

1986

Synthesis and electron spin resonance spectroscopy of organo-sulfur radical cations

Wing Cheung Law
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**SYNTHESIS AND ELECTRON SPIN RESONANCE SPECTROSCOPY OF
ORGANO-SULFUR RADICAL CATIONS**

Iowa State University

PH.D. 1986

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**Synthesis and electron spin resonance spectroscopy
of organo-sulfur radical cations**

by

Wing Cheung Law

**A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY**

**Department: Chemistry
Major: Organic Chemistry**

Approved:

Signatures have been redacted for privacy.

**Iowa State University
Ames, Iowa**

1986

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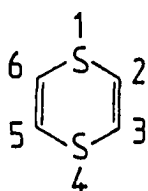
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CHAPTER I. REVIEW OF LITERATURE

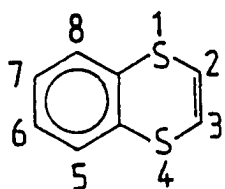
Stable sulfur-centered radical cations have been studied for more than three decades.

Numerous radical cations have been derived from the following representative systems.

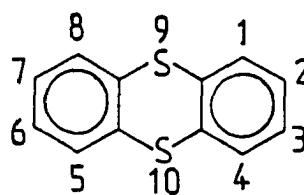
Table 1 lists the hyperfine splittings and *g*-value of some representative sulfur-centered



1,4-Dithiin



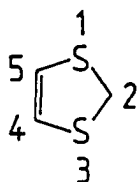
1,4-Benzodithiin



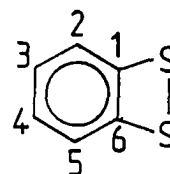
Thianthrene



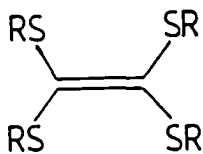
1,2-Dithiete



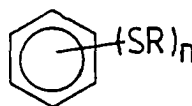
1,3-Dithiole



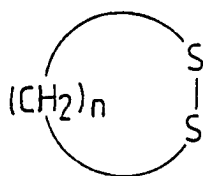
Benzodithiete^a



Tetrakis(alkylthio)ethylene



n=2-6 (Alkylthio)benzene



n=2 1,2-Dithietane

n=3 1,2-Dithiolane

n=4 1,2-Dithiane

^aThe CA Index name for this compound is 7,8-dithiabicyclo[4.2.0]octa-triene.

Table 1. Values of a^H and g for some sulfur-centered radical cations


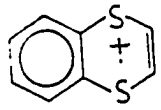
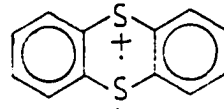
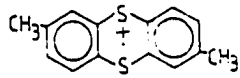
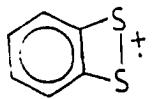
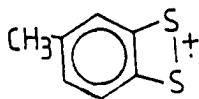
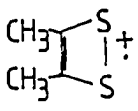
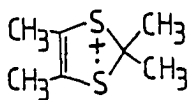

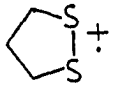
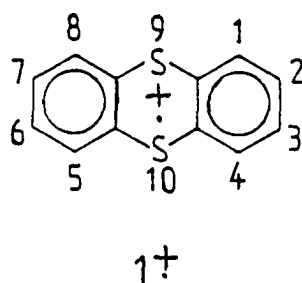
Radical Cations	$a^H(G)$	g	References
	2.84(4H)	2.0089	1
	3.32(2H)(2,3) 1.06(2H)(6,7) 0.201(2H)(5,8)		2
	1.30(4H)(2,3,6,7)	2.0084	3
	1.68(8H)(3,8;2,6-CH ₃)	2.0080	3
	1.15(2H)(2,3)	2.0150	3
	1.51(4H)(4;3-CH ₃)	2.0150	3

Table 1. (continued)

Radical Cations	$a^H(G)$	g	References
	2.17(6H)	2.0155	1
	6.15(6H)	2.0089	1
	3.7(4H)	2.0193	4
	25 °C 10(4H) ⁴ 9.5(4H) ^{5,6} -93 °C 16.25(2H) 3.9(2H)	2.0183	4,5,6
$n\text{-C}_5\text{H}_{11}\text{S—SC}_5\text{H}_{11}\text{-n}^+$ (glass)		2.018	7
$\text{HO}_2\text{CCH}_2\text{S—SCH}_2\text{CO}_2\text{H}^+$ (crystalline)		2.018	8
$(\text{CH}_3)_2\text{S—S}(\text{CH}_3)_2^+$	6.8(12H)	2.0103	9

radical cations.

It was found that a solution of thianthrene in concentrated sulfuric acid was purple in color and was paramagnetic.¹⁰ The formation of a paramagnetic species in this system has been interpreted as an one-electron oxidation to give thianthrene radical cation $1^{\cdot+}$. The pentet ESR spectrum was consistent with the symmetrical radical cation $1^{\cdot+}$ in



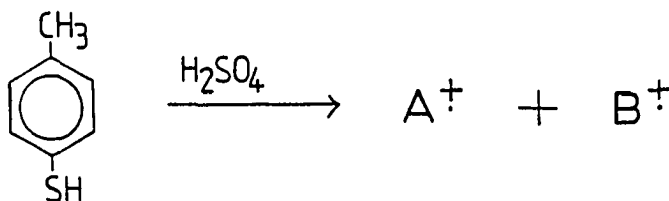
which the spin coupling of only four hydrogens was observed. The four effective hydrogens were assigned as those in the 2-, 3-, 7-, and 8-position. The ESR spectra of 2,6-dimethylthianthrene ($a^H=1.68(8H)$ G, $g=2.0080$) and 2,6-dichlorothianthrene ($a^H=1.45(2H)$ G) proved the above assignment. Theoretical calculation performed by Sullivan² also supported this assignment.

Shine, Dais, and Small¹⁰ also prepared a series of 1-, 2-, and 2,7-substituted thianthrenes. They found that the thianthrenes all gave ESR signals in sulfuric acid, but they were unable to explain some of the spectra they observed. For example, both 1-amino and 2-aminothianthrenes gave essentially the same pentet spectrum, as did both 2-hydroxythianthrene and 2,7-dihydroxythianthrene (Table 2). It is difficult to understand the pentet and triplet hyperfine splittings observed for 2-aminothianthrene and 2-hydroxythianthrene radical cations, respectively. It is possible that some kind of additional chemical change occurred during the oxidation of 2-aminothianthrene and/or 2-hydroxythianthrene by H_2SO_4 . The pentet and triplet could have been rearrangement products from the respective parent radical cations.

Table 2. Values of a^H and g of radical cations obtained by dissolving 1-aminothianthrene, 2-aminothianthrene, 2-hydroxythianthrene, 2,7-dihydroxythianthrene in H_2SO_4

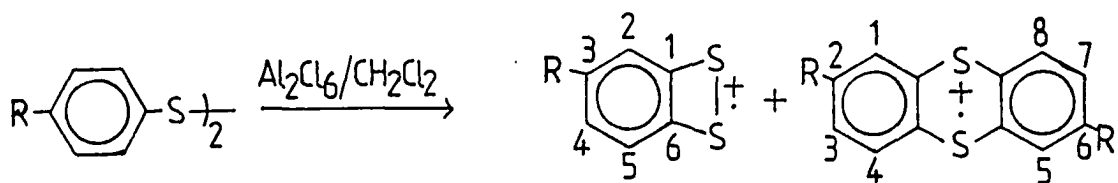
Thianthrene derivatives	a^H (G)	g
1-NH ₂	1.31 (4H)	2.0081
2-NH ₂	1.27 (4H)	2.0080
2-OH	1.91 (2H)	2.0077
2,7-(OH) ₂	1.90 (2H)	2.0076

Thianthrene radical cations can also be prepared by rearrangement methods. In 1955, Wertz and Vivo¹¹ were able to observe two well-resolved ESR signals (A⁺ and B⁺) by dissolving *p*-thiocresol in concentrated H_2SO_4 . They suggested that B⁺ (9 lines,



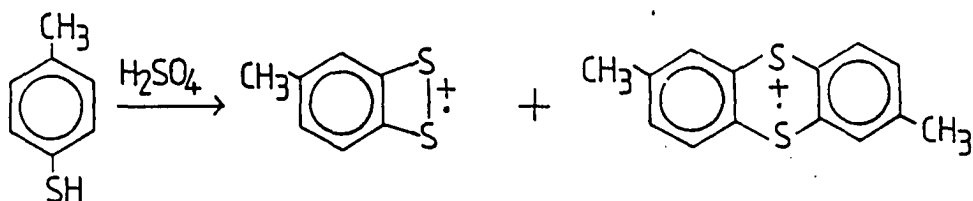
$g=2.0081$) was the radical cation of the thianthrene derivative, but they were unable to suggest a structure for A⁺ (5 lines, $g=2.0151$).

Giordan and Bock³ reported that a series of *p*-substituted aryl disulfides reacted with Al_2Cl_6 in CH_2Cl_2 at low temperature ($\sim -60^\circ C$) to form radical cations of the corresponding thianthrenes; warming of these solutions produced a second ESR signal which was assigned as the corresponding benzodithiete radical cations.



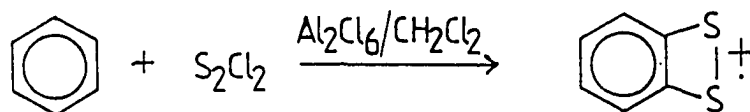
R=H,CH ₃ ,F,OCH ₃	R	g	a ^H (G)	g	a ^H (G)
	H	2.0150	1.15 (2H)	2.0084	1.30 (4H)
	CH ₃	2.0150	1.51 (4H)	2.0080	1.68 (8H)
	F	2.0160	3.30 (1F)	2.0083	3.30 (2F)
			1.20 (1H)		1.45 (2H)
	OCH ₃	not determined		2.0071	0.19 (6H)
					2.45 (2H)
					1.48 (2H)
					1.33 (2H)

For R = CH₃, the benzodithiete radical cation had the same *g*-value and hyperfine splitting pattern as the radical A⁺ produced by Wertz and Vivo by dissolving *p*-thiocresol in concentrated H₂SO₄. Therefore, both 2,6-dimethylthianthrene and 3-methylbenzodithiete radical cations can be generated by dissolving *p*-thiocresol in concentrated H₂SO₄.

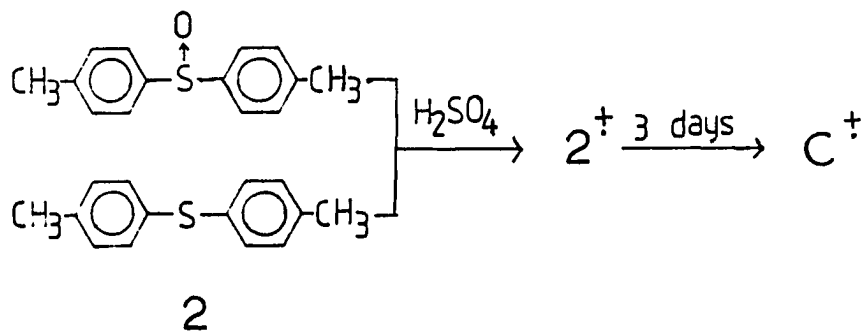


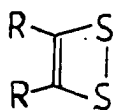
The mechanisms of generation of benzodithiete and thianthrene radical cations from aryl disulfide or thiophenol are not known. No further work in this area has been reported.

Giordan and Bock³ also reported that benzodithiete radical cation was generated by reaction of benzene with S_2Cl_2 in Al_2Cl_6/CH_2Cl_2 .



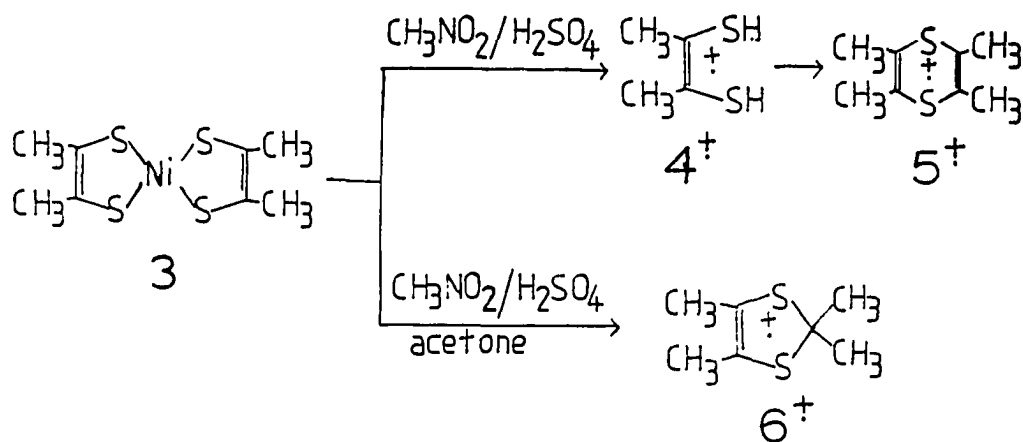
Shine, Rahman, Seeger, Wu¹² reported that a solution of either di-*p*-tolylsulfoxide or di-*p*-tolylsulfide **2** in sulfuric acid first produced a radical cation which they assigned as $2^{\cdot+}$ ($a^H=4.9(6H,CH_3)$, $2.7(4H)$, $0.61(4H)$ G, $g=2.00738$). After three days, $2^{\cdot+}$ disappeared while another seven-line signal $C^{\cdot+}$ ($a^H=1.6$ G, $g=2.00786$) appeared. The authors didn't assign any structure to this radical cation. Based on its g -value and hyperfine splitting constant, it appears that this radical cation is the 2,6-dimethylthianthrene radical cation (which has a nonet ESR signal). The same seven line spectrum was also reported by Schmidt.¹³





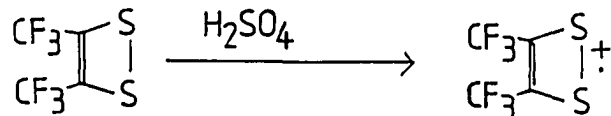
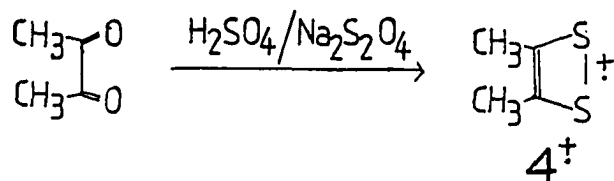
1,2-Dithiete

1,2-Dithietes contain an unsaturated four-membered ring. Owing to the strong lone pair interaction between two adjacent sulfur atoms, these compounds are generally very unstable. Only when R is strong electron withdrawing group such as CF_3 or bulky group such as *tert*-butyl can the 1,2-dithietes be synthesized as stable compounds. Therefore, the accessible sources for 1,2-dithiete radical cations cannot be the parent compounds. Several routes for the generation of dithiete radical cations were reported in the 1970s. Schrauzer

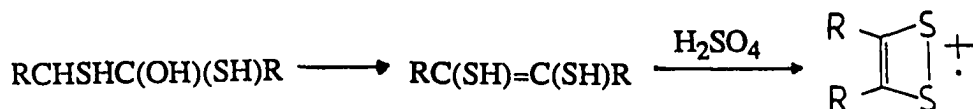
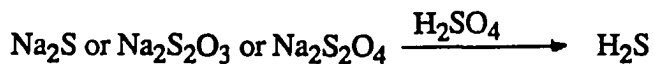


and Rabinowitz¹⁴ reacted metal complex **3** with $\text{CH}_3\text{NO}_2/\text{H}_2\text{SO}_4$ (1:1) to obtain a heptet ESR signal ($a^{\text{H}}=2.06$ (6H) G, $g=2.014$) which they assigned as *cis*-2-butene-2,3-dithiol radical cation **4⁺**. On standing, rearrangement to form tetramethyl-1,4-dithiin radical cation **5⁺** occurred. Reaction of **3** with acetone in $\text{CH}_3\text{NO}_2/\text{H}_2\text{SO}_4$ produced a new seven-line ESR signal ($a^{\text{H}}=5.75$ (6H) G, $g=2.009$) which they assigned as 2,2,4,5-tetramethyldithiole radical cation, **6⁺**.

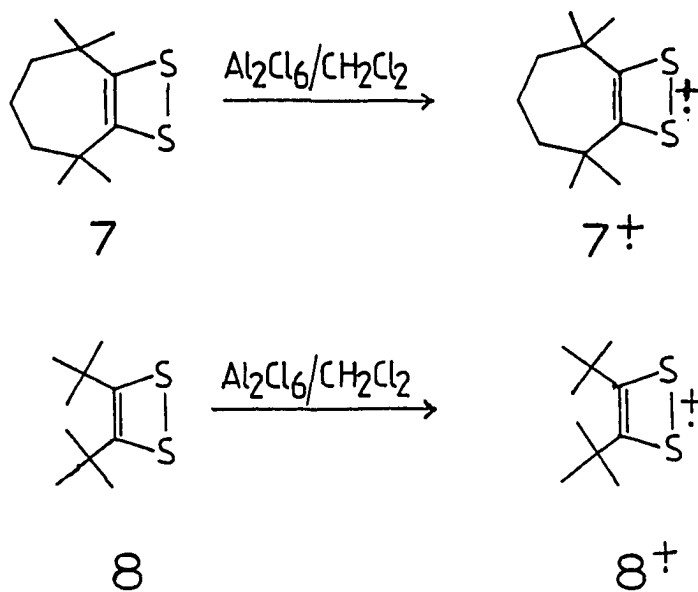
Russell, Tanikaga, and Talaty¹ found that treatment of biacetyl with sulfuric acid and $\text{Na}_2\text{S}_2\text{O}_4$ yielded a radical cation which was identical with 4^+ generated by Schrauzer and Rabinowitz. The surprisingly low value of α^{H} for 4^+ and the absence of cis/trans isomers led them to propose dimethyl-1,2-dithiete radical cation as the structure for 4^+ . Indeed, bis(trifluoromethyl)-1,2-dithiete when dissolved in sulfuric acid yielded its radical cation directly.



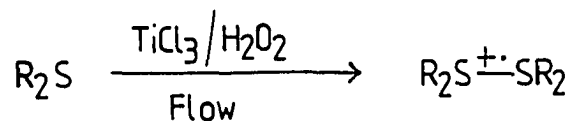
Russell, Tanikaga and Talaty also found that as a general procedure, dithiete radical cations could be generated by reaction of α -hydroxy ketones with H_2SO_4 and sodium dithionite, sodium thiosulfate or sodium sulfide. The reaction sequence was proposed to involve the following steps:



Recently, Bock, Rittmeyer, Krebs, Schütz, Voss and Köpke¹⁵ reported that two 1,2-dithiete derivatives **7** and **8** were readily oxidized by one-electron transfer system $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$ to their radical cations $7^{\cdot+}$ ($g=2.157$) and $8^{\cdot+}$ ($g=2.0159$), respectively.

