.06
126.0	0.027	0.19	185.0	0.025	0.18

1-(5-Ethyl-2-thienyl)-1-thiahexane

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
186.0	0.009	0.06	212.0	0.022	0.16
187.0	0.007	0.05	213.0	0.018	0.13
199.0	0.793	5.56	214.0M	3.608	25.31
200.0	0.107	0.75	215.0	0.463	3.25
201.0	0.080	0.56	216.0	0.321	2.25
202.0	0.009	0.06	217.0	0.049	0.34
203.0	0.004	0.03	218.0	0.013	0.09

$C_{11}S_2H_{18}$



M.W: 214.08499

1-(5-Ethyl-2-thienyl)-4-methyl-1-thiapentane

Purity: GLC Frac. 99.99%

Date: 10/17/74

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
37.2	0.006	0.028	63.0	0.263	1.26
38.0	0.018	0.086	63.5	0.003	0.014
38.1	0.370	1.77	64.0	0.039	0.19
39.0	4.780	22.86	64.1	0.069	0.33
39.3m*	0.015	0.071	64.2m*	0.003	0.014
40.1	0.550	2.64	64.5	0.003	0.014
41.1	8.455	40.43	65.0	1.524	7.29
42.0	0.650	3.09	66.0	0.514	2.46
43.1	20.910	100.00	67.0	0.837	4.00
44.0	0.089	0.43	68.0	0.018	0.09
44.1	0.687	3.29	68.1	0.128	0.61
45.0	4.840	23.14	69.0	1.464	7.00
46.0	0.236	1.13	69.1	0.314	1.50
47.0	0.460	2.20	70.0	0.651	3.11
48.0	0.042	0.20	70.1	0.143	0.69
49.0	0.050	0.23	71.0	1.613	7.71
50.0	0.311	1.49	71.1	2.749	13.14
51.0	0.896	4.29	71.5	0.003	0.014
52.0	0.361	1.73	72.0	0.128	0.61
53.0	1.554	7.43	72.1	0.150	0.71
54.0	0.143	0.69	73.0	0.272	1.30
54.5	0.003	0.014	74.0	0.102	0.49
55.0	2.360	11.29	75.0	0.036	0.17
56.0	0.006	0.028	76.0	0.206	0.99
56.1	2.272	1.30	76.1	0.027	0.13
57.0	0.224	1.07	77.0	0.131	0.63
57.1	0.248	1.19	77.1	0.487	2.33
58.0	0.556	2.66	78.0	0.021	1.00
58.1	0.015	0.071	78.1	0.409	1.96
59.0	3.017	14.43	79.0	0.018	0.09
60.0	0.203	0.97	79.1	0.158	0.76
61.0	0.006	1.09	80.0	0.027	0.13
62.0	0.087	0.41	81.0	0.072	0.34
62.5	0.003	0.014	81.1	0.027	0.13

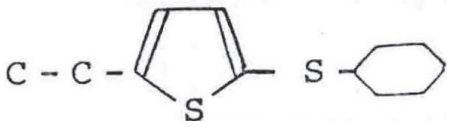
1-(5-Ethyl-2-thienyl)-4-methyl-1-thiapentane

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
82.0	0.197	0.94	117.8m*	0.015	0.071
83.1	0.173	0.83	118.0	0.033	0.16
84.0	0.678	3.24	119.0	0.009	0.043
85.0	0.729	3.49	120.0	0.003	0.14
86.0	0.081	0.39	121.0	0.015	0.071
87.0	0.152	0.73	122.0	0.012	0.058
88.0	0.078	0.37	123.0	0.066	0.31
89.0	0.057	0.27	124.0	0.093	0.44
90.0	0.036	0.17	125.0	0.105	0.50
91.0	0.096	0.46	126.0	0.018	0.086
92.0	0.027	0.13	127.0	0.096	0.49
93.0	0.054	0.26	128.0	0.120	0.58
94.0	0.015	0.071	129.0	7.110	34.00
95.0	0.263	1.26	130.0	0.433	2.07
96.0	0.150	0.71	131.0	0.574	2.74
96.5	0.006	0.028	132.0	0.039	0.19
97.0	1.255	6.00	133.0	0.021	0.10
98.0	0.120	0.57	134.0	0.006	0.028
99.0	1.703	8.14	135.0	0.009	0.043
99.5	0.009	0.043	136.0	0.006	0.028
100.0	0.003	0.50	137.0	0.012	0.058
101.0	0.120	0.57	138.0	0.012	0.058
102.0	0.206	0.99	139.0	0.012	0.058
103.0	0.057	0.27	140.0	0.015	0.071
103.1	0.054	0.26	141.0	0.075	0.36
104.0	0.018	0.086	142.0	0.158	0.76
105.0	0.012	0.058	143.0	0.986	4.71
105.1	0.012	0.058	144.0	8.126	38.86
106.0	0.006	0.028	145.0	0.687	3.29
106.5	0.003	0.014	146.0	0.657	3.14
107.0	0.012	0.058	147.0	0.054	0.26
107.5	0.003	0.014	148.0	0.021	0.10
108.0	0.087	0.41	149.0	0.006	0.028
109.0	0.287	1.37	150.0	0.003	0.014
110.0	0.645	3.09	151.0	0.006	0.028
111.0	0.765	3.66	152.0	0.003	0.014
112.0	1.105	5.29	153.0	0.170	0.81
113.0	0.347	1.66	154.0	0.024	0.11
114.0	0.212	1.01	155.0	0.051	0.24
115.0	0.125	0.60	156.0	0.009	0.043
116.0	0.191	0.91	157.0	0.269	1.29
117.0	0.048	0.23	158.0	0.036	0.17