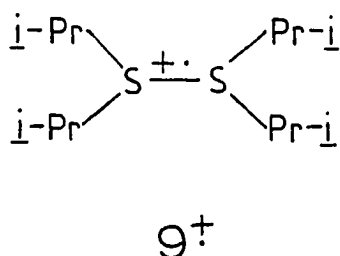


It was shown by Gilbert, Hodgeman, and Norman⁹ that alkyl sulfides (R_2S) could be oxidized by $\text{TiCl}_3/\text{H}_2\text{O}_2$ under flow condition to form dimeric radical cations $\text{R}_2\text{S}\text{-SR}_2^{\cdot+}$. The dimeric structure was established by the fact that dimethyl sulfide was oxidized to give a



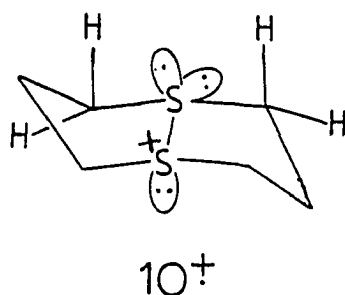
thirteen-line ESR spectrum with a g -value of 2.0103 and a splitting constant of 6.8 gauss.

It was then discovered that dimeric sulfide radical cations could also be generated by photolysis of solutions containing R_2S , t -BuOOBu- t and CF_3CO_2H and by low temperature electrolysis.¹⁶ These methods provided a way to study these radical cations over a wide range of temperature. It was found that the radical cation 9^+ had a conformation preference at low temperature. At 0 °C, the ESR spectrum of 9^+ was a pentet ($a^H=8.9$ G, $g=2.0112$), while at -104 °C, the ESR spectrum was a triplet of triplets ($a^H=13.8$ (2H), 5.8 (2H) G).



Asmus used pulse radiolysis technique¹⁷ to identify the σ to σ^* absorption band of $R_2S-SR_2^+$ and proved the three electron σ bond character of $R_2S-SR_2^+$. His work provided a way for studying short-life radical species.

In 1976, Musker and Wolford¹⁸ reported that a long-lived radical cation could be formed by oxidation of 1,5-dithiacyclooctane (DTCO) **10** by oxidizing reagent such as $NOBF_4$. They suggested a structure for $DTCO^+$ in which the spin was localized in only one sulfur atom. They attributed the unusual stability of $DTCO^+$ to the transannular interaction between the two sulfur atoms in the same molecule.



Brown, Hirschon, and Musker¹⁹ later reported that DTCO could be oxidized by H_2SO_4 to give a pentet ESR spectrum with a g -value of 2.012 and a splitting constant of 9.9 G. They again assigned this radical cation as DTCO^+ , and explained that the significantly different ESR spectra obtained when the oxidation was carried out in different solvents was due to strong solvent effects. A deuterium labeling experiment showed that their previous suggested structure for DTCO^+ was wrong, and that the two sulfur atoms in the DTCO^+ had to be equivalent.

It has been a controversial issue whether the hyperfine splitting of a hydrogen β to a sulfur atom with unpaired spin density result mainly from angle-dependent hyperconjugative interaction or from an angle-independent spin polarization effect. Zweig and Hodgson²⁰ investigated the cation radicals of 1,4-bis(methylthio)benzene and 1,2,4,5-tetrakis(methylthio)benzene and suggested that coupling constants of the methyl hydrogen β to the sulfur were related to ρ_s by the expression (Equation 1).

$$a^{\text{H}} = Q_{\text{SCH}_3} \cdot \rho_s \quad (1)$$

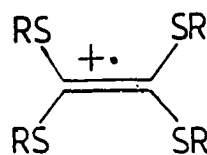
where

$$Q_{\text{SCH}_3} = 21 \text{ G}$$

In a reexamination of Zweig and Hodgson's work, Sullivan and Forbes²¹ suggested a value

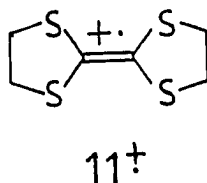
of $Q_{SCH_3} = 18.5$ G from a comparison of the experimental coupling constants with those calculated from ρ_s . They also implied that the magnitude of the alkyl hydrogen coupling is dependent upon the dihedral angle between the plane of the C-H bond and the p_z - π orbital of the adjacent sulfur.

Geske and Merritt²² studied the cation radicals of some tetrakis(alkylthio)ethylenes and suggested that the alkyl hydrogen coupling constant arises mainly from angle-dependent hyperconjugative model (Equation 2), but they failed to make an estimation of Q_{S-C-H}



$$a^H = Q_{S-C-H} \cdot \rho_s \langle \cos^2\theta \rangle \quad (2)$$

based on their results. Chambers, Canfield, Williams and Coffen²³ reported the ESR spectrum of $\Delta^{2,2'}$ -bi-1,3-dithiolanylidene radical cation **11**⁺ ($a^H = 2.41(8H)$ G, $g = 2.0089$). Since a^H was small, they concluded that coupling constants of alkyl hydrogens linked to a π^+ system by a bivalent sulfur atom don't arise predominantly from a hyperconjugation

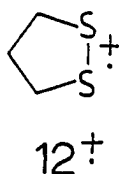


mechanism similar to that found for hydrocarbons. They concluded that, for thioether radical cations, the alternative spin polarization mechanism is more important. They explained their conclusion by pointing out that the known weaker overlap in S-C 3p-2p π bonds than C-C 2p-2p π bonds which decreases the spin delocalization in a hyperconjugation mechanism.

Bock, Brähler, Henkel, Schlecker and Seebach²⁴ studied several examples of tetrakis (alkylthio)ethylene radical cations and suggested the hyperfine splitting of hydrogens β to the sulfur atoms arise mainly from an angle-independent spin polarization effect; all their examples were reasonably well-correlated by Equation 3. Nevertheless, Bock, Stein, and

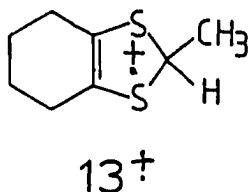
$$a_{\alpha}^{\text{H}} = |17\rho_{\text{S}}| \text{ G} \quad (3)$$

Semkow^{5,6} reported the temperature dependent ESR spectrum of 1,2-dithiolane radical cation 12^+ . At -93 °C, the ESR spectrum of 12^+ was a triplet of triplets ($a^{\text{H}}=16.25(2\text{H})$, 3.9(2H) G, $g=2.0183$), while at -30 °C the spectrum of 12^+ was a pentet ($a^{\text{H}} = 9.5$ G). Their results provided evidence for the non-planar structure of 12^+ as well as an example

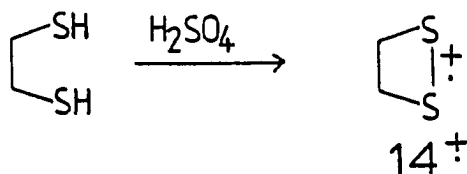


that hyperfine splitting by hydrogen atoms β to sulfur atom possessing unpaired spin density was angle-dependent.

Russell and Zaleta⁴ prepared 2-methyl-4,5-tetramethylene-1,3-dithiole radical cation 13^+ ($a^{\text{H}}=24.2(1\text{H})$, 8.4(4H) G) and showed that hyperconjugation was important in this



system. Furthermore, they found that ethane-1,2-dithiol could be oxidized by concentrated H_2SO_4 to form 1,2-dithietane radical cation 14^+ ($a^{\text{H}}=3.7(4\text{H})$ G, $g=2.0193$). Surprisingly, the hydrogens of 14^+ have a very small hyperfine splitting (3.7 G) comparing to the 1,2-dithiolane radical cation (10.0 G). They explained this observation by pointing out that since 12^+ and 14^+ had antisymmetrical SOMOs, the value of a^{H} would be determined by hyperconjugative 1,2-interactions and homohyperconjugative (W plan) 1,3 interaction.²⁵ In 14^+ , the 1,3-interaction was more important than 12^+ . Because of the antisymmetric SOMO in 14^+ and the favorable geometry, the 1,3-interaction partially cancelled the 1,2-hyperconjugative interaction and resulted in a rather small hyperfine splitting.

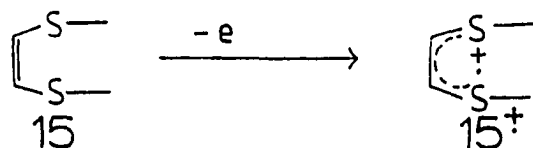
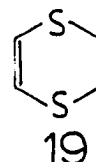
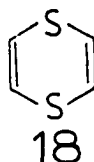
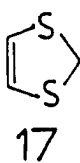
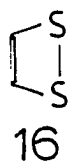
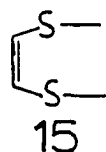


In summary, although the first sulfur centered radical cation was reported several decades ago, a detailed understanding of the structure and bonding of sulfur centered radical cations hasn't been achieved, and there has been controversy over the issue whether the hyperfine splitting of hydrogen β to sulfur atom possessing spin density is determined mainly by hyperconjugation.

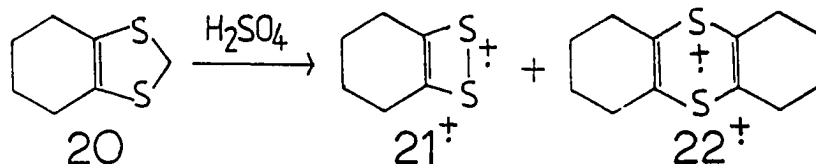
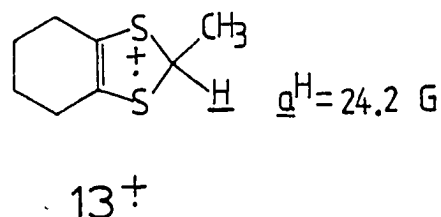
**CHAPTER II. RADICAL CATIONS DERIVED FROM ETHYLENE
DITHIOL AND DERIVATIVES**

Introduction

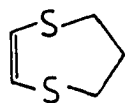
Compounds having the structural unit **15** can be classified as derivatives of ethylene dithiol. Some representative examples are 1,2-dithiete **16**, 1,3-dithiole **17**, 1,4-dithiin **18**, and 2,3-dihydro-1,4-dithiin **19**. When **16-19** are oxidized to form the radical cations, the spin density is delocalized over a π system involving four atoms. Delocalization should help to stabilize these radical cations, and therefore one would expect that persistent radical cations could be derived from **16-19**.



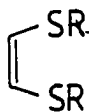
There are a number of reports ^{1-4,8,12,13} on dithiete, benzodithiete, 1,4-dithiin, thianthrene radical cations. However, their structure and chemistry have not been fully explored. Only a few examples of 1,3-dithiole radical cations are reported. Russell and Zaleta⁴ prepared **13**⁺ in H₂SO₄ and showed that hyperconjugation makes a very important contribution to the hyperfine splitting of the methine hydrogen. However, treatment of **20** with H₂SO₄ didn't yield 1,3-dithiole radical cation,²⁶ instead, the methylene group was expelled to yield the corresponding dithiete and 1,4-dithiin radical cations **21**⁺ and **22**⁺. No other examples of 1,3-dithiole radical cations containing hydrogen atoms at the 2-position have been reported.



This work was undertaken to study the radical cations derived from **16-19** as well as from other new systems such as **23** and **24**, in order to obtain information about the structure of these radical cations, the nature of the splitting mechanisms operating, and finally, if possible, to study their chemistry.



23



24

Results and Discussion

1,3-Dithiole radical cations

In spite of the instability of 20^+ in H_2SO_4 at ambient temperature, it was hoped that 20^+ might be stable at low temperature. Therefore, the oxidation was carried out at low temperature in Al_2Cl_6/CH_2Cl_2 . Indeed, at $-30^\circ C$ or below, the dithiole radical cations 20^+ was observed (Figure 1). At $-90^\circ C$, 20^+ gave a hyperfine splitting (hfs) pattern of $t \times t \times t$

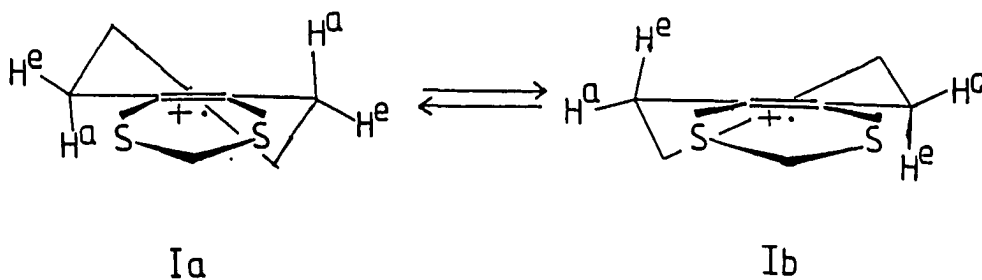
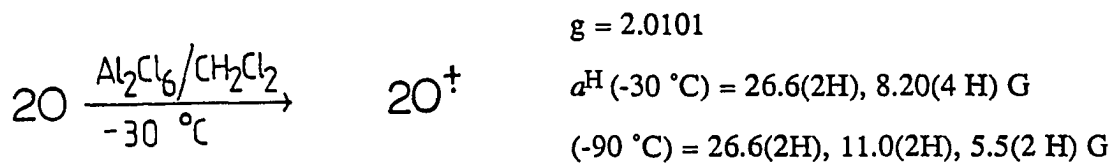
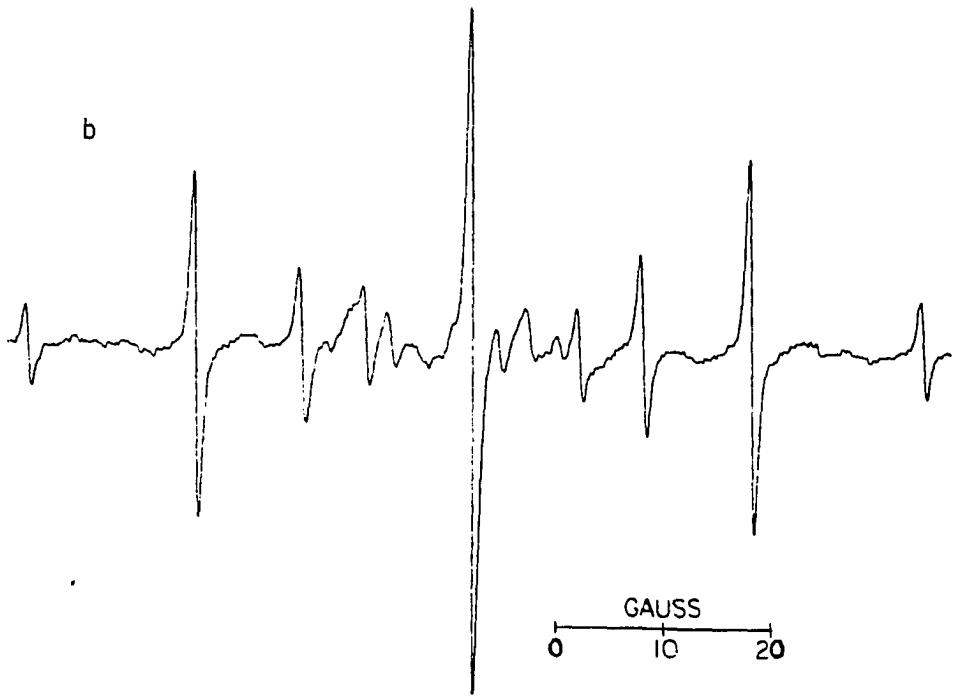
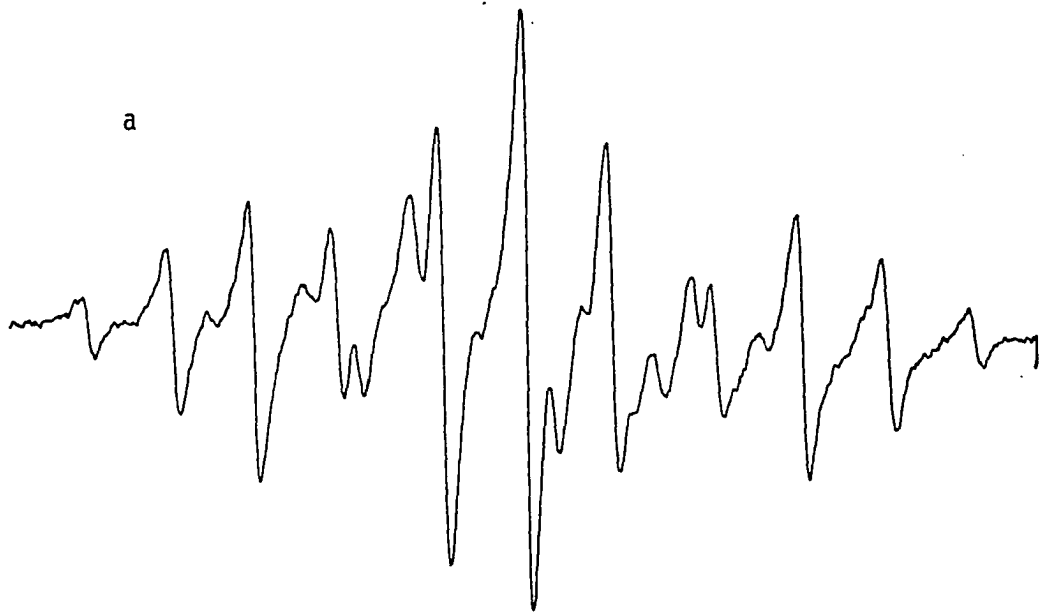


Figure 1. First derivative ESR spectra of 4,5-tetramethylene-1,2-dithiolenyl radical cation, 20^+ . (a) At $-30\text{ }^\circ\text{C}$, (b) At $-80\text{ }^\circ\text{C}$, (c) At $-90\text{ }^\circ\text{C}$



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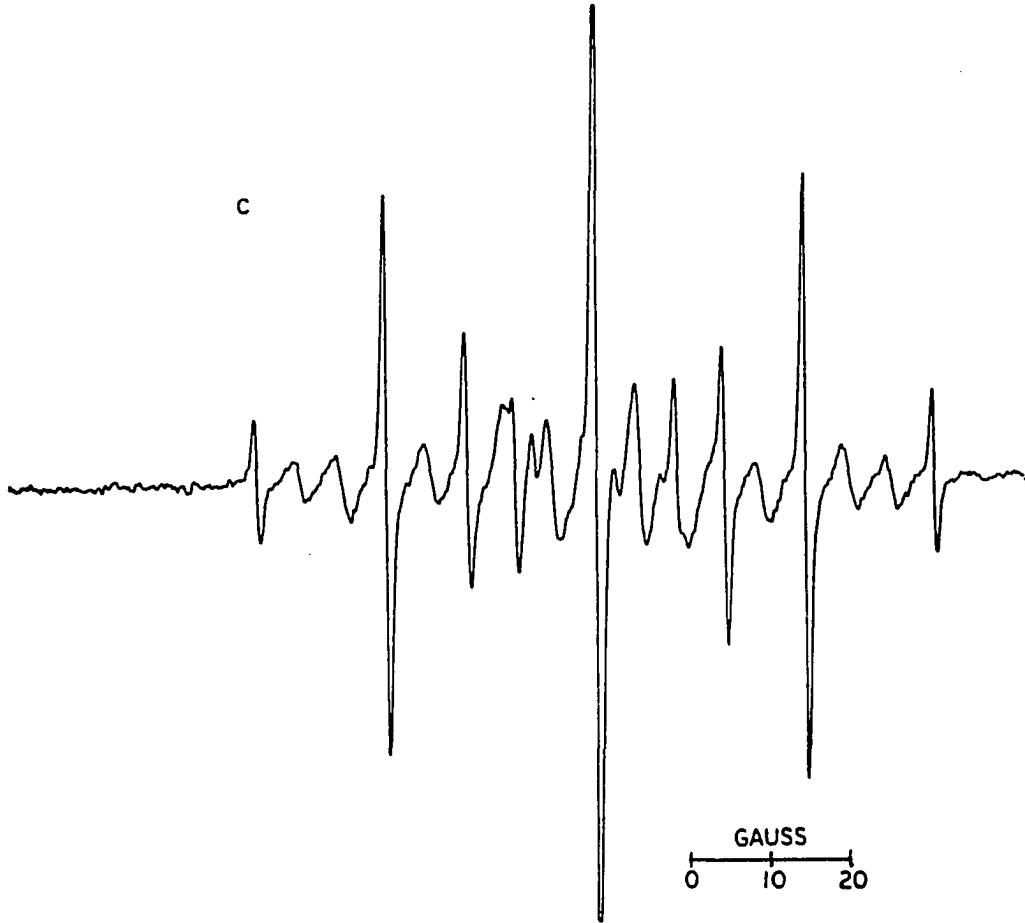


Figure 1. (continued)

with selective line broadening in the slow exchange mode. At -30 to -40 °C, the spectrum was a triplet of pentets, and at intermediate temperatures, selective line broadening was observed because of the half-chair cyclohexene ring flip which interconverted the quasi-equatorial and quasi-axial hydrogen atoms.

By studying the effect of temperature on the ESR spectrum of the radical cation one can obtain thermodynamic parameters for the ring inversion process.²⁷ Above the coalescence temperature, the rate of ring inversion may be such that line-width alternation will occur. The rate constant for ring inversion (k in sec^{-1}) is given by Equation 4, where

$$k = 2.54 \times 10^6 (a_A^H - a_B^H)^2 / \Delta \text{ width} \quad (4)$$

a_A^H and a_B^H are hyperfine splitting constants (hfsc) of axial hydrogens and equatorial hydrogens, respectively, and Δ width is the difference between widths of the second peak and the wing peak. Below the coalescence temperature, separate coupling constants can be observed for hydrogen atoms that spend most of their time in axial ($\langle a_a^H \rangle$) or equatorial ($\langle a_e^H \rangle$) positions. The rate constant under this condition of slow exchange is given by Equation 5. Plot of $\ln(k/T)$ versus $1/T$ give a straight line from which ΔH^\ddagger and ΔS^\ddagger can be

$$k = 6.22 \times 10^6 [(a_A^H - a_B^H)^2 - (\langle a_a^H \rangle - \langle a_e^H \rangle)^2]^{1/2} \quad (5)$$

calculated from the following relationships (Equations 6 and 7)

$$\Delta H^\ddagger = -\text{slope} \times R \quad (6)$$

$$\Delta S^\ddagger = R \times (\text{intercept} - \ln(k_b/h)) \quad (7)$$

where

$$h = \text{Planck's constant} = 6.626 \times 10^{-34} \text{J}\cdot\text{S}$$

$$k_b = \text{Boltzmann's constant} = 1.381 \times 10^{-23} \text{J}\cdot\text{K}^{-1}$$

$$R = \text{Gas constant} = 8.314 \text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$$

A calculation of the thermodynamic parameters for the ring inversion from the line broadening data obtained above the coalescence temperature will be referred to as a

measurement in the fast exchange mode while a calculation of the thermodynamic parameters for the ring inversion from the peak separation data obtained below the coalescence temperature will be referred to as a measurement in the slow exchange mode.

When the line broadening of 20^+ was measured in fast exchange mode, a value of $\Delta H^\ddagger = 6.2$ kcal/mole and $\Delta S^\ddagger = 5.6$ eu was calculated for 20^+ with a coalescence temperature at ~ -80 °C (Figure 2).

Table 3. The temperature dependence of rate constant k for the cyclohexene ring inversion of 20^+

Temp, K	1000/T, K ⁻¹	k , sec ⁻¹	ln(k/T)	Δ width, G
203	4.93	2.07×10^7	11.5	0.59
208	4.81	2.71×10^7	11.8	0.45
213	4.69	2.97×10^7	11.9	0.41
218	4.59	4.06×10^7	12.1	0.30
223	4.48	8.13×10^7	12.8	0.15
233	4.29	1.74×10^8	13.5	0.07
243	4.12	2.44×10^8	13.8	0.05

At room temperature, 20^+ decomposed to the dithiete radical cation 21^+ ($a^H = 3.04$ (4H) G, $g = 2.0155$) which upon cooling below -50 °C gave the line broadening expected for the cyclohexene ring flip (Figure 3). When the line broadening was measured in the fast exchange mode, a value of $\Delta H^\ddagger = 6.0$ kcal/mol and $\Delta S^\ddagger = 3.8$ eu was calculated for the cyclohexene ring inversion in 21^+ (see Experimental Section).

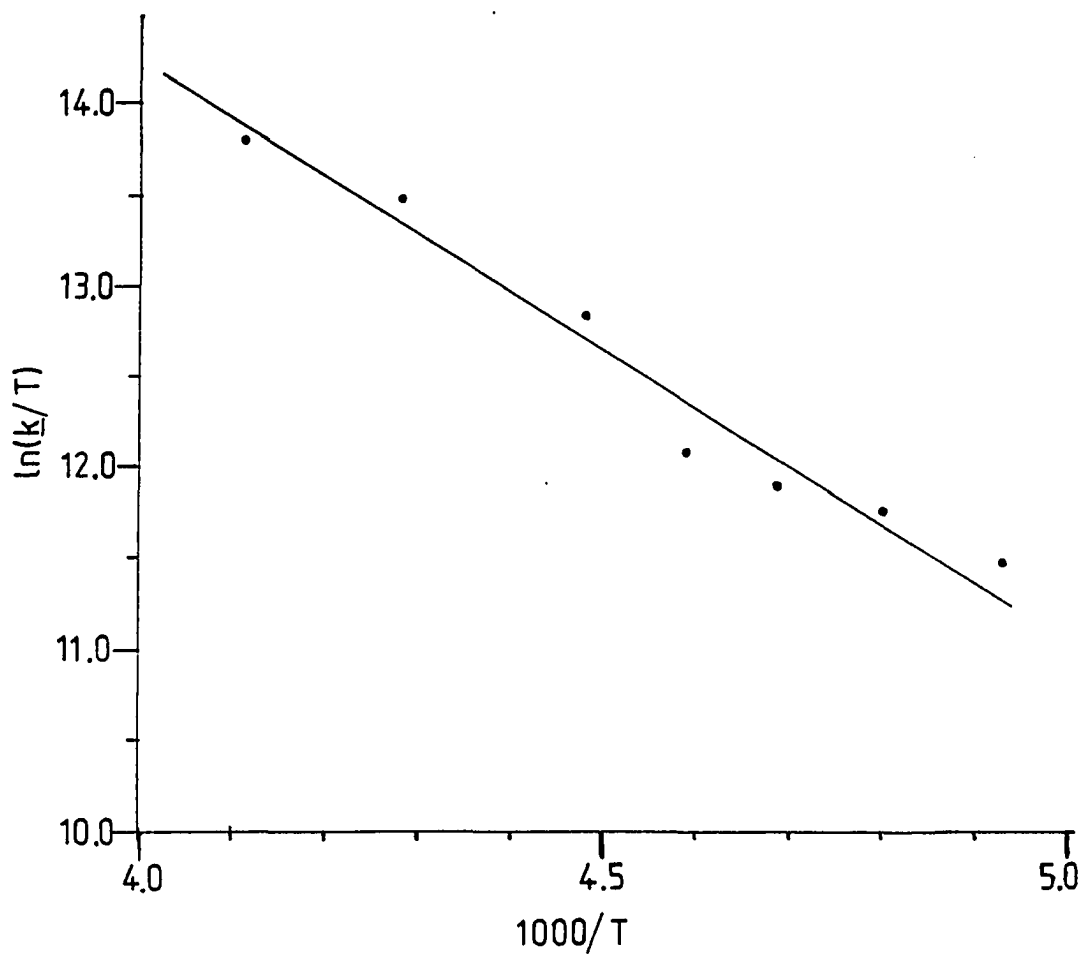
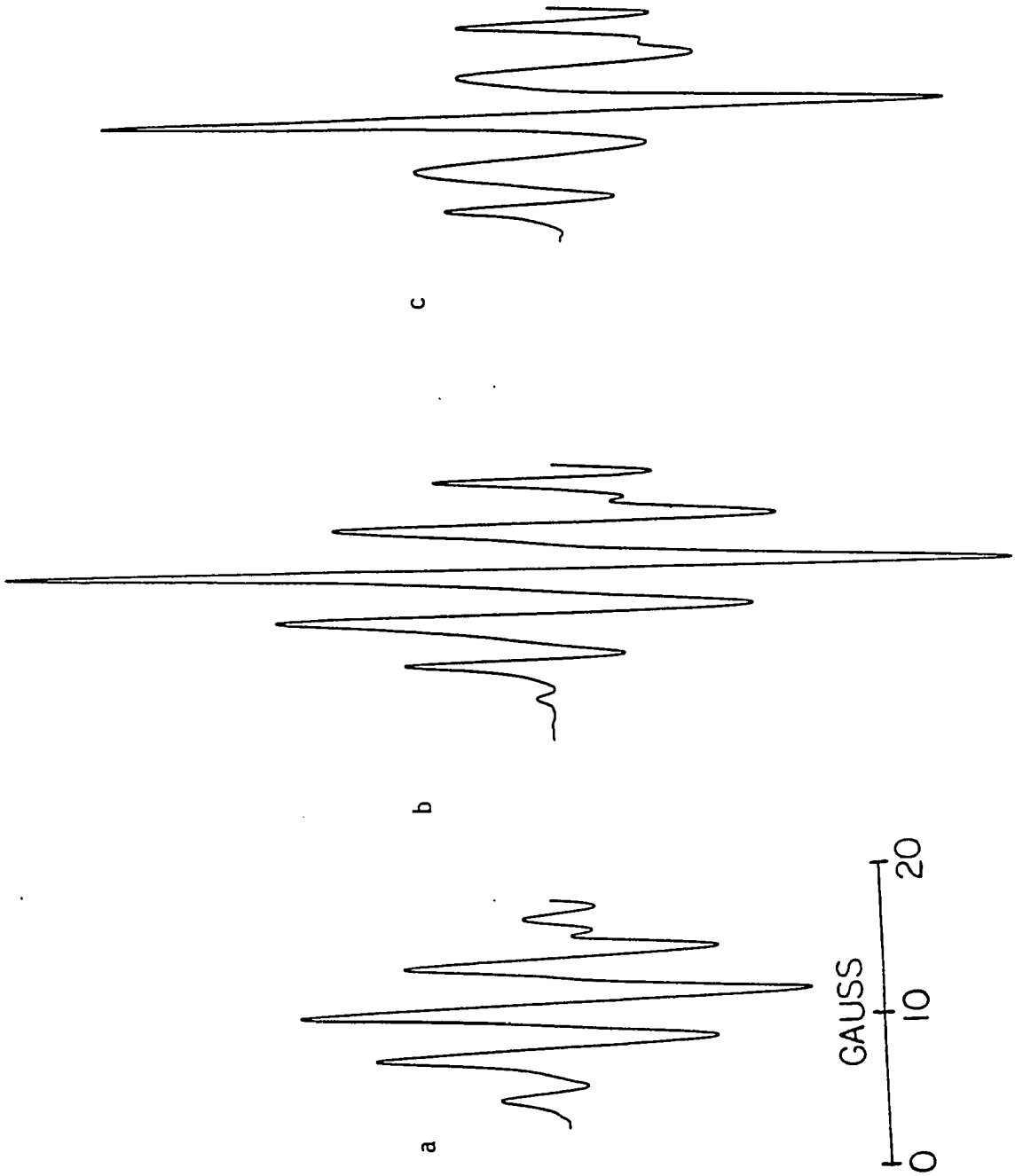
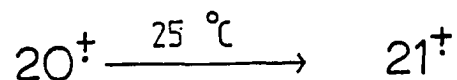


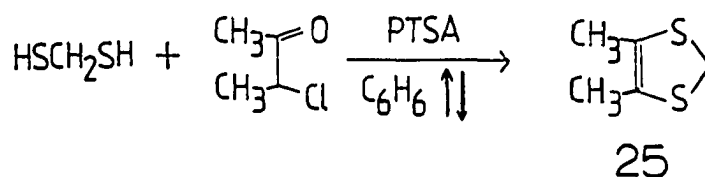
Figure 2. Plot of $\ln(k/T)$ versus $1/T$ for the cyclohexene ring inversion of 20^+ . Data were obtained from Table 3. The slope of the straight line = -3.10×10^3 and the intercept = 26.6. Correlation coefficient = -0.987

Figure 3. First derivative ESR spectra of 3,4-tetramethylene-1,2-dithiete radical cation, 21^{\ddagger} . (a) At $-50\text{ }^{\circ}\text{C}$, (b) At $-80\text{ }^{\circ}\text{C}$, (c) At $-90\text{ }^{\circ}\text{C}$



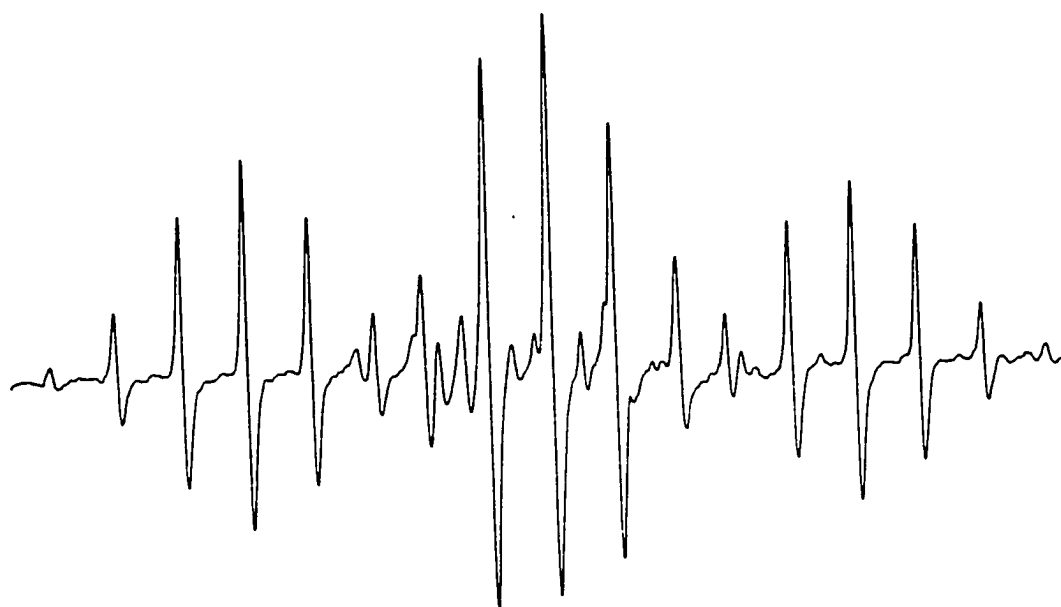


4,5-Dimethyl-1,3-dithiole **25** was made by reaction of methanedithiol with 3-chlorobutanone in refluxing benzene with *p*-toluenesulfonic acid (PTSA) as catalyst. The 1,3-dithiole **25** was oxidized by Al_2Cl_6 in CH_2Cl_2 at -70°C to form 25^{\ddagger} . The ESR spectrum of 25^{\ddagger} (Figure 4) was a triplet of heptets ($a^{\text{H}} = 27.2(2\text{H}), 5.75(6\text{H})$ G, $g = 2.0100$). Similar to 20^{\ddagger} , the two hydrogen atoms of the methylene group in 25^{\ddagger} also have large hyperfine splitting (27.2 G).

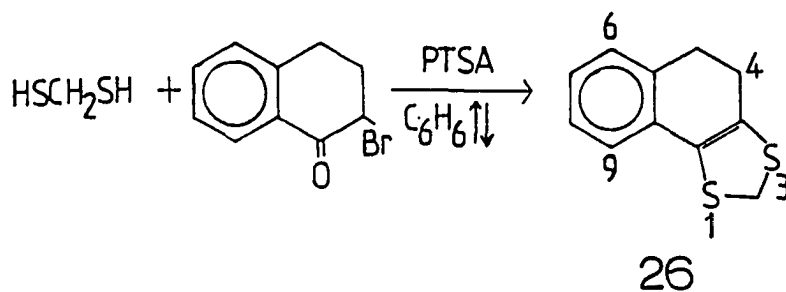


The compound **26** was synthesized by a similar strategy from reaction of methanedithiol with 2-bromo- α -tetralone. Treatment of **26** with $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$ afforded radical cation 26^{\ddagger} . At above -30°C , the ESR spectrum of 26^{\ddagger} (Figure 5) was a triplet of triplets of pentets pattern ($a^{\text{H}} = 21.2$ (2H), 7.7 (2H), 1.55 (4H) G, $g = 2.0086$). The large triplet (21.2 G) was assigned to the methylene hydrogens in the C-2 position, another triplet was assigned to the methylene hydrogens in the C-4 position, and the small pentet was assigned to the hydrogens in the C-5, 7, and 9 positions. At below -30°C , the ESR

Figure 4. First derivative ESR spectrum of 4,5-dimethyl-1,3-dithiole radical cation, 25^\dagger

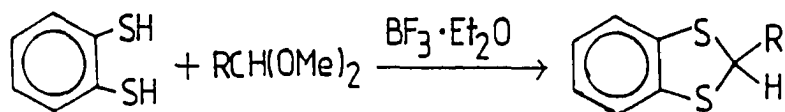


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spectrum of $26^{\cdot+}$ showed selective line broadening which appeared to be connected with the ring flip of cyclohexadiene ring. The selective line broadening was measured in the fast exchange mode; a ΔH^{\ddagger} of 5.2 kcal/mol was obtained.