1-(5-Ethyl-2-thienyl)-4-methyl-1-thiapentane

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
159.0	0.028	0.13	200.0	0.069	0.33
160.0	0.005	0.023	201.0	0.048	0.23
164.0	0.003	0.014	202.0	0.006	0.028
166.0	0.006	0.014	207.0	0.012	0.058
167.0	0.003	0.014	208.0	0.006	0.028
168.0	0.006	0.023	212.0	0.021	0.10
169.0	0.003	0.014	213.0	0.018	0.086
170.0	0.009	0.043	214.0M	2.838	13.57
171.0	0.009	0.043	215.0	0.418	2.00
172.0	0.018	0.086	216.0	0.254	1.21
173.0	0.006	0.028	217.0	0.033	0.16
199.0	0.454	2.17	218.0	0.012	0.058

$C_{12}S_2H_{18}$



1-(5-Ethyl-2-thienyl)-cyclohexyl sulfides

Purity: GLC Frac. 99.99%

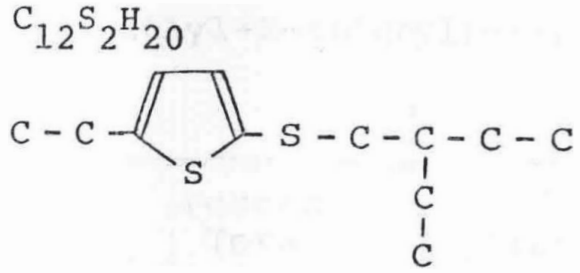
M.W: 226.08499

Date: 10/21/74

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
38.0	0.264	1.62	70.0	0.515	3.15
39.0	5.094	31.18	71.0	1.466	8.97
40.1	0.528	3.23	72.0	0.113	0.69
41.1	12.985	79.49	73.0	0.264	1.62
42.0	0.543	3.32	74.0	0.042	0.26
43.1	0.880	5.38	75.0	0.025	0.15
44.0	0.063	0.38	76.0	0.168	1.03
44.1	0.038	0.23	76.1	0.017	0.10
45.0	3.309	20.26	77.0	0.117	0.72
46.0	0.159	0.97	77.1	0.595	3.64
47.0	0.314	1.92	78.0	0.025	0.15
48.0	0.025	0.15	78.1	0.360	2.21
49.0	0.042	0.26	79.0	0.017	0.10
50.0	0.293	1.79	79.1	0.385	2.36
51.0	0.838	5.13	80.0	0.067	0.41
52.0	0.410	2.51	81.0	0.058	0.36
53.0	2.388	14.62	81.1	0.511	3.13
54.0	0.716	4.38	82.0	0.159	0.97
55.1	12.985	79.49	82.1	0.126	0.77
56.0	0.553	3.38	83.1	2.723	16.67
57.0	0.163	1.00	84.0	0.586	3.59
57.1	0.071	0.44	84.1	0.205	1.26
58.0	0.469	2.87	85.1	0.612	3.74
59.0	2.513	15.38	86.0	0.071	0.44
60.0	0.126	0.70	87.0	0.042	0.26
61.0	0.176	1.08	88.0	0.067	0.41
62.0	0.075	0.46	89.0	0.046	0.28
63.0	0.218	1.33	90.0	0.042	0.26
64.0	0.038	0.23	91.0	0.058	0.36
64.1	0.063	0.38	92.0	0.013	0.08
65.0	1.382	8.46	92.1	0.017	0.10
66.0	0.519	3.18	93.0	0.042	0.26
67.0	1.424	8.72	94.0	0.017	0.10
68.0	0.017	0.10	95.0	0.209	1.28
68.1	0.096	0.59	96.0	0.109	0.67
69.0	1.081	6.62	97.0	0.628	3.85

1-(5-Ethyl-2-thienyl)-cyclohexyl sulfides

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
98.0	0.080	0.49	137.0	0.008	0.05
99.0	1.424	8.72	138.0	0.004	0.025
100.0	0.096	0.59	139.0	0.004	0.025
101.0	0.092	0.56	140.0	0.008	0.05
102.0	0.017	0.10	141.0	0.063	0.38
103.0	0.029	0.18	142.0	0.138	0.85
104.0	0.008	0.05	143.0	0.666	4.08
105.0	0.008	0.05	144.0	16.336	100.00
105.1	0.010	0.06	145.0	1.424	8.72
106.0	0.008	0.05	146.0	1.508	9.23
107.0	0.010	0.06	147.0	0.113	0.69
108.0	0.080	0.49	148.0	0.046	0.28
109.0	0.260	1.59	149.0	0.013	0.08
110.0	0.603	3.69	150.0	0.008	0.05
111.0	0.733	4.49	151.0	0.013	0.08
112.0	0.130	0.79	152.0	0.007	0.04
113.0	0.080	0.49	153.0	0.015	0.09
114.0	0.176	1.08	154.0	0.007	0.04
115.0	0.121	0.74	155.0	0.042	0.26
116.0	0.214	1.31	156.0	0.008	0.05
117.0	0.050	0.31	157.0	0.017	0.10
117.8m*	0.017	0.10	159.0	0.007	0.04
118.0	0.034	0.21	160.0	0.005	0.03
119.0	0.008	0.05	163.0	0.007	0.04
120.0	0.004	0.025	167.0	0.007	0.04
121.0	0.017	0.10	168.0	0.005	0.03
122.0	0.017	0.10	169.0	0.008	0.05
123.0	0.025	0.15	170.0	0.007	0.04
124.0	0.017	0.10	181.0	0.005	0.03
125.0	0.038	0.23	183.0	0.008	0.05
126.0	0.007	0.04	191.0	0.004	0.025
127.0	0.080	0.49	192.0	0.005	0.03
128.0	0.117	0.72	193.0	0.004	0.025
129.0	8.981	54.97	212.0	0.010	0.06
130.0	0.586	3.59	224.0	0.017	0.10
131.0	0.729	4.46	225.0	0.007	0.04
132.0	0.054	0.33	226.0M	2.471	15.13
133.0	0.025	0.15	227.0	0.343	2.10
134.0	0.017	0.10	228.0	0.180	1.10
135.0	0.017	0.10	229.0	0.038	0.23
136.0	0.008	0.05	230.0	0.007	0.04
			231.0	0.003	0.02



$C_{12}S_2H_{20}$

1-(5-Ethyl-2-thienyl)-3-ethyl-1-thiapentane

Purity: GLC Frac. 99.40%

M.W: 228.10064

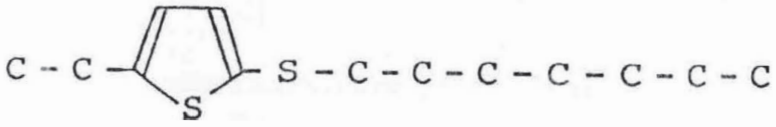
Date: 10/24/74

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
38.0	0.010	0.042	64.1	0.056	0.23
38.1	0.210	0.86	65.0	1.382	5.68
39.0	3.455	14.21	66.0	0.486	2.00
40.1	0.394	1.62	67.0	0.921	3.79
41.1	7.678	31.58	68.0	0.010	0.04
42.0	0.468	1.93	68.1	0.066	0.27
43.1	24.313	100.00	69.0	1.177	4.84
44.0	0.061	0.25	69.1	0.282	1.16
44.1	0.845	3.47	70.0	0.532	2.19
45.0	4.064	16.72	70.1	0.056	0.23
45.1	0.015	0.06	71.0	1.331	5.47
46.0	0.166	0.68	71.1	0.084	0.35
47.0	0.384	1.58	72.0	0.107	0.44
48.0	0.028	0.115	73.0	0.282	1.16
49.0	0.038	0.16	74.0	0.051	0.21
50.0	0.225	0.93	75.0	0.033	0.14
51.0	0.653	2.68	76.0	0.151	0.62
52.0	0.303	1.25	76.1	0.018	0.07
53.0	1.484	6.11	77.0	0.110	0.45
54.0	0.138	0.57	77.1	0.476	1.96
55.1	2.324	9.56	78.0	0.023	0.09
56.0	0.010	0.04	78.1	0.379	1.56
56.1	0.292	1.20	79.0	0.018	0.67
57.0	0.161	0.66	79.1	0.169	0.69
57.1	2.610	10.74	80.0	0.028	0.12
58.0	0.435	1.79	81.0	0.054	0.22
58.1	0.113	0.46	81.1	0.046	0.19
59.0	2.815	11.58	82.0	0.161	0.66
60.0	0.179	0.74	82.1	0.051	0.21
61.0	0.210	0.86	83.0	0.159	0.65
62.0	0.061	0.25	83.1	0.069	0.28
63.0	0.251	1.03	84.0	0.630	2.59
64.0	0.033	0.14	85.0	0.845	3.47

1-(5-Ethyl-2-thienyl)-3-ethyl-1-thiapentant

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
85.1	2.329	9.58	129.0	6.449	26.53
86.0	0.077	0.32	130.0	0.425	1.75
86.1	0.141	0.58	131.0	0.537	2.22
87.0	0.077	0.32	132.0	0.036	0.15
88.0	0.066	0.27	133.0	0.018	0.07
89.0	0.051	0.21	135.0	0.010	0.04
90.0	0.031	0.13	139.0	0.036	0.15
91.0	0.102	0.42	140.0	0.010	0.04
92.0	0.028	0.12	141.0	0.069	0.28
93.0	0.038	0.16	142.0	0.154	0.63
94.0	0.015	0.06	143.0	0.947	3.89
95.0	0.235	0.97	144.0	11.770	48.42
96.0	0.131	0.54	145.0	1.049	4.32
97.0	0.973	4.00	146.0	1.049	4.32
98.0	0.102	0.42	147.0	0.079	0.33
99.0	1.894	7.79	148.0	0.031	0.13
100.0	0.115	0.47	155.0	0.023	0.09
101.0	0.110	0.45	157.0	0.253	0.21
102.0	0.015	0.06	158.0	0.031	0.13
103.0	0.038	0.16	159.0	0.026	0.105
108.0	0.082	0.34	213.0	0.033	0.14
109.0	0.279	1.15	214.0	0.018	0.07
110.0	0.645	2.65	226.0	0.018	0.07
111.0	0.632	2.60	227.0	0.010	0.04
112.0	0.368	1.52	228.0M	2.160	8.88
113.0	0.297	1.22	229.0	0.302	1.24
114.0	0.184	0.76	230.0	0.197	0.81
115.0	0.125	0.52	231.0	0.031	0.13
116.0	0.174	0.72	232.0	0.010	0.04
117.0	0.046	0.19			
117.8m*	0.015	0.06			
118.0	0.026	0.105			
121.0	0.015	0.0631			
122.0	0.013	0.0526			
123.0	0.069	0.2842			
124.0	0.010	0.4105			
125.0	0.066	0.2736			
126.0	0.010	0.0421			
127.0	0.089	0.37			
128.0	0.128	0.53			