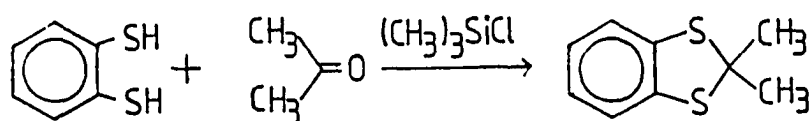
Other easily available benzodithiole compounds **27-30** were also synthesized. All of them could be oxidized to form the corresponding radical cations by treatment with Al_2Cl_6 at $-60\text{ }^{\circ}\text{C}$ (Figure 6). Table 4 lists the hyperfine splittings and g -values of the radical cations $27^{\cdot+}$ - $30^{\cdot+}$.



27, R=H

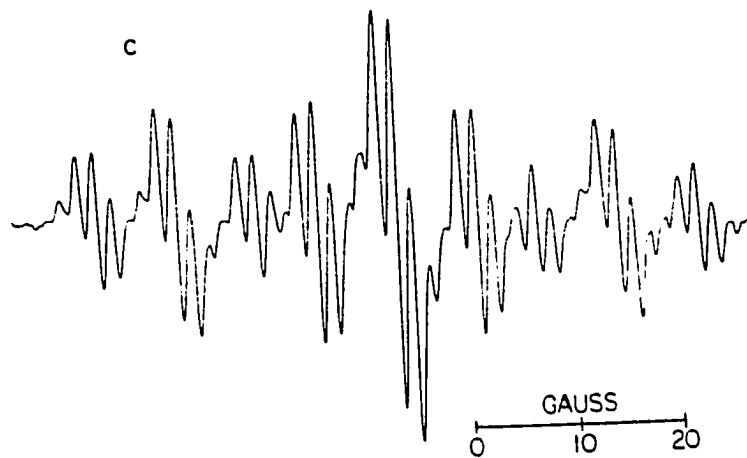
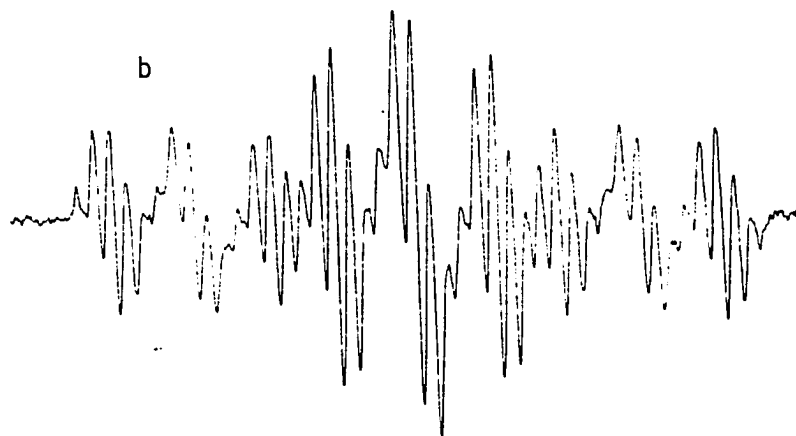
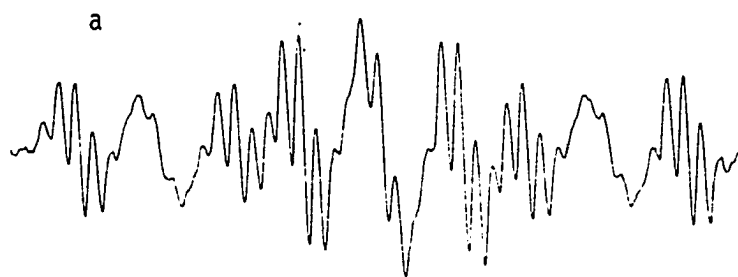
28, R=CH₃

29, R=C₆H₅



30

Figure 5. First derivative ESR spectra of 4,5-Dihydronaphtho[1,2-d]-1,3-dithiole radical cation, 26^+ . (a) At $-95\text{ }^\circ\text{C}$, (b) At $-70\text{ }^\circ\text{C}$, (c) At $-40\text{ }^\circ\text{C}$



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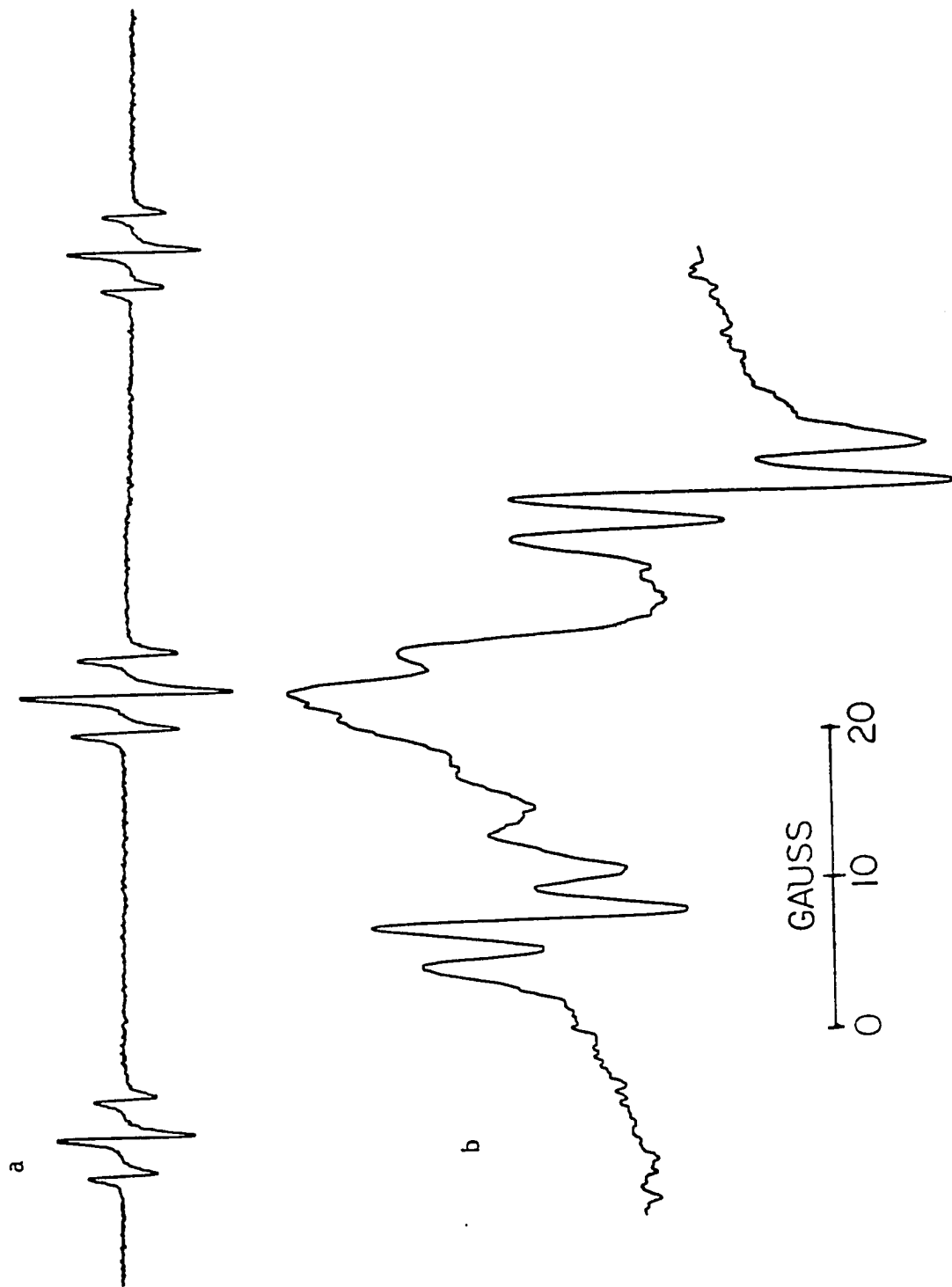
Figure 6. First derivative ESR spectra of

(a) 1,3-benzodithiole radical cation, 27⁺

(b) 2-methyl-1,3-benzodithiole radical cation, 28⁺

(c) 2-phenyl-1,3-benzodithiole radical cation, 29⁺

(d) 2,2-dimethyl-1,3-benzodithiole radical cation, 30⁺



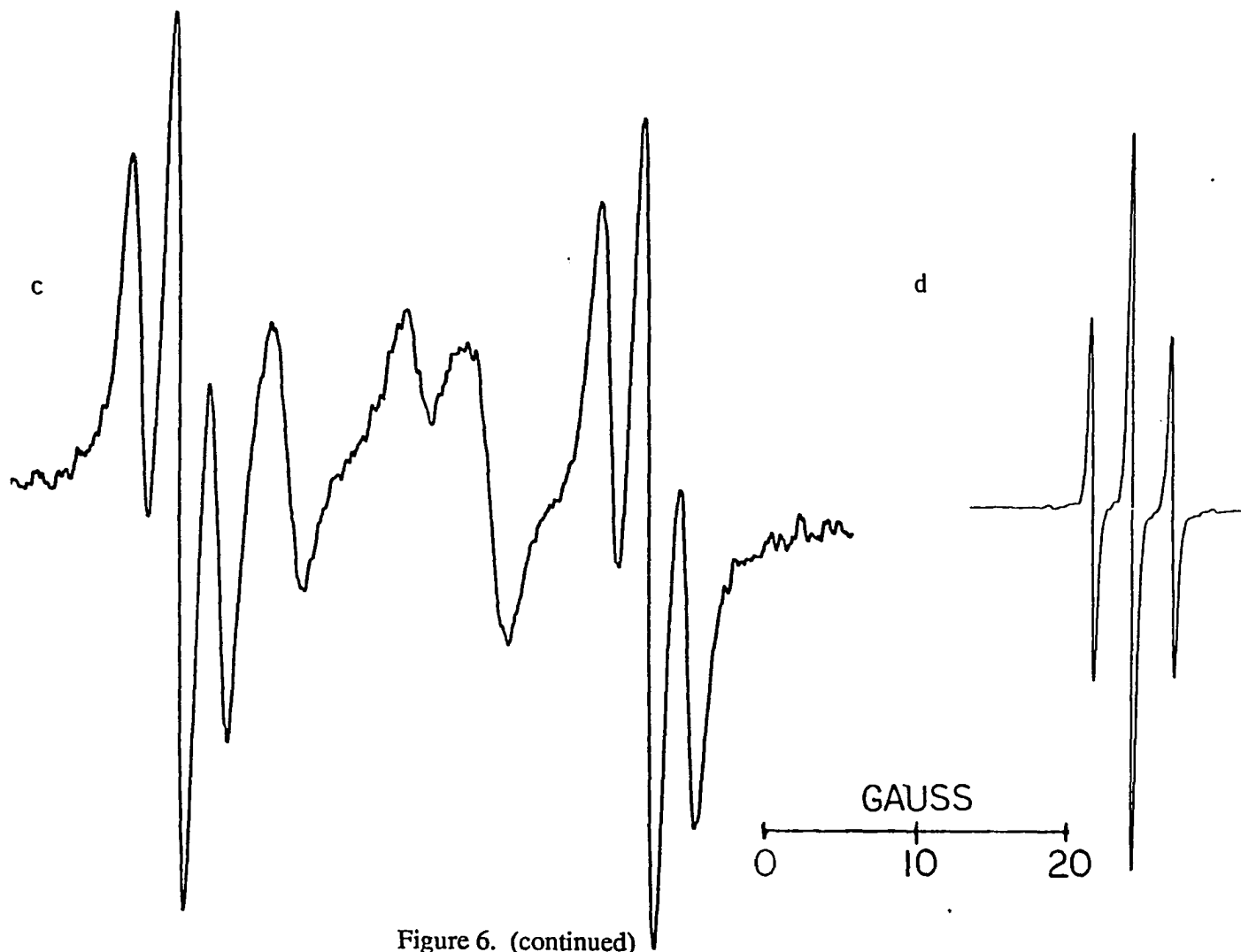


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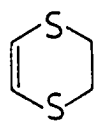
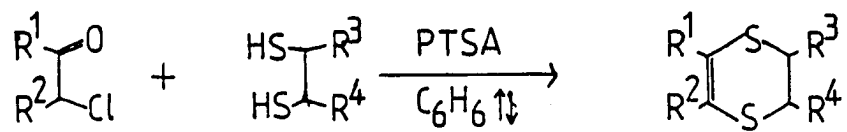
Table 4. Values of a^H and g for 1,3-benzodithiole radical cations **27**⁺-**30**⁺

Radical Cations	a^H (G)	g
27 ⁺	30.24 (2H), 2.56 (2H)	2.0103
28 ⁺	29.4 (1H), 2.7 (2H)	2.0102
29 ⁺	32.0 (1H), 2.83 (2H)	2.0101
30 ⁺	2.7 (2H)	2.0099

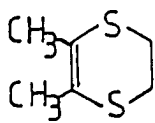
For all the 1,3-dithiole radical cations **20**⁺, **25**⁺-**30**⁺, the hydrogen atoms in the C-2 position have large hfsc (24-32 G). Since it was demonstrated by Russell and Zaleta⁴ that hyperconjugation had to be important for 1,3-dithiole radical cations, the above results convincingly prove that all 1,3-dithiole radical cations have symmetrical SOMO since otherwise hydrogens at C-2 would be in the nodal plane of the SOMO and have very small hfsc.

2.3-Dihydro-1,4-dithiin radical cations

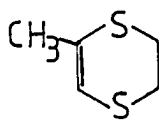
A series of substituted 2,3-dihydro-1,4-dithiins were synthesized by reacted 1,2-dithiols with α -chloro ketones in refluxing benzene with *p*-toluenesulfonic acid (PTSA) as catalyst. Compounds **31-36** were synthesized by the above procedure in good yields. In some cases, the corresponding 1,3-dithiolanes were isolated, and Al_2Cl_6 was used to convert the 1,3-dithiolane to the corresponding 2,3-dihydro-1,4-dithiins. Compounds **38** and **39** were synthesized in this way.



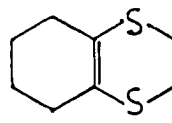
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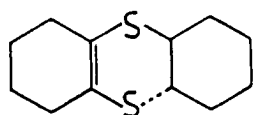
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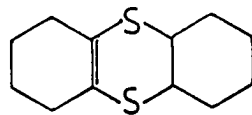
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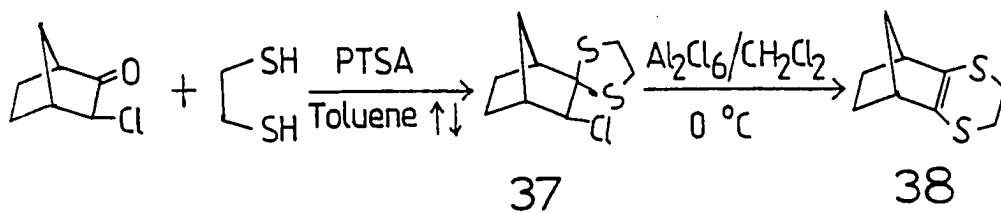
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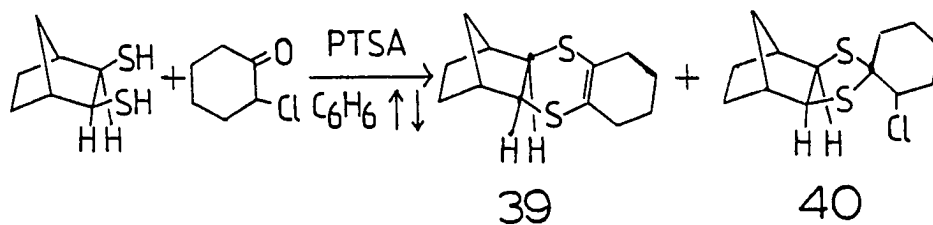


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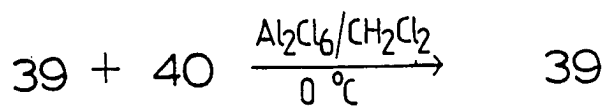
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2,3-Dihydro-1,4-dithiin **31** is reported to give $\Delta^{2,2'}$ -bi-1,3-dithiolanylidene radical cation **11**⁺ when treated with concentrated H₂SO₄ at room temperature.²⁶ However, treatment of **31** with Al₂Cl₆ in CH₂Cl₂ at -70 °C gave rise to **31**⁺ ($a^H = 8.15$ (2H), 3.4 (2H), 2.7 (2H) G, $g = 2.0092$). The ESR spectrum (Figure 7) was somewhat surprising since the four methylene hydrogens were differentiated into two groups with different hfscs. The spectrum suggests that **31**⁺ is not a planar system and that at low temperature it is locked in a half chair conformation with non-equivalent quasi-axial and quasi-equatorial hydrogen atoms.

5,6-Dimethyl-1,4-dithiin **32** gave the radical cation **32**⁺ at -60 °C when treated with either Al₂Cl₆/CH₂Cl₂ or SbCl₃/CH₂Cl₂. The methylene hydrogens were again found to be divided into two groups with different hfscs ($a^H = 5.7$ (6H), 6.9 (2H), 2.1 (2H) G, $g = 2.0080$). The compound **32** also gave **32**⁺ in H₂SO₄ at -20 °C to 70 °C with selective line broadening above -10 °C and a coalescence temperature of ~ 70 °C (Figure 8). The value of

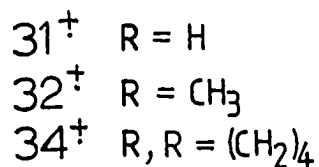
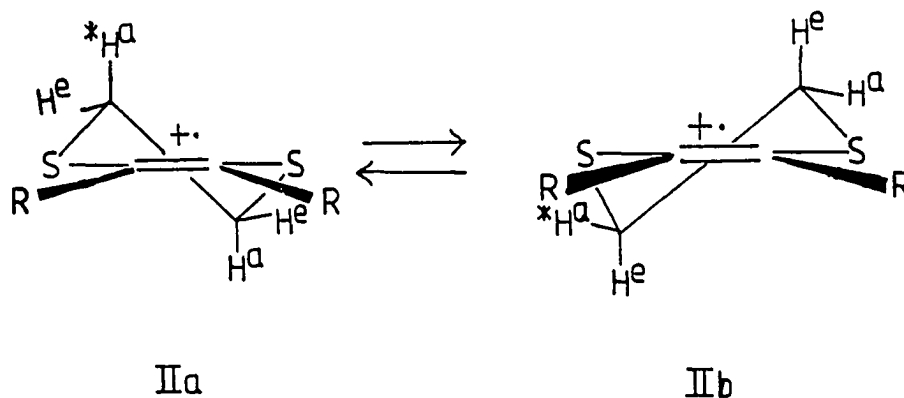
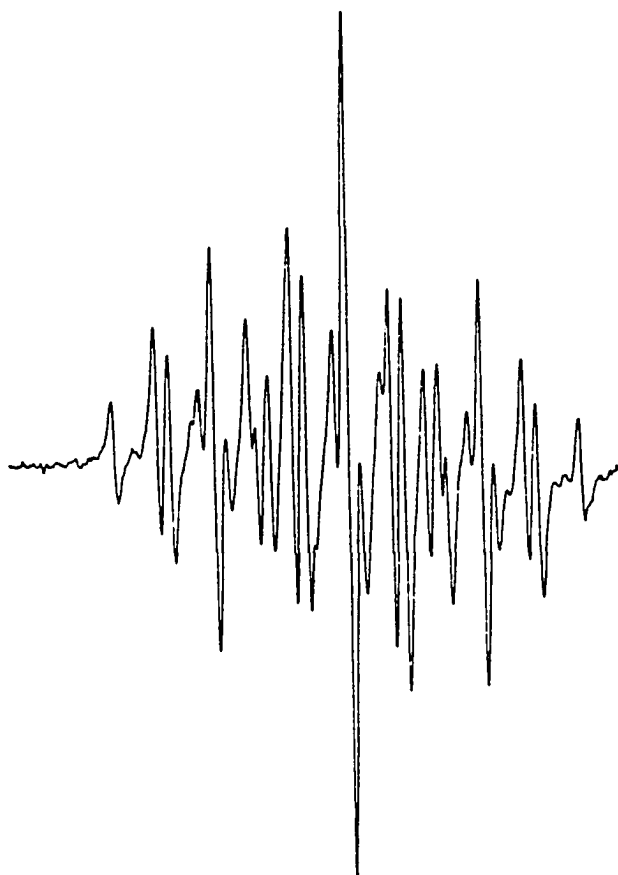


Figure 7. First derivative ESR spectrum of 2,3-dihydro-1,4-dithiin radical cation, **31⁺**



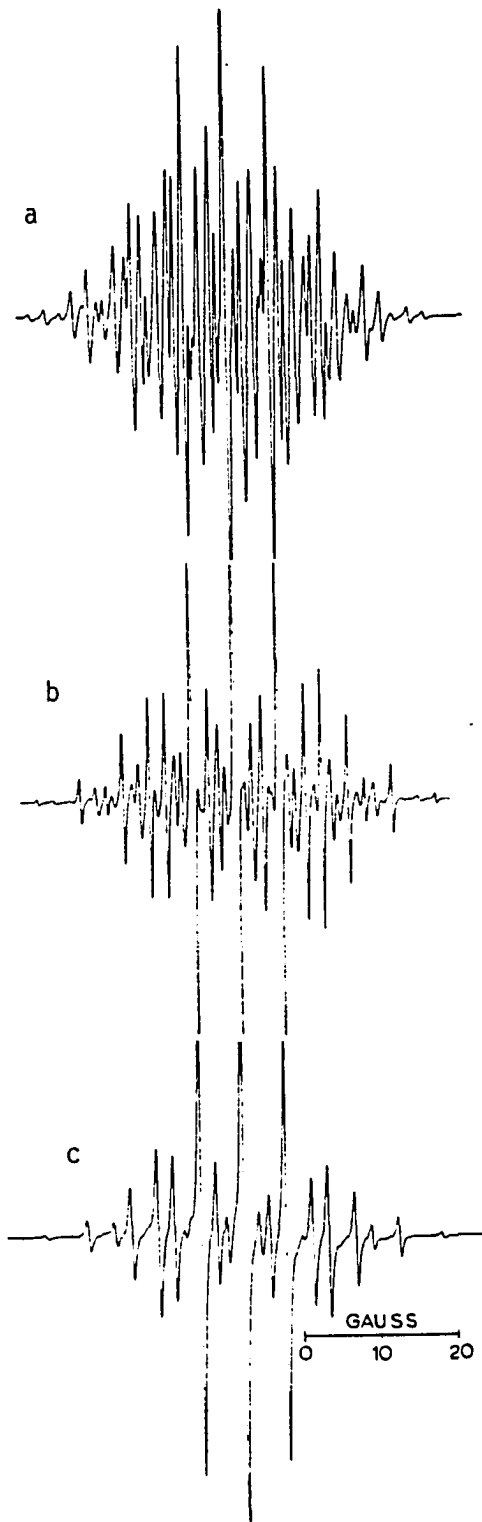
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Figure 8. First derivative ESR spectra of 5,6-dimethyl-2,3-dihydro-1,4-dithiin radical cation, **32⁺**.

(a) At -60 °C in $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$

(b) At 20 °C in H_2SO_4

(c) At 70 °C in H_2SO_4



a^H (apparent) of the quasi-equatorial and quasi-axial hydrogen atoms of 32^+ were measured in the slow exchange mode, and the conformational motion ($\text{IIa} \rightleftharpoons \text{IIb}$) was calculated to have $\Delta H^\ddagger = 2.3$ kcal/mol and $\Delta S^\ddagger = -20$ eu with $\Delta G^\ddagger = 9.2$ kcal/mol at the coalescence temperature (Figure 9). Based on the ESR spectrum of 32^+ , the methylene hydrogen atoms in 31^+ were assigned as 8.15 (axial) and 2.7 (equatorial) G.

Table 5. The temperature dependence of rate constant k for the ring inversion of 32^+

Temp, K	1000/T K ⁻¹	k sec ⁻¹	ln(k/T)	$[(a_A^H - a_B^H)^2 - (\langle a_a^H \rangle - \langle a_e^H \rangle)^2]^{1/2}$, G
273	3.66	4.73×10^6	9.76	0.76
283	3.53	5.79×10^6	9.92	0.93
308	3.25	8.40×10^6	10.21	1.35
318	3.14	1.01×10^7	10.37	1.63
323	3.10	1.05×10^7	10.39	1.69

Similarly, radical cation 34^+ displayed selective line broadening at above -10 °C in H_2SO_4 (Figure 10). At -20 °C in H_2SO_4 , 34^+ had $a^H = 7.35$ (4H), 6.85 (2H), 2.26 (2H), 0.65 (2H) G, and $g = 2.0080$. The 7.35 G pentet was assigned to the α -methylene hydrogens in the cyclohexene ring, the 6.85 G triplet was assigned to the quasi-axial hydrogens of the 2,3-dihydro-1,4-dithiin ring, while the 2.26 G triplet was assigned to the quasi-equatorial hydrogens of the 2,3-dihydro-1,4-dithiin ring, the other small triplet was assigned to two of the β -methylene hydrogens in the cyclohexene ring. The values of a^H (apparent) for the quasi-equatorial and quasi-axial hydrogen atoms of 34^+ were measured in the slow exchange mode, and the conformational motion ($\text{IIa} \rightleftharpoons \text{IIb}$) was calculated to have $\Delta H^\ddagger = 2.3$ kcal/mol and $\Delta S^\ddagger = -20$ eu (see Experimental section).

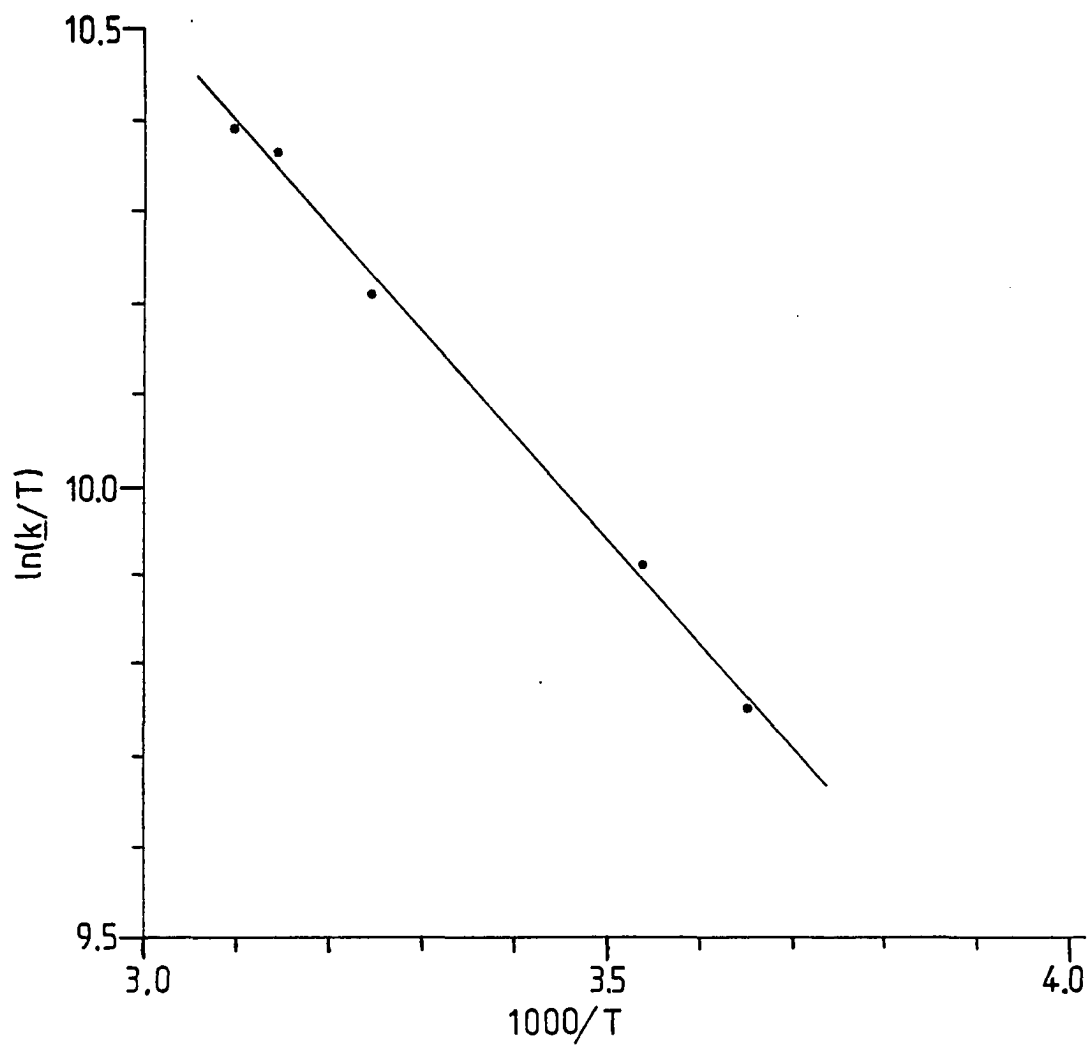


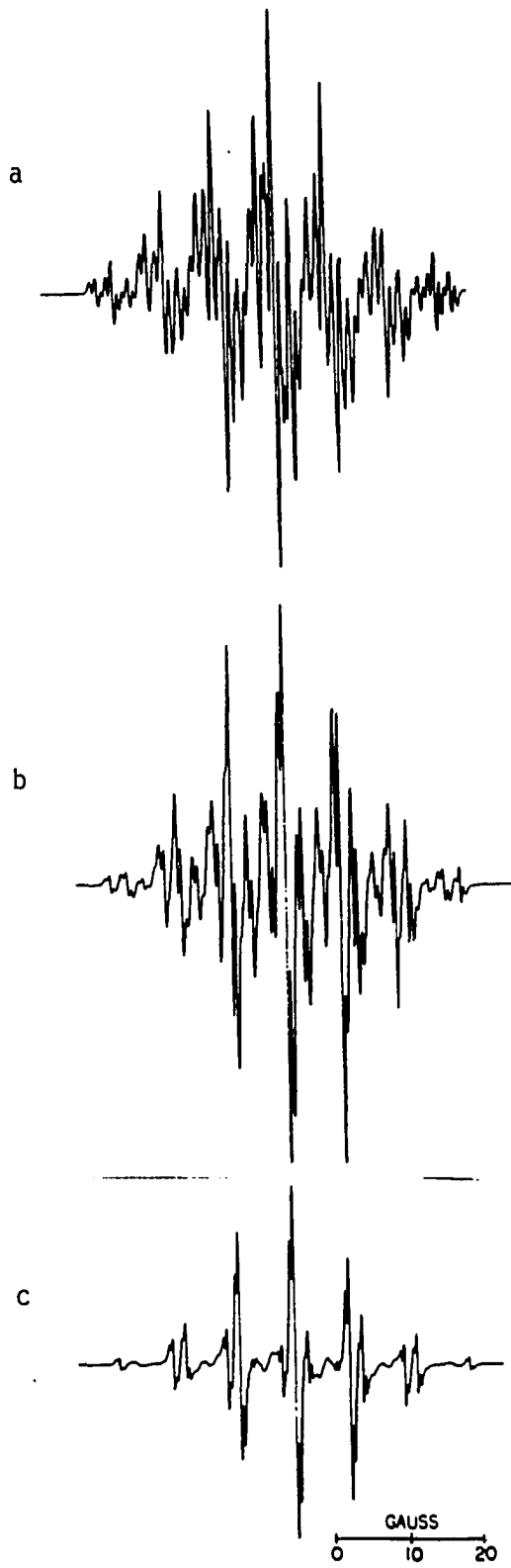
Figure 9. Plot of $\ln(k/T)$ versus $1/T$ for the ring inversion process of 32^+ . Data were obtained from Table 5. The slope of the straight line = -1.13×10^3 and the intercept = 13.9. Correlation coefficient = -0.9987

Figure 10. First derivative ESR spectra of 5,6-tetramethylene-2,3-dihydro-1,4-dithiin radical cation, 34⁺.

(a) At -95 °C in Al₂Cl₆/CH₂Cl₆

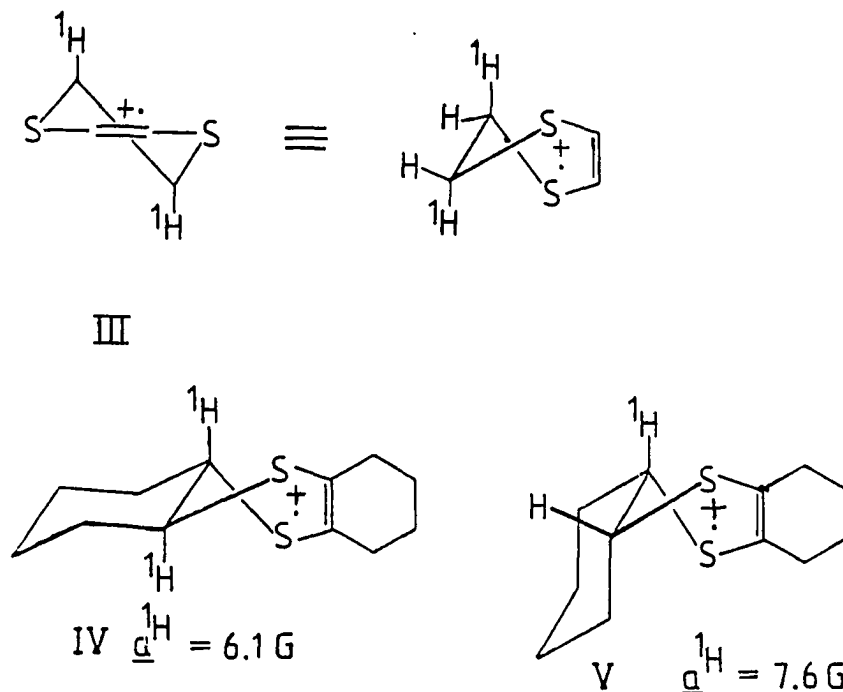
(b) At 10 °C in H₂SO₄

(c) At 40 °C in H₂SO₄



Compound **39** was oxidized to form **39⁺** ($a^H = 7.7$ (4H), 4.8 (2H), 0.8 (1H) G, $g = 2.0077$) in H_2SO_4 (Figure 11).

The half chair structure for 2,3-dihydro-1,4-dithiin ring (III) with a large hfs by the quasi-axial hydrogen atoms (1H) was firmly established by the observation that **35⁺** ($a^H = 7.9$ (4H), 6.1 (2H) G, $g = 2.0082$) had a large hfsc for two cyclohexene hydrogen atoms (IV), but **36⁺** ($a^H = 7.6$ (5H), 1.6 (2H) G, $g = 2.0082$) had a large α -coupling to only one cyclohexane hydrogen atom in the quasi-axial position relative to the heterocyclic ring (V) (Figure 11).



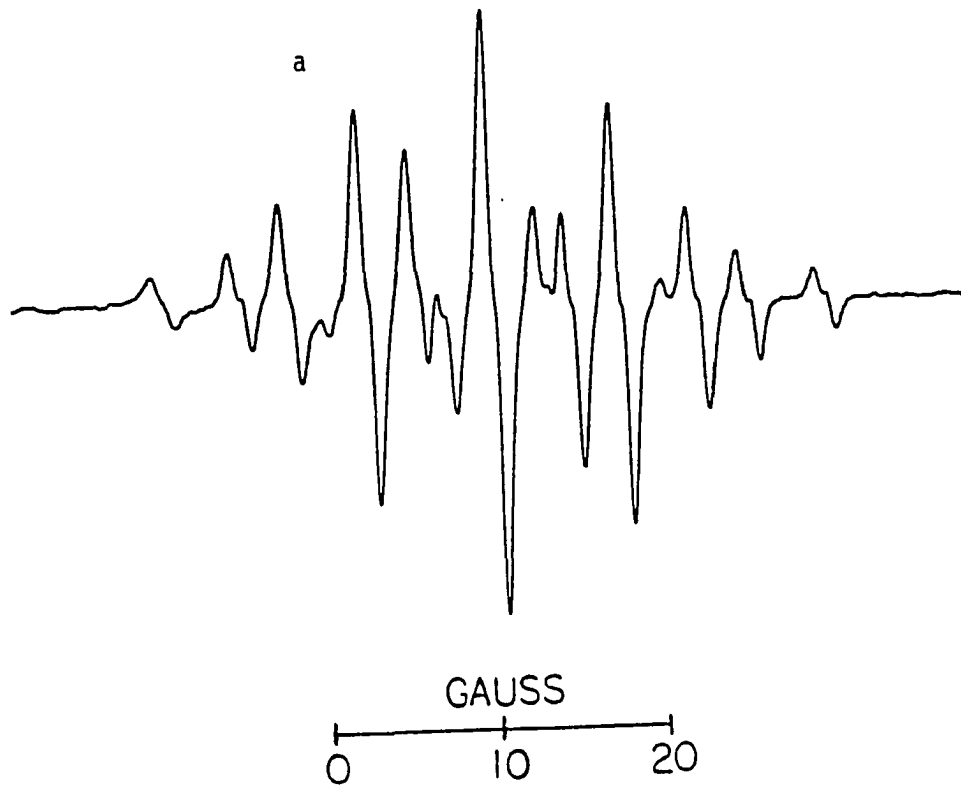
Surprisingly, **34⁺**, **36⁺** and **39⁺** didn't show selective broadening for the cyclohexene ring inversion even at -95 °C in CH_2Cl_2 and four equivalent α -hydrogen atoms were observed for the cyclohexene ring. This suggests that the energy barrier for the cyclohexene ring inversion of these radical cations is very low.