$C_{13}S_2H_{22}$



1-(5-Ethyl-2-thienyl)-
1-thiaoctane

Purity: GLC Frac.
99.99%

M.W: 242.11629

Date: 10/23/74

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
38.0	0.022	0.18	67.0	1.030	8.73
38.1	0.252	2.14	68.0	0.113	0.95
39.0	4.237	35.91	69.0	0.955	8.09
39.3m*	0.011	0.09	69.1	0.397	3.36
40.1	0.579	4.91	70.0	0.467	4.23
41.1	11.800	100.00	70.1	0.107	0.91
42.0	1.148	9.73	70.5	-	-
43.1	9.440	80.00	71.0	1.175	9.95
44.0	0.198	1.68	71.1	0.150	1.27
44.1	0.300	2.55	71.4	-	-
45.0	4.452	37.73	72.0	0.107	0.91
46.0	0.215	1.82	73.0	0.316	2.68
47.0	0.466	3.95	74.0	0.059	0.50
48.0	0.048	0.41	75.0	0.048	0.41
49.0	0.059	0.50	76.0	0.215	1.82
50.0	0.241	2.05	76.1	0.027	0.23
51.0	0.633	5.36	77.0	0.107	0.91
52.0	0.300	2.55	77.1	0.526	4.45
53.0	1.341	11.36	78.0	0.027	0.23
54.0	0.193	1.64	78.1	0.424	3.59
55.1	3.862	32.73	79.0	0.0215	0.18
56.0	0.016	0.14	79.1	0.193	1.64
56.1	0.392	3.32	80.0	0.032	0.27
57.1	11.479	97.27	81.0	0.054	0.45
58.0	0.440	3.73	81.1	0.080	0.68
58.1	0.472	4.00	82.0	0.150	1.27
59.0	3.165	26.82	83.0	0.150	1.27
60.0	0.188	1.59	83.1	0.043	0.36
61.0	0.231	1.95	84.0	0.600	5.09
62.0	0.064	0.55	85.1	0.708	6.00
63.0	0.188	1.59	86.0	0.086	0.73
64.0	0.037	0.32	87.0	0.408	3.45
64.1	0.054	0.45	88.0	0.064	0.55
65.0	1.395	11.82	88.1	0.048	0.41
66.0	0.488	4.14	89.0	0.054	0.45
			89.1	0.038	0.32

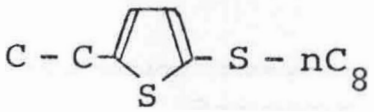
1-(5-Ethyl-2-thienyl)-1-thiaoctane

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
90.0	0.032	0.27	125.0	0.118	1.00
90.1	0.011	0.09	126.0	0.022	0.18
91.0	0.102	0.86	127.0	0.086	0.73
92.0	0.032	0.27	128.0	0.134	1.14
93.0	0.043	0.36	129.0	6.705	56.82
93.1	0.027	0.23	130.0	0.451	3.82
94.0	0.016	0.14	131.0	0.558	4.73
95.0	0.236	2.00	132.0	0.043	0.36
96.0	0.134	1.14	133.0	0.022	0.18
97.0	0.982	8.32	134.0	0.011	0.09
98.0	0.123	1.05	135.0	0.016	0.14
99.0	2.092	17.73	136.0	0.011	0.09
100.0	0.129	1.09	137.0	0.022	0.18
101.0	0.263	2.23	138.0	0.022	0.18
102.0	0.032	0.27	139.0	0.022	0.18
103.0	0.043	0.36	140.0	0.016	0.14
104.0	0.011	0.09	141.0	0.086	0.73
104.1	0.011	0.09	142.0	0.182	1.55
105.0	0.011	0.09	143.0	0.912	7.73
105.1	0.016	0.14	144.0	9.440	80.00
106.0	0.011	0.09	145.0	0.778	6.59
106.1	0.011	0.09	146.0	0.746	6.32
107.0	0.016	0.14	147.0	0.064	0.55
108.0	0.091	0.77	148.0	0.027	0.23
109.0	0.288	2.44	149.0	0.005	0.045
110.0	0.670	5.68	150.0	0.005	0.045
111.0	0.713	6.05	151.0	0.016	0.14
112.0	0.638	5.41	152.0	0.011	0.09
113.0	0.338	2.86	153.0	0.016	0.14
114.0	0.288	1.55	154.0	0.011	0.09
115.0	0.134	1.14	155.0	0.059	0.50
116.0	0.193	1.64	156.0	0.016	0.14
117.0	0.064	0.55	157.0	0.268	2.27
117.8m*	0.022	0.18	158.0	0.038	0.32
118.0	0.027	0.23	159.0	0.032	0.27
119.0	0.011	0.09	160.0	0.009	0.07
120.0	0.005	0.045	165.0	0.005	0.045
121.0	0.016	0.14	166.0	0.009	0.07
122.0	0.016	0.14	167.0	0.022	0.18
123.0	0.080	0.68	168.0	0.009	0.07
124.0	0.102	0.86	169.0	0.016	0.14

1-(5-Ethyl-2-thienyl)-1-thiaoctane

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
170.0	0.011	0.09	205.0	0.009	0.07
171.0	0.016	0.14	213.0	0.009	0.07
179.0	0.005	0.045	214.0	0.009	0.07
181.0	0.022	0.18	227.0	0.338	2.86
182.0	0.011	0.09	228.0	0.054	0.45
183.0	0.011	0.09	229.0	0.043	0.36
184.0	0.011	0.09	230.0	0.009	0.07
185.0	0.022	0.18	240.0	0.022	0.18
186.0	0.011	0.09	241.0	0.027	0.23
187.0	0.009	0.07	242.0M	2.253	19.09
195.0	0.009	0.07	243.0	0.349	2.95
198.0	0.009	0.07	244.0	0.215	1.82
199.0	0.016	0.14	245.0	0.038	0.32
200.0	0.016	0.14	246.0	0.011	0.09
201.0	0.009	0.07			
202.0	0.005	0.045			

$C_{14}S_2H_{24}$



1-(5-Ethyl-2-thienyl)-1-thianonane

Purity: GLC Frac. 99.99%

M.W: 256.13194

Date: 11/14/74

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
37.0	0.053	0.38	64.1	0.046	0.33
37.3m*	0.007	0.05	64.5	0.0035	0.025
38.0	0.204	1.49	65.0	1.228	8.97
39.0	3.931	28.72	66.0	0.425	3.10
39.3m*	0.018	0.13	67.0	1.228	8.97
40.1	0.512	3.74	68.0	0.007	0.05
41.1	13.689	100.00	68.1	0.147	1.08
42.0	1.439	10.51	69.0	0.832	6.08
43.1	13.689	100.00	69.1	1.404	10.26
44.0	0.088	0.64	70.0	0.421	3.08
44.1	0.407	2.97	70.1	0.235	1.72
45.0	4.001	29.23	71.0	1.278	9.33
46.0	0.165	1.20	71.1	3.264	23.85
47.0	0.404	2.95	72.0	0.098	0.72
47.1	0.063	0.46	72.1	0.165	1.21
48.0	0.025	0.18	73.0	0.288	2.10
49.0	0.032	0.23	74.0	0.039	0.28
50.0	0.164	1.20	75.0	0.032	0.23
51.0	0.535	3.91	76.0	0.090	0.66
52.0	0.254	1.86	76.1	0.018	0.13
53.0	1.404	10.26	77.0	0.091	0.67
54.0	0.207	1.51	77.1	0.484	3.54
55.1	4.247	31.03	78.0	0.376	2.74
56.0	0.010	0.08	79.0	0.183	1.33
56.1	0.593	4.33	80.0	0.032	0.23
57.0	0.175	1.28	81.0	0.046	0.33
57.1	7.792	56.92	81.1	0.095	0.69
58.0	0.344	2.51	82.0	0.130	0.95
58.1	0.305	2.23	82.1	0.053	0.38
59.0	2.983	21.79	83.0	0.130	0.95
60.0	0.165	1.21	83.1	0.137	0.10
61.0	0.214	1.56	84.0	0.515	3.76
61.5	tr	tr	84.1	0.126	0.92
62.0	0.053	0.38	85.0	0.611	4.46
63.0	0.162	1.18	85.1	0.095	0.69
64.0	0.025	0.18	86.0	0.067	0.49

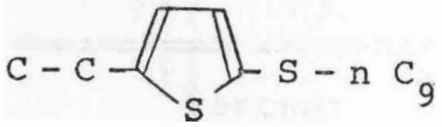
1-(5-Ethyl-2-thienyl)-1-thianonane

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
87.0	0.376	2.74	119.1	0.007	0.05
88.0	0.049	0.36	120.0	tr	tr
88.1	0.042	0.31	121.0	0.018	0.13
89.0	0.039	0.28	122.0	0.010	0.08
89.1	0.032	0.23	123.0	0.067	0.49
90.0	0.028	0.20	124.0	0.088	0.64
90.1	0.014	0.10	125.0	0.102	0.74
91.0	0.095	0.69	126.0	0.025	0.18
92.0	0.025	0.18	127.0	0.074	0.54
93.0	0.032	0.23	128.0	0.112	0.82
93.1	0.021	0.15	129.0	5.054	36.92
94.0	0.010	0.08	130.0	0.324	2.37
94.1	0.007	0.05	131.0	0.399	2.91
95.0	0.193	1.41	132.0	0.028	0.20
96.0	0.119	0.87	133.0	0.018	0.13
97.0	0.839	6.13	134.0	0.010	0.08
98.0	0.109	0.79	135.0	0.063	0.46
99.0	1.966	14.36	136.0	0.010	0.08
100.0	0.112	0.82	137.0	0.060	0.44
101.0	0.200	1.46	138.0	0.018	0.13
102.0	0.025	0.18	139.0	0.025	0.18
103.0	0.035	0.26	140.0	0.014	0.10
104.0	0.0035	0.025	141.0	0.060	0.44
104.1	0.007	0.05	142.0	0.102	0.74
105.0	0.010	0.08	143.0	0.828	6.05
106.0	0.007	0.05	144.0	7.511	54.87
107.0	0.010	0.08	145.0	0.639	4.67
108.0	0.067	0.49	146.0	0.590	4.31
109.0	0.246	1.79	147.0	0.055	0.40
110.0	0.565	4.13	148.0	0.021	0.15
111.0	0.604	4.41	149.0	0.010	0.08
112.0	0.534	3.90	150.0	0.0035	0.025
112.4	0.0035	0.025	151.0	0.015	0.11
113.0	0.288	2.10	152.0	0.0035	0.025
113.5	0.0035	0.025	153.0	0.010	0.08
114.0	0.140	1.02	154.0	0.0035	0.025
115.0	0.130	0.95	155.0	0.070	0.51
116.0	0.158	1.15	156.0	0.010	0.08
117.0	0.062	0.45	157.0	0.228	1.67
117.8m*	0.014	0.10	158.0	0.035	0.26
118.0	0.028	0.20	159.0	0.025	0.18
119.0	0.010	0.08	160.0	0.0035	0.025