Figure 11. First derivative ESR spectra of

(a) $\Delta^{4,9}$ -*cis-exo*-3,10-dithiatetracyclo[10.2.1.0.2,110^{4,9}]pentadecene radical cation, **39⁺**

(b) $\Delta^{3,8}$ -*trans*-2,9-dithiatricyclo[8.4.0.0^{3,8}]tetradecene radical cation, **35⁺**

(c) $\Delta^{3,8}$ -*cis*-2,9-dithiatricyclo[8.4.0.0^{3,8}]tetradecene radical cation, **36⁺**



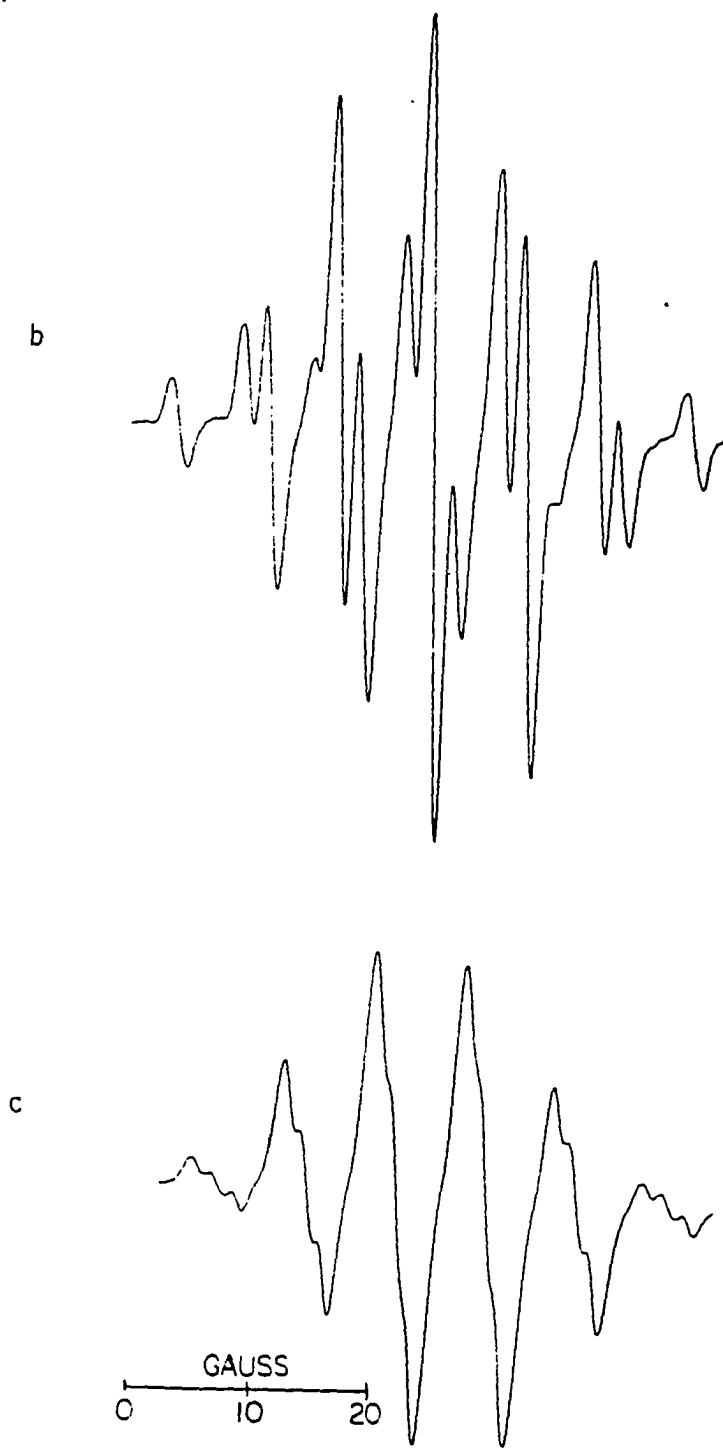


Figure 11. (continued)

4-Methyl-2,3-dihydro-1,4-dithiin **33** was oxidized in either $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$ or H_2SO_4 to give radical cation $33^{\cdot+}$ which gave a complicated ESR spectrum and showed line broadening corresponding to the expected ring flip above $-10\text{ }^\circ\text{C}$ (in H_2SO_4) with a coalescence temperature at $\sim 70\text{ }^\circ\text{C}$. No attempt was made to assign the hfsc (Figure 12).

2,3-Dihydro-1,4-dithiin radical cation was also prepared in the bicyclo[2.2.1]heptane system ($38^{\cdot+}$). The ESR spectrum observed for $38^{\cdot+}$ in H_2SO_4 changed with temperature below $70\text{ }^\circ\text{C}$ but was independent of temperature from 70 to $120\text{ }^\circ\text{C}$. At $100\text{ }^\circ\text{C}$, $38^{\cdot+}$ had $a^{\text{H}} = 5.0$ (1H), 3.6 (4H), 1.55 (4H) G, $g = 2.0075$ (Figure 13). The time-averaged methylene hydrogens were assigned as 3.6 G, the large coupling (5.0 G) was assigned to the *7-anti* hydrogen while the *5,6-exo* and the bridgehead hydrogens were assigned as 1.55 G. The large $a^{\text{H}}_{7\text{-anti}}/a^{\text{H}}_{\text{exo}}$ ratio (3.2) indicates the 2,3-dihydro-1,4-dithiin radical cation has a symmetrical SOMO.²⁶

1,4-Dithiepin radical cations

The previous success in the synthesis of 2,3-dihydro-1,4-dithiins stimulated an interest in utilizing the same methodology to synthesize derivatives of 1,4-dithiepin. However, treatment of α -chloro ketones with 1,3-propanedithiol in refluxing benzene with PTSA as catalyst failed to produce derivative of 1,4-dithiepin. Therefore, other routes were developed for this system. 2,3-Tetramethylene-1,4-dithiepin **42** was synthesized by basic hydrolysis of **41** followed by reaction of the dithiolate with 1,3-dibromopropane.

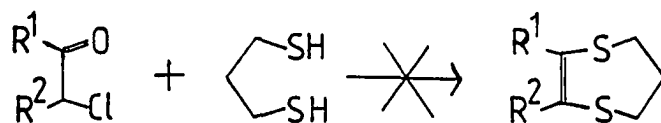


Figure 12. First derivative ESR spectra of 5-methyl-2,3-dihydro-1,4-dithiin radical cation,

33⁺.

(a) At -70 °C in $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$

(b) At 20 °C in H_2SO_4

(c) At 70 °C in H_2SO_4

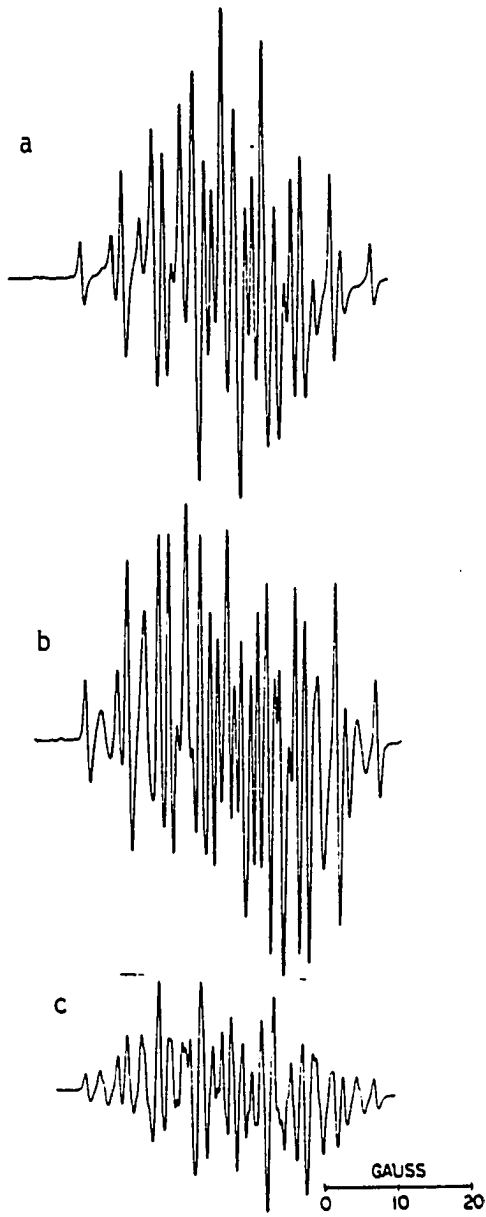
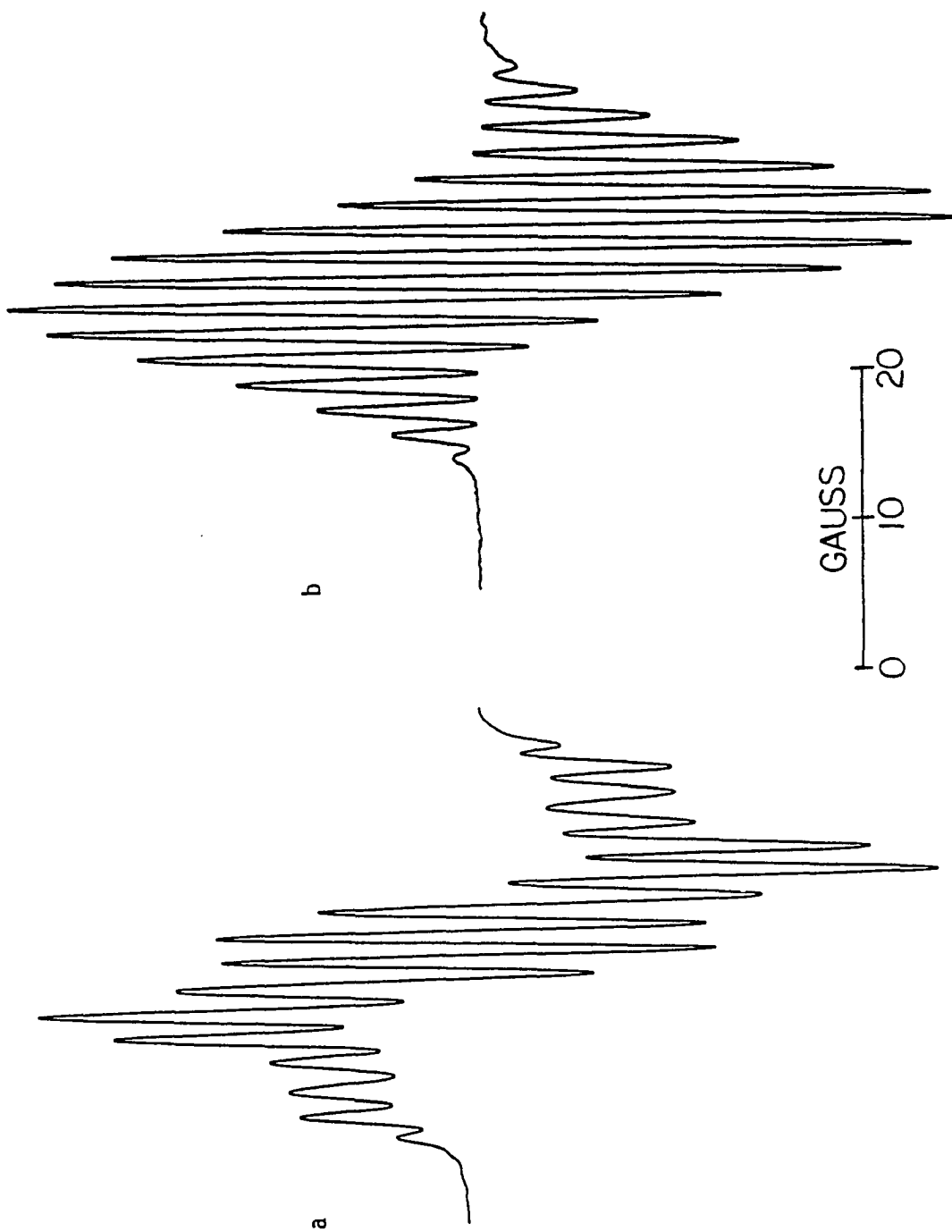
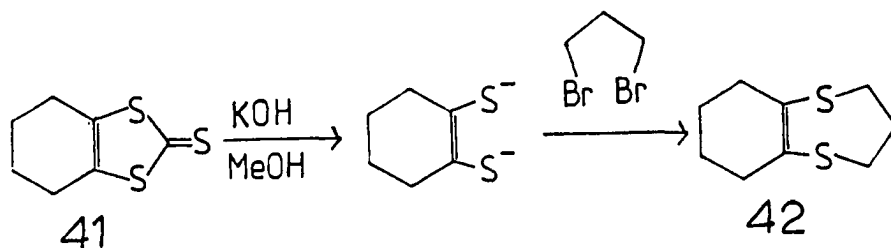


Figure 13. First derivative ESR spectra of $\Delta^{2,7}$ -3,6-dithiatricyclo[6.2.1.0^{2,7}]undecene radical cation, **38⁺**.

(a) At 25 °C in H₂SO₄

(b) At 100 °C in H₂SO₄





When **42** was dissolved in H_2SO_4 at room temperature, a complicated ESR spectrum for radical cation $\text{42}^{\cdot+}$ with selective line broadening was observed. The spectrum was too complicated to be analyzed, presumably due to the fact that β -methylene hydrogens of the cyclohexene ring also had a small hyperfine splitting. A poorly resolved spectrum was obtained for $\text{42}^{\cdot+}$ at -95°C in $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$ (Figure 14). It appeared that a simpler system had to be chosen to avoid complication from long range interactions. 2,3-Dimethyl-1,4-dithiepin **43** turned out to be an ideal candidate.

The synthesis and mechanism of formation of **43** is outlined in Scheme I. The second step involves a new type of carbocation rearrangement wherein the migration center is a sulfur atom. It is of interest that in this case the sulfur atom has a greater tendency than alkyl or hydrogen to migrate.

Scheme I.

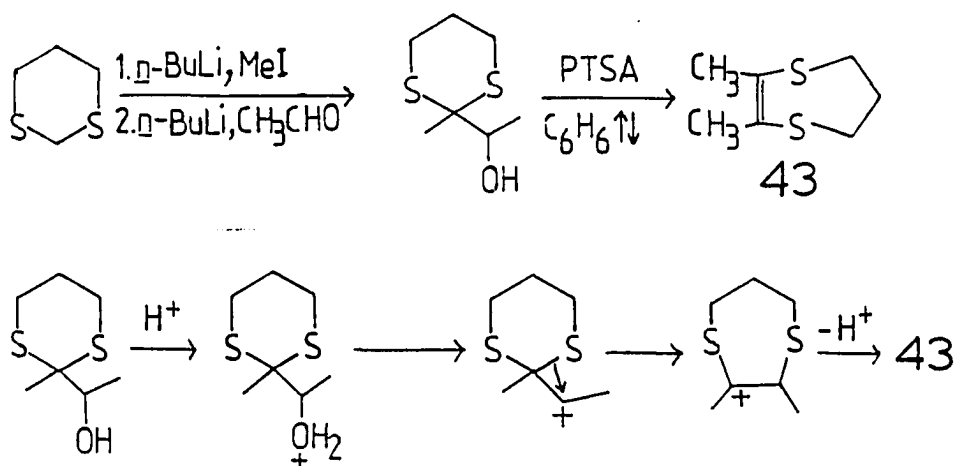
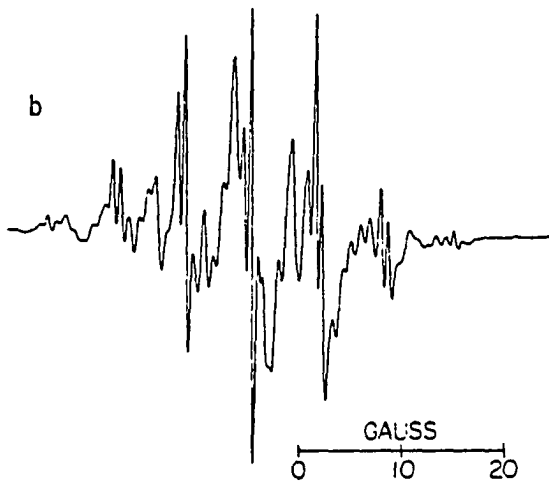
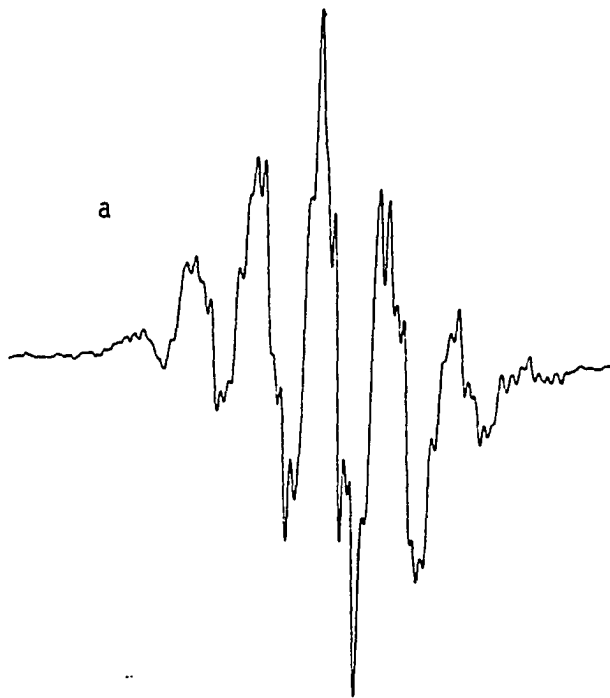


Figure 14. First derivative ESR spectra of 2,3-tetramethylene-1,4-dithiepin radical cation,

42⁺.

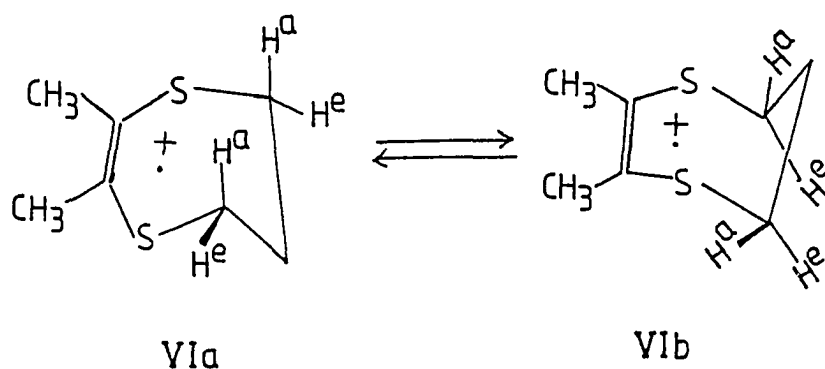
(a) At -95 °C in Al₂Cl₆/CH₂Cl₂

(b) At 25 °C in H₂SO₄



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Compound **43** gave a well-resolved ESR spectrum of a nonet of triplets ($a^H = 5.3$ (8H), 1.85 (2H) G) at -70 °C in Al_2Cl_6/CH_2Cl_2 (Figure 15). The spectrum can be easily explained by a frozen conformation with the two axial hydrogen atoms of the methylene groups (α to sulfur atoms) having the same hfsc as the methyl hydrogen atoms. In H_2SO_4 , 43^+ showed selective line broadening above -10 °C. The value of a^H (apparent) for the quasi-equatorial and quasi-axial hydrogen atoms were measured in the slow exchange mode to give $\Delta H^\ddagger = 5.8$ kcal/mol and $\Delta S^\ddagger = -9.5$ eu for the ring flip ($VIa \rightleftharpoons VIb$).