1-(5-Ethyl-2-thienyl)-1-thianonane

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
163.0	0.0035	0.025	205.0	0.0035	0.025
165.0	0.006	0.04	206.0	0.0035	0.025
166.0	0.0035	0.025	207.0	0.021	0.13
167.0	0.007	0.05	208.0	0.0035	0.025
168.0	0.006	0.04	209.0	0.0035	0.025
169.0	0.010	0.08	211.0	0.0035	0.025
170.0	0.010	0.08	213.0	0.010	0.08
171.0	0.014	0.10	214.0	0.010	0.08
172.0	0.013	0.09	220.0	0.0035	0.025
173.0	0.0035	0.025	221.0	0.010	0.08
174.0	tr	tr	222.0	0.007	0.05
176.0	0.0035	0.025	223.0	0.0035	0.025
179.0	0.0035	0.025	224.0	0.010	0.08
181.0	0.018	0.13	225.0	0.007	0.05
182.0	0.006	0.04	226.0	0.008	0.06
183.0	0.007	0.05	227.0	0.010	0.08
184.0	0.006	0.04	239.0	0.028	0.20
185.0	0.021	0.13	240.0	0.007	0.05
186.0	0.010	0.08	241.0	0.228	1.67
187.0	0.0035	0.025	242.0	0.046	0.33
192.0	0.007	0.05	243.0	0.025	0.18
193.0	0.0035	0.025	244.0	0.007	0.05
194.0	0.0035	0.025	254.0	0.032	0.23
195.0	0.010	0.08	255.0	0.021	0.13
196.0	0.0035	0.025	256.0M	1.966	14.36
197.0	0.0035	0.025	257.0	0.298	2.18
198.0	0.0035	0.025	258.0	0.176	1.28
199.0	0.010	0.08	259.0	0.032	0.23
200.0	0.018	0.13	260.0	0.010	0.08
201.0	0.0035	0.025			
202.0	tr	tr			

$C_{15}S_2H_{28}$



1-(5-Ethyl-2-thienyl)-1-thiadecane

Purity: GLC Frac. 99.99%

N.W: 270.14758

Date: 10/25/74

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
37.0	0.028	0.17	68.0	0.195	1.17
38.0	0.125	0.75	69.0	0.695	4.17
39.0	2.419	14.50	69.1	1.098	6.58
39.3m*	0.028	0.17	69.2	1.154	6.92
40.1	0.403	2.42	70.0	0.306	1.83
41.1	11.261	67.50	70.1	0.695	4.17
42.0	1.599	9.58	71.0	0.820	4.92
43.1	16.683	100.00	71.1	4.727	28.33
44.0	0.056	0.33	72.0	0.083	0.50
44.1	0.542	3.25	72.1	0.250	1.50
45.0	2.280	13.67	73.0	0.306	1.83
46.0	0.111	0.67	74.0	0.056	0.33
47.0	0.306	1.83	75.0	0.028	0.17
48.0	0.028	0.17	76.0	0.069	0.42
49.0	0.028	0.17	77.0	0.083	0.50
50.0	0.125	0.75	77.1	0.375	2.25
51.0	0.417	2.50	78.0	0.306	1.83
52.0	0.195	1.17	79.0	0.167	1.00
53.0	0.987	5.92	80.0	0.028	0.17
54.0	0.334	2.00	81.0	0.056	0.33
55.1	5.005	30.00	81.1	0.139	0.83
56.0	1.349	8.08	82.0	0.097	0.58
57.1	10.010	60.00	82.1	0.097	0.58
58.0	0.250	1.50	83.0	0.111	0.67
58.1	0.431	2.58	83.1	0.431	2.58
59.0	1.835	11.00	84.0	0.403	2.42
60.0	0.139	0.83	84.1	0.348	2.08
61.0	0.181	1.08	85.0	0.500	3.00
62.0	0.028	0.17	85.1	2.044	12.25
63.0	0.125	0.75	86.0	0.069	0.42
64.0	0.028	0.17	86.1	0.153	0.92
64.1	0.042	0.25	87.0	0.320	1.92
65.0	0.779	4.67	88.0	0.042	0.25
66.0	0.320	1.92	88.1	0.042	0.25
67.0	0.876	5.25	89.0	0.042	0.25

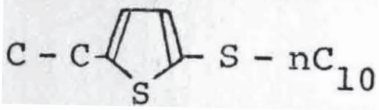
1-(5-Ethyl-2-thienyl)-1-thiadecane

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
89.1	0.042	0.25	127.1	0.083	0.50
90.0	0.022	0.13	128.0	0.083	0.50
91.0	0.056	0.33	129.0	3.643	21.83
92.0	0.022	0.13	130.0	0.306	1.83
93.0	0.028	0.17	131.0	0.361	2.17
94.0	0.022	0.13	132.0	0.028	0.17
95.0	0.167	1.00	133.0	0.014	0.08
96.0	0.111	0.67	134.0	0.014	0.08
97.0	0.695	4.17	135.0	0.014	0.08
98.0	0.195	1.17	136.0	0.014	0.08
99.0	1.390	8.33	137.0	0.022	0.13
100.0	0.125	0.75	138.0	0.014	0.08
101.0	0.167	1.00	139.0	0.022	0.13
102.0	0.028	0.17	140.0	0.042	0.25
103.0	0.028	0.17	141.0	0.069	0.42
104.0	0.014	0.08	141.1	0.083	0.50
105.0	0.022	0.13	142.0	0.139	0.83
106.0	0.014	0.08	143.0	0.779	4.47
107.0	0.014	0.08	144.0	6.951	41.67
108.0	0.056	0.33	145.0	0.626	3.75
109.0	0.208	1.25	146.0	0.570	3.42
110.0	0.473	2.83	147.0	0.069	0.42
111.0	0.500	3.00	148.0	0.022	0.13
112.0	0.473	2.83	149.0	0.014	0.08
113.0	0.278	1.67	150.0	tr	tr
114.0	0.139	0.83	151.0	0.022	0.13
115.0	0.125	0.75	152.0	tr	tr
116.0	0.139	0.83	153.0	0.014	0.08
117.0	0.056	0.33	154.0	0.028	0.17
117.8m*	tr	tr	155.0	0.042	0.25
118.0	0.014	0.08	155.1	0.056	0.33
119.0	0.042	0.25	156.0	0.014	0.08
119.5	tr	tr	157.0	0.222	1.33
120.0	tr	tr	158.0	0.028	0.17
120.5	tr	tr	159.0	0.028	0.17
121.0	0.022	0.13	168.0	0.022	0.13
122.0	0.022	0.13	169.0	0.028	0.17
123.0	0.042	0.25	169.1	0.042	0.25
124.0	0.069	0.42	170.0	tr	tr
125.0	0.083	0.50	171.0	tr	tr
126.0	0.069	0.42	181.0	0.028	0.17
127.0	0.069	0.42	183.0	0.022	0.13

1-(5-Ethyl-2-thienyl)-1-thiadecane

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
185.0	0.022	0.13	229.0	0.022	0.13
195.0	0.014	0.08	239.0	0.111	0.67
196.0	0.014	0.08	240.0	0.028	0.17
197.0	0.014	0.08	241.0	0.028	0.17
199.0	0.014	0.08	242.0	0.195	1.17
200.0	0.014	0.08	243.0	0.042	0.25
207.0	0.028	0.17	244.0	0.022	0.13
209.0	0.022	0.13	254.0	0.097	0.58
210.0	0.014	0.08	255.0	0.208	1.25
214.0	0.056	0.33	256.0	0.056	0.33
215.0	tr	tr	257.0	0.028	0.17
221.0	0.022	0.13	269.0	0.022	0.13
225.0	0.028	0.17	270.0M	1.738	10.42
226.0	0.069	0.42	271.0	0.348	2.08
226.1	0.069	0.42	272.0	0.208	1.25
227.0	0.042	0.25	273.0	0.042	0.25
228.0	0.056	0.33			

$C_{16}S_2H_{28}$



1-(5-Ethyl-2-thienyl)-thiaundecane

Purity: GLC Frac. 99.99%

N.W: 284.16323

Date: 3/26/75

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
37.0	0.067	0.52	64.1	0.040	0.31
37.2m*	0.0045	0.035	64.5	0.0045	0.035
38.0	0.206	1.59	65.0	0.470	3.63
39.0	3.668	28.37	66.0	0.210	1.63
39.3m*	0.013	0.10	67.0	0.752	5.81
40.1	0.510	3.94	68.0	0.850	6.57
41.1	12.168	94.12	69.0	0.434	3.36
42.0	2.774	21.45	69.1	3.042	23.53
43.1	12.929	100.00	70.0	0.210	1.63
44.0	0.031	0.24	70.1	2.371	18.34
44.1	0.403	3.11	71.0	0.599	4.64
45.0	1.968	15.23	71.1	2.505	19.38
45.1	0.353	2.73	71.4	0.0045	0.035
46.0	0.112	0.87	72.0	0.067	0.52
46.1	0.027	0.21	72.1	0.143	1.11
47.0	0.309	2.39	73.0	0.174	1.35
47.1	1.083	8.37	74.0	0.054	0.42
48.0	0.022	0.17	75.0	0.063	0.48
48.1	0.031	0.24	76.0	0.072	0.55
49.0	0.036	0.28	76.1	0.022	0.17
50.0	0.174	1.35	77.0	0.031	0.24
51.0	0.429	3.32	77.1	0.349	2.70
52.0	0.188	1.45	78.0	0.201	1.56
53.0	1.002	7.75	79.0	0.009	0.07
54.0	0.514	3.98	79.1	0.143	1.11
54.8	0.0045	0.035	80.0	0.009	0.07
55.0	6.979	53.98	80.1	0.027	0.21
55.1	0.0045	0.035	81.0	0.040	0.31
56.0	3.176	24.57	81.1	0.143	1.11
57.1	8.142	62.98	82.0	0.090	0.70
58.0	0.228	1.76	82.1	0.599	4.64
58.1	0.344	2.66	82.5	0.0045	0.035
59.0	5.905	45.67	83.0	0.090	0.70
60.0	0.098	0.76	83.1	1.700	13.15
60.1	0.192	1.49	83.5	0.0045	0.035
61.0	0.353	2.73	84.0	0.215	1.66
62.0	0.067	0.52	84.1	0.854	6.61
63.0	0.148	1.14	84.5	0.0045	0.035
63.5	0.0045	0.035	85.0	0.286	2.21
64.0	0.013	0.10	85.1	1.566	12.11

1-(5-Ethyl-2-thienyl)-thiaundecane

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
86.0	0.027	0.21	113.0	0.121	0.93
86.1	0.098	0.76	114.0	0.063	0.48
87.0	0.130	0.10	115.0	0.067	0.52
88.0	0.022	0.17	116.0	0.331	2.56
88.1	0.027	0.21	117.0	0.045	0.70
89.0	0.022	0.17	118.0	0.036	0.28
89.1	0.063	0.48	119.0	0.045	0.35
89.5	0.0045	0.035	120.0	0.0045	0.035
90.0	0.013	0.10	120.1	0.009	0.07
90.1	0.013	0.10	121.0	0.027	0.21
90.5	-	-	122.0	0.011	0.08
91.0	0.125	0.97	123.0	0.098	0.76
92.0	0.027	0.21	124.0	0.358	2.77
93.0	0.031	0.24	125.0	0.094	0.73
93.1	0.022	0.17	126.0	0.072	0.55
94.0	0.009	0.07	127.0	0.036	0.28
95.0	0.098	0.76	128.0	0.045	0.35
95.1	0.045	0.35	129.0	1.655	12.80
96.0	0.094	0.73	130.0	0.102	0.83
96.1	0.098	0.76	131.0	0.139	1.07
96.5	0.007	0.055	132.0	0.011	0.08
97.0	1.168	9.03	133.0	0.009	0.07
97.1	0.581	4.50	134.0	0.013	0.10
98.0	0.295	2.28	135.0	0.626	4.84
98.1	0.300	2.32	136.0	0.036	0.28
99.0	0.608	4.71	137.0	0.599	4.64
100.0	0.063	0.48	138.0	0.036	0.28
101.0	0.081	0.62	139.0	0.085	0.66
102.0	0.022	0.17	140.0	0.259	2.01
102.5	0.0045	0.035	141.1	0.054	0.42
103.0	0.174	1.35	142.0	0.045	0.35
104.0	0.013	0.10	143.0	0.344	2.66
105.0	0.49	0.38	144.0	2.326	17.99
106.0	0.027	0.21	145.0	0.219	1.70
107.0	0.045	0.70	146.0	0.188	1.45
108.0	0.031	0.24	147.0	0.027	0.21
109.0	0.116	0.90	148.0	0.011	0.08
110.0	0.318	2.46	149.0	0.090	0.70
111.0	0.492	3.81	150.0	0.011	0.08
112.0	0.277	2.15	151.0	0.085	0.66
112.1	0.403	3.11	152.0	0.011	0.08
112.5	0.007	0.055	153.0	0.031	0.24