The radical cations 31^+ - 36^+ and 43^+ all have large $a^H_{axial}/a^H_{equatorial}$ ratios (~ 3) for the heterocyclic rings. The large ratios clearly indicate that for 2,3-dihydro-1,4-dithiin and 1,4-dithiepin radical cations, the hyperfine splitting of a hydrogen atom β to a sulfur atom with unpaired spin density arises mainly from an angle-dependent hyperconjugative interactions.

2.5-Dithiabicyclo[4.2.1]non-3-ene radical cation

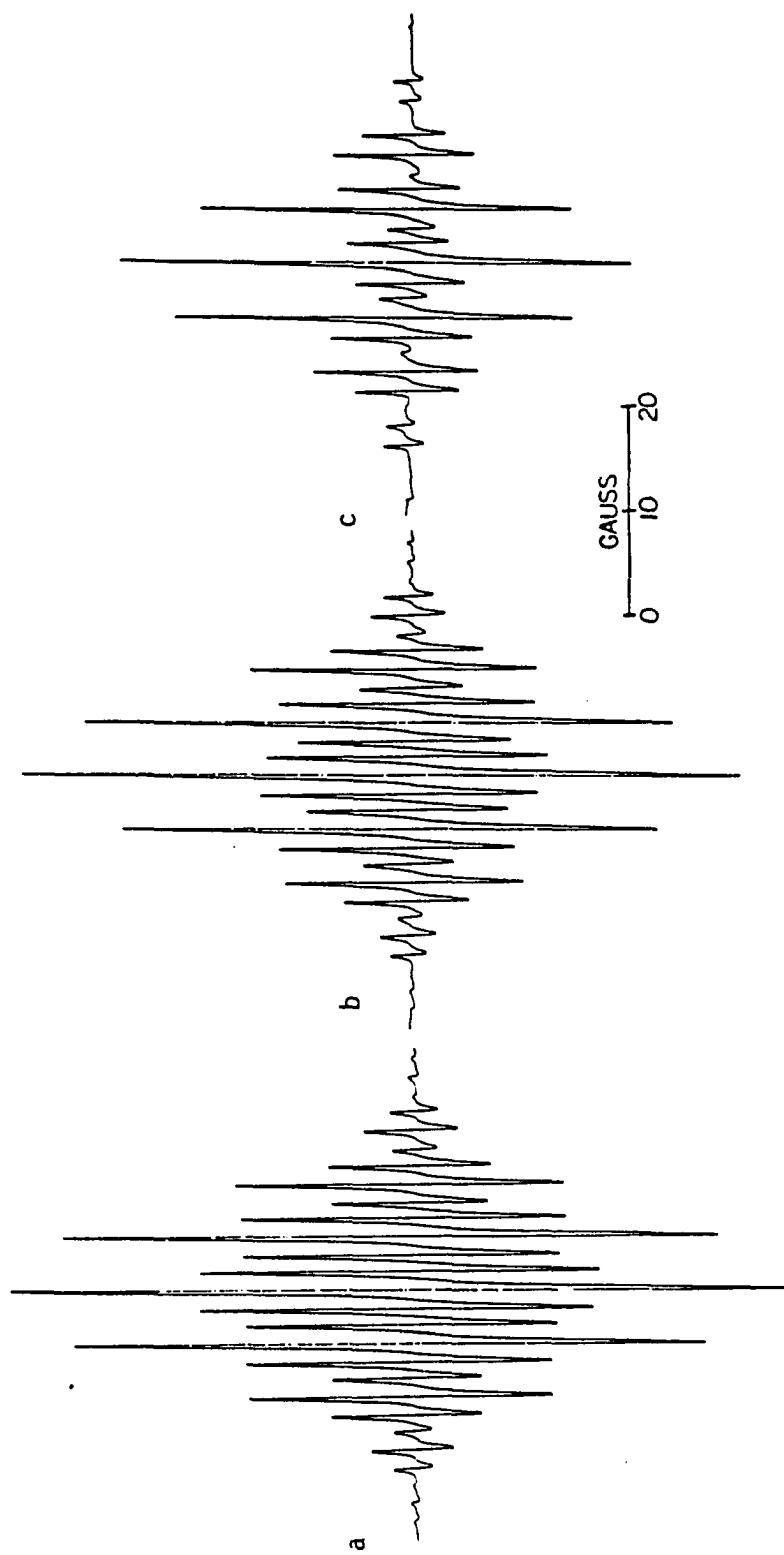
2,5-Dithiabicyclo[4.2.1]non-3-ene **44** was prepared by basic hydrolysis of **45**, followed by reaction of the dithiolate with *cis*-1,2-dichloroethylene. Compound **44** reacted with H_2SO_4 to form the 1,4-dithiin radical cation 46^+ ($a^H = 2.8$ (4H) G, $g = 2.0089$), but

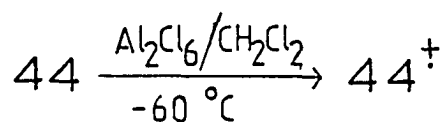
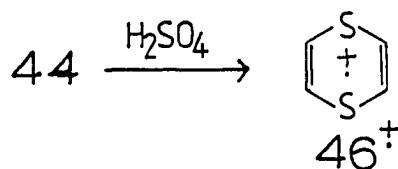
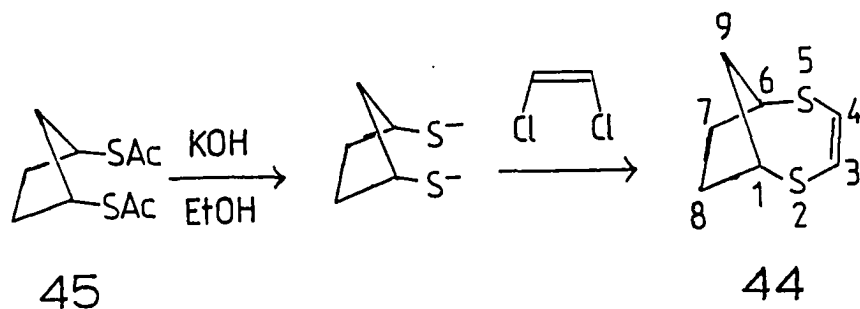
Figure 15. First derivative ESR spectra of 2,3-dimethyl-1,4-dithiepin radical cation, 43^+ .

(a) At $-70\text{ }^\circ\text{C}$ in $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$

(b) At $20\text{ }^\circ\text{C}$ in H_2SO_4

(c) At $60\text{ }^\circ\text{C}$ in H_2SO_4





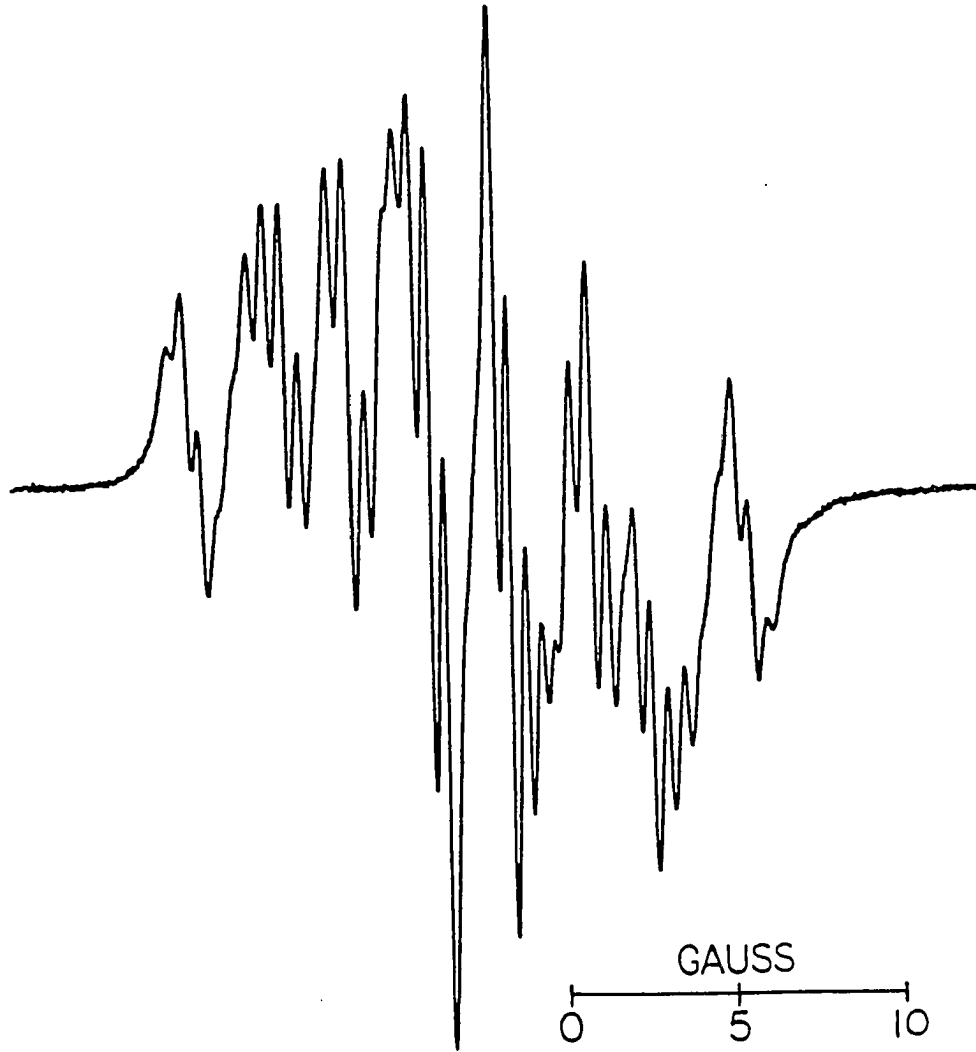
with $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$ at -60°C to form 44^+ ($a^{\text{H}} = 5.10$ (2H), 2.85 (2H), 1.80 (1H), 0.51 (3H) G, $g = 2.0099$) (Figure 16). The *anti*-hydrogen at C-9 is assigned the 1.8 G doublet splitting and the *syn*-hydrogen as 0.51 G. The vinyl hydrogens are assigned as the 2.85 G triplet splitting and the bridgehead hydrogens as 5.10 G by comparison with 31^+ and 32^+ . This leaves 0.51 G (2H) for the *exo* hydrogen atoms at C-7, 8 and a ratio of $a^{\text{H}}_{\text{anti}}/a^{\text{H}}_{\text{exo}}$ of 3.5.

The ESR spectrum of 44^+ shows that sulfur-centered radicals like carbon, oxygen, and nitrogen-center radicals are capable of showing sizable long range couplings. The large $a^{\text{H}}_{\text{anti}}/a^{\text{H}}_{\text{exo}}$ ratio (3.5) clearly indicates that the SOMO of 44^+ is symmetrical.²⁶

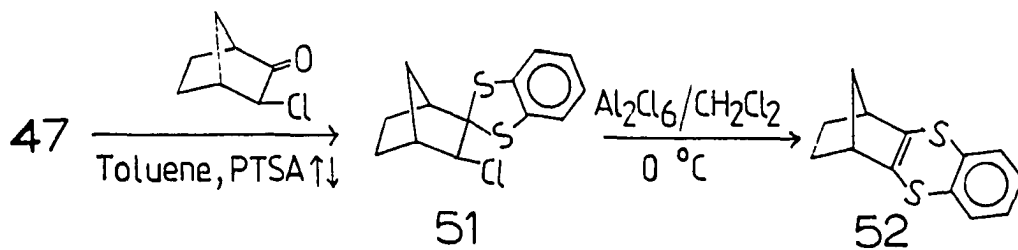
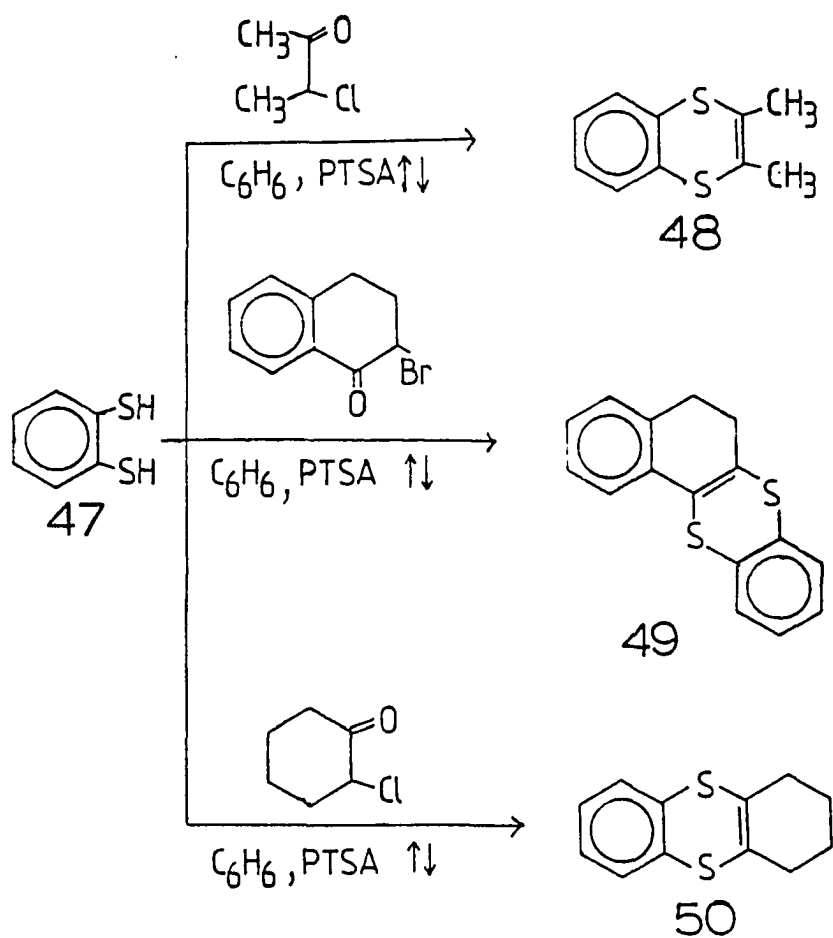
1,4-Dithiin radical cations

Benzo-derivatives of 1,4-dithiin could be synthesized by reaction of 1,2-benzenedithiol 47 with α -halo ketones. Thus, compounds 48-50 were synthesized by this

Figure 16. First derivative ESR spectrum of 2,5-dithiabicyclo[4.2.1]non-3-ene radical cation, **44⁺**

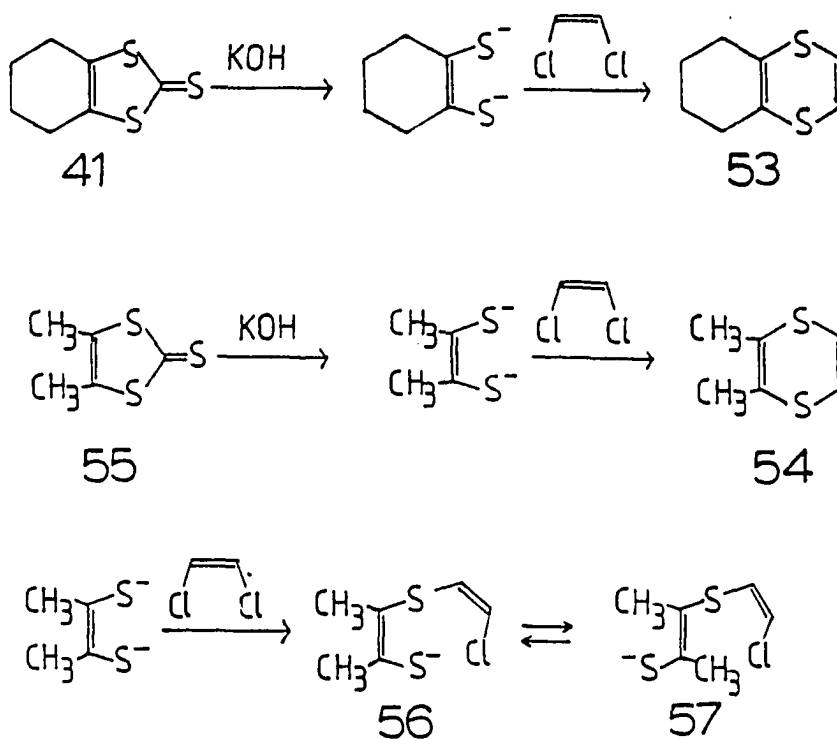


methodology. However, when 3-chloro-2-norbornanone was reacted with **47**, compound **51** was formed. In this case, Al_2Cl_6 was used to convert **51** to the 1,4-benzodithiin compound **52**.

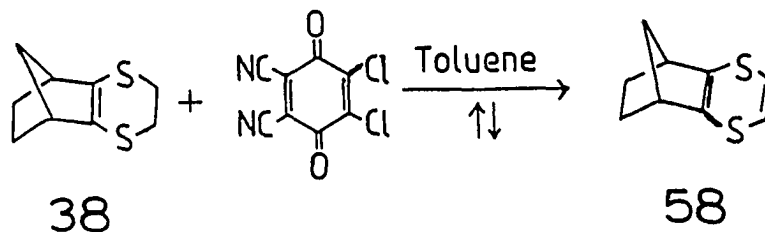


Another way to synthesize the unsymmetrical 1,4-dithiin **53** and **54** is described in Scheme II, in which **41** and **55** were hydrolyzed under basic conditions, and the dithiolates reacted with *cis*-1,2-dichloroethylene to form the corresponding 1,4-dithiins. For the synthesis of **54**, the yield was low (23%) due to the fact that the intermediate **56** could rearrange to the trans isomer **57**, which could react with another molecule of **57** to form an oligomer.

Scheme II.



A third method employed for synthesis of unsymmetrical 1,4-dithiin was the oxidation of the corresponding 2,3-dihydro-1,4-dithiin by 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ). Compound **58** was synthesized by this method.



Treatment of **49** with $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$ at -70°C gave a broad doublet ESR signal of 49^\ddagger ($a^{\text{H}} = 7.2\text{ G}$, $g = 2.0075$). In the temperature range from -60 to -40°C , line broadening was observed with a coalescence temperature at $\sim -50^\circ\text{C}$. At -30°C the signal became a triplet (3.8 G)(Figure 17). It is obvious that the line broadening is connected with the ring flip of the cyclohexene ring in 49^\ddagger . Although the combination of large line width and small a^{H} doesn't allow the measurement of ΔH^\ddagger for the ring inversion of 49^\ddagger , it is concluded that 49^\ddagger has a larger ΔH^\ddagger than 26^\ddagger , since 49^\ddagger shows selective line broadening over a narrower temperature range than 26^\ddagger .