1-(5-Ethyl-2-thienyl)-thiaundecane

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
154.0	0.018	0.14	195.0	0.0045	0.035
155.0	0.022	0.17	196.0	0.018	0.14
155.1	0.027	0.21	197.0	0.0045	0.035
156.0	0.007	0.055	198.0	0.0045	0.035
157.0	0.148	1.14	199.0	0.007	0.055
158.0	0.067	0.52	200.0	0.157	1.21
159.0	0.022	0.17	201.0	0.022	0.17
160.0	0.009	0.07	202.0	0.018	0.14
161.0	0.0045	0.035	203.0	tr	tr
162.0	0.0045	0.035	204.0	tr	tr
163.0	0.009	0.07	205.0	0.007	0.055
164.0	0.0045	0.035	206.0	0.009	0.07
165.0	0.009	0.07	207.0	0.067	0.52
166.0	0.009	0.07	208.0	0.009	0.07
167.0	0.040	0.31	209.0	0.009	0.07
168.0	0.018	0.14	210.0	0.0045	0.035
169.0	0.007	0.055	211.0	0.007	0.055
170.0	0.0045	0.035	212.0	0.0045	0.035
171.0	0.009	0.07	213.0	tr	tr
172.0	0.063	0.48	214.0	0.036	0.28
173.0	0.009	0.07	215.0	0.009	0.07
174.0	0.007	0.055	216.0	0.0045	0.035
175.0	0.0045	0.035	220.0	0.007	0.055
176.0	0.0045	0.035	221.0	0.102	0.08
177.0	0.0045	0.035	222.0	0.036	0.28
178.0	tr	tr	223.0	0.009	0.07
179.0	0.009	0.07	224.0	0.007	0.055
180.0	0.007	0.055	225.0	0.009	0.07
181.0	0.027	0.21	226.0	0.018	0.14
182.0	0.009	0.07	227.0	0.007	0.055
183.0	0.009	0.07	228.0	0.007	0.055
184.0	0.018	0.14	239.0	0.063	0.48
185.0	0.018	0.14	240.0	0.009	0.07
186.0	0.045	0.35	241.0	0.009	0.07
187.0	0.009	0.07	242.0	0.018	0.14
188.0	0.007	0.055	243.0	0.0045	0.035
190.0	0.0045	0.035	244.0	0.0045	0.035
191.0	0.0045	0.035	254.0	0.063	0.48
192.0	0.018	0.14	255.0	0.013	0.10
193.0	0.0045	0.035	256.0	0.013	0.10
194.0	0.0045	0.035	257.0	0.0045	0.035

1-(5-Ethyl-2-thienyl)-thiaundecane

m/e	Percent Total Ionization	Relative Abundance	m/e	Percent Total Ionization	Relative Abundance
258.0	-	-	284.0M	0.564	4.36
269.0	0.049	0.38	285.0	0.121	0.93
270.0	0.013	0.10	286.0	0.063	0.48
271.0	0.007	0.055	287.0	0.013	0.10
281.0	-	-	288.0	0.0045	0.035
282.0	0.0045	0.035			
283.0	0.009	0.07			

APPENDIX II

HEXADECANE REFERENCE PATTERN (11-18-74)

m/e	Relative intensity	m/e	Relative intensity
43	78.13	141	1.44
57	100.00	155	1.03
71	54.69	169	0.78
85	31.56	183	0.41
99	6.41	197	0.22
113	3.22	226M	1.03
127	2.03		

Sensitivity at m/e 57 = 1600 div./µl.

VITA

Pisal Chandrasurin, born in Phrae, Thailand, is the son of Nikom and Chamkam Chandrasurin. He finished high school from Bangsaen Boys' School, Cholburi, Thailand. He earned his Diploma of Public Health Sciences from the University of Medical Sciences (now Mahidol University), Bangkok, Thailand, in April, 1968. He received a B. A. in Chemistry from Park College, Kansas City, Missouri, in May, 1971.

ABSTRACT

Chandrasurin, Pisal

The Mass Spectra and Correlations with Structure for Some 1-(5-ethyl-2-thienyl)-1-thiaalkanes

Directed by Dr. Norman G. Foster, May, 1975

Submitted for Master of Science Degree

The mass spectra of fifteen members of the 1-(5-ethyl-2-thienyl)-1-thiaalkanes have been obtained. Fragmentation paths, rearrangement mechanisms supported by low ionization voltage data have been discussed.

The parent peaks are moderately strong. The rearrangement ion at m/e 144 is prominent for all spectra of the compounds. A large amount of hydrocarbon fragment ions and only a small amount of typical alkylsulfide ions are observed. Short chain compounds do not follow the correlations developed.

Suggestions for further studies of synthesis with positions of deuterium atom and carbon-13 on molecules have been made.