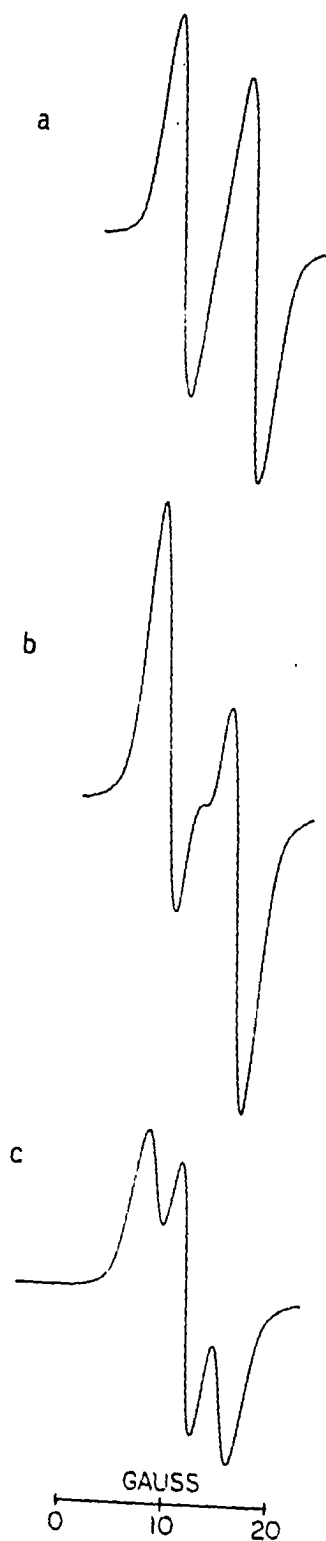
The unexpectedly high energy barrier for the ring inversion of the cyclohexene rings in both 26^\ddagger and 49^\ddagger is surprising. For simple cyclohexene rings, one would expect the barrier for ring inversion to be too low to be measured. As a matter of fact, no activation parameter has been reported for conformational equilibria of cyclohexene or its derivatives or for radicals containing the cyclohexadiene unit. An examination of a molecular model of 49^\ddagger indicates that in 49^\ddagger , ^1H and the lone pair of S^* are close enough to interact with each other. This interaction leads to a distortion of the planarity of the π system of the cyclohexene unit, and make the non-planar half-chair conformation of cyclohexene ring energetically more favorable than the plan transition state in which a strong interaction between ^1H and the lone pair of S^* exists (see VII). This interaction also explains why ΔH^\ddagger for 49^\ddagger is larger than for 26^\ddagger since 49^\ddagger has a larger (six-member) heterocyclic ring and the lone pair S^* is more extended. Thus, the interaction with ^1H is larger for 49^\ddagger and this larger interaction results in higher value for ΔH^\ddagger .

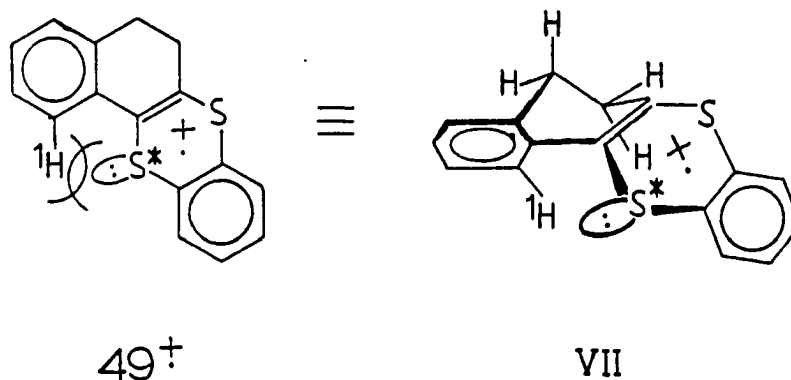
Figure 17. First derivative ESR spectra of 4,5-dihydronaphtho[1,2-d]-1,4-benzodithiin radical cation, 49^+ .

(a) At $-70\text{ }^\circ\text{C}$ in $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$

(b) At $-50\text{ }^\circ\text{C}$ in $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$

(c) At $-30\text{ }^\circ\text{C}$ in $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$

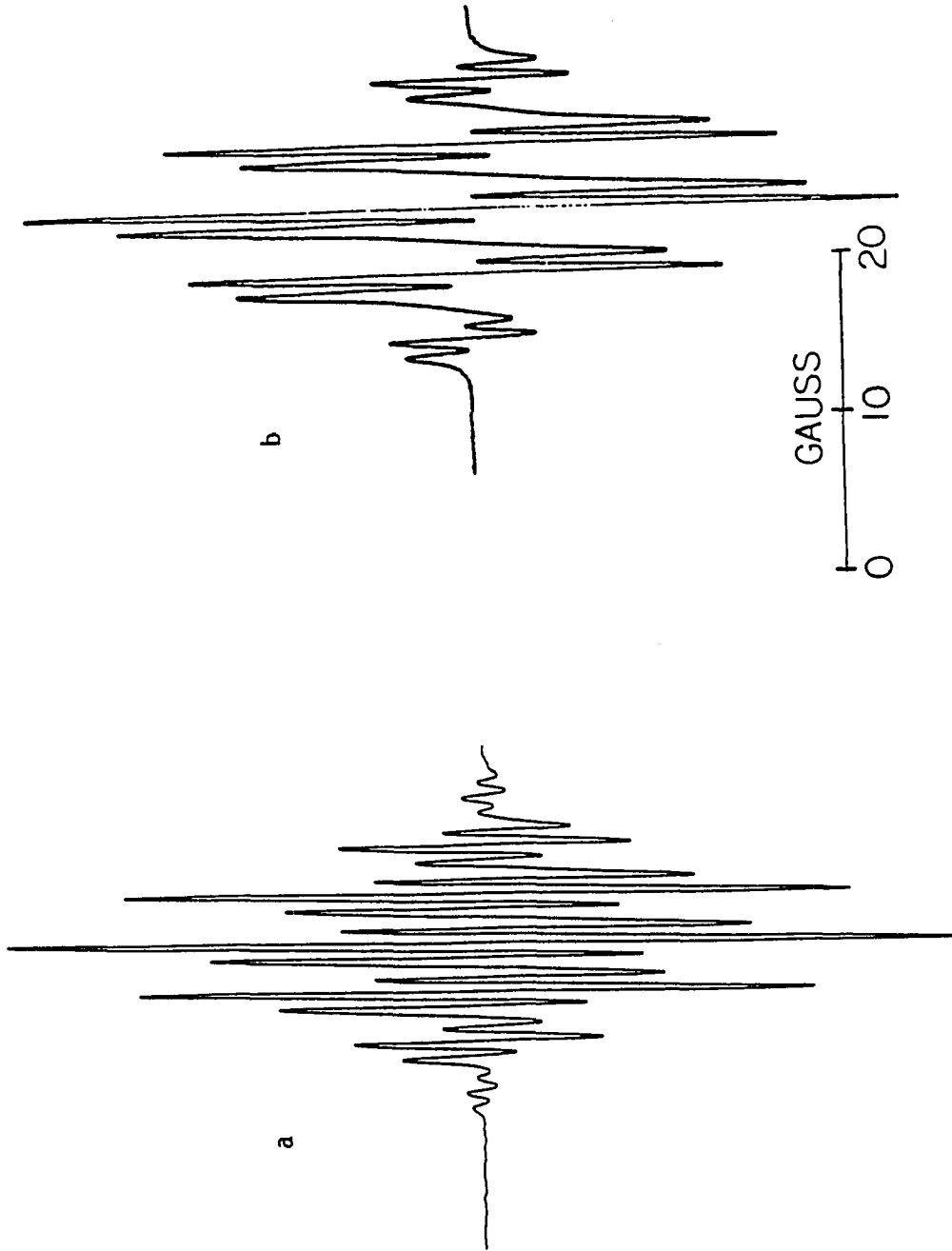




Compounds, 48, 50, 52-54, and 58 all gave their corresponding radical cations when treated with $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$ (Table 6, Figure 18). Surprisingly, like the 2,3-dihydro-1,4-dithiin radical cation 34⁺-36⁺ and 39⁺, no selective line broadening corresponding to the cyclohexene ring inversion was observed for 50⁺, 53⁺ and 22⁺ even at -95 °C. The barrier to cyclohexene ring flip seems to be a function of the C=C-S angle with larger angles giving rise to a lower barrier. The non-bonded interaction between the π system and the cyclohexene α -methylene hydrogen atoms is believed to be responsible for the low barrier. Since the 3p orbital of the sulfur atom used to form the π system is large in size, if the C=C-S angle is also large, the non-bonded interaction between the π system and the cyclohexene α -methylene hydrogens could be sizable. In the half chair conformation VIIIa the π system interacts with all four cyclohexene α -methylene hydrogens, while in the boat form transition state VIIIb, two of the four α -methylene hydrogens lie in the nodal plane of the π system and have a weaker interaction with the π system. Thus, it is concluded that the non-bonded interaction between the cyclohexene α -methylene hydrogens and the π system (of either 1,4-dithiin or 2,3-dihydro-1,4-dithiin) destabilizes the ground state more than the transition state for the ring flip of the cyclohexene ring and as a result of this interaction, 34⁺-36⁺, 39⁺, 50⁺, 53⁺, and 22⁺ have low energy barriers for the cyclohexene ring inversion.

Figure 18. First derivative ESR spectra of

- (a) 2,3-dimethyl-1,4-benzodithiin radical cation, **48⁺**
- (b) 2,3-tetramethylene-1,4-benzodithiin radical cation, **50⁺**
- (c) 2,3-(1,3-cyclopentanediy1)-1,4-benzodithiin radical cation, **52⁺**
- (d) 2,3-tetramethylene-1,4-dithiin radical cation, **53⁺**
- (e) 2,3-dimethyl-1,4-dithiin radical cation, **54⁺**
- (f) $\Delta^{2,7}, \Delta^{4,5}$ -3,6-dithiatricyclo[6.2.1.0^{2,7}]undecadiene radical cation, **58⁺**



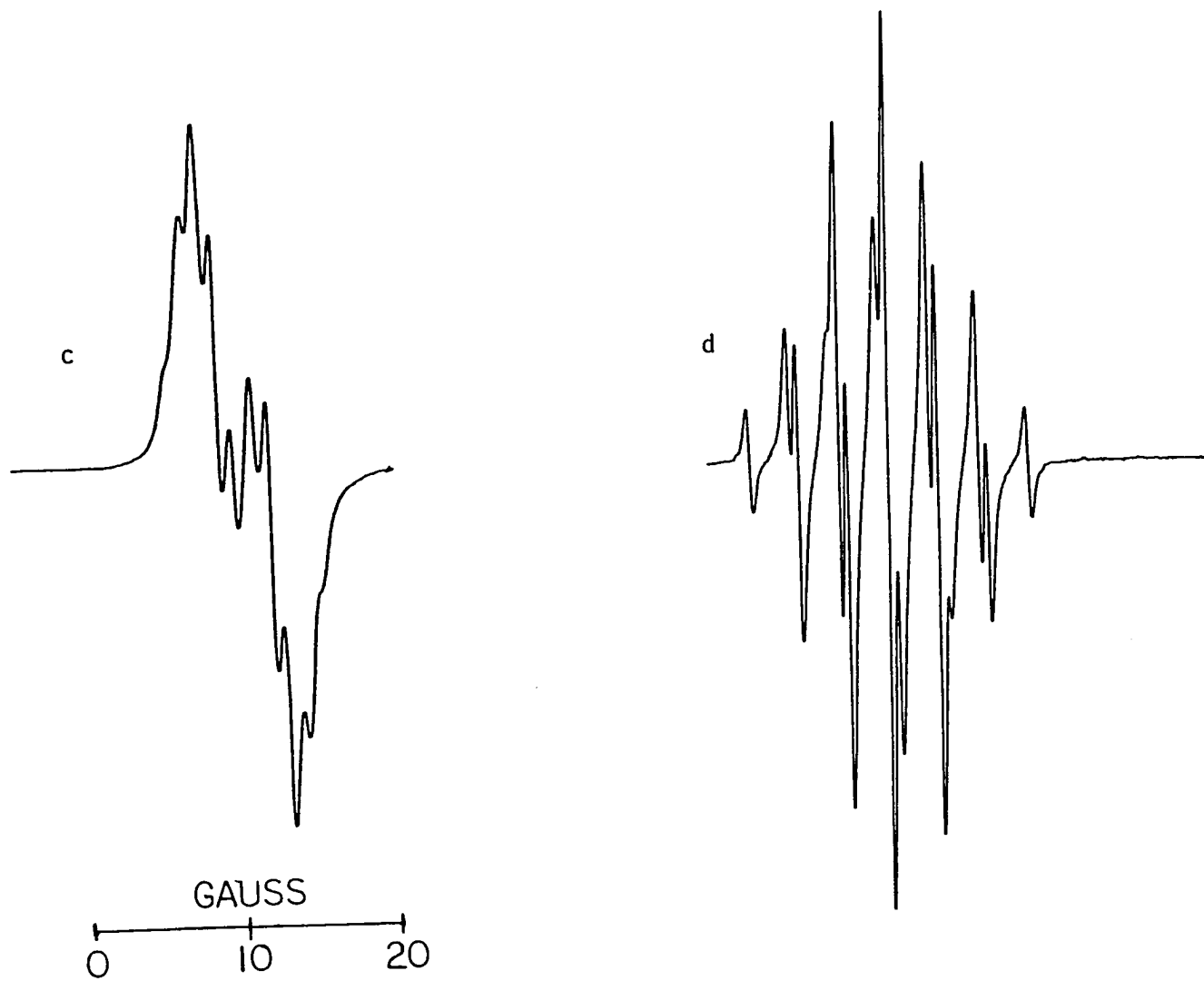


Figure 18. (continued)

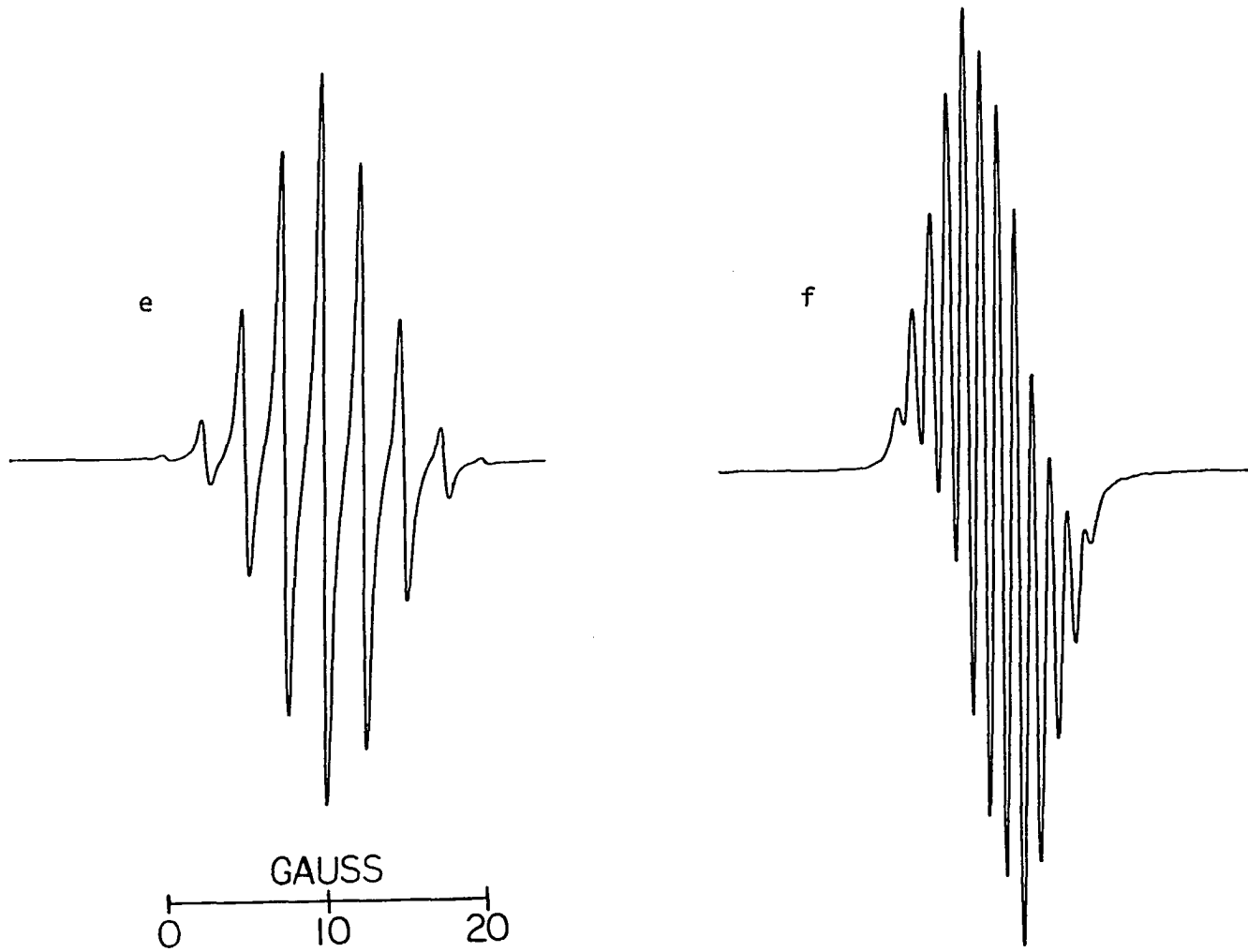
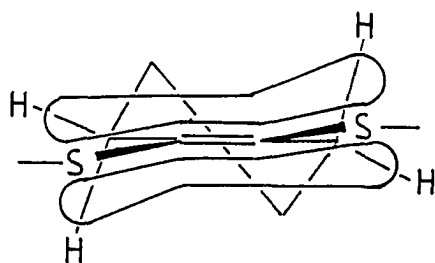


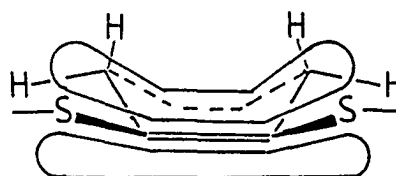
Figure 18. (continued)

Table 6. Values of a^H and g for 1,4-dithiin radical cations 50^+ , 52^+ - 54^+ , and 58^+

Radical Cations	a^H (G)	g
48^+	3.9 (6H), 0.9 (2H)	2.0081
50^+	4.1 (4H), 0.95 (2H)	2.0082
52^+	3.6 (1H), 1.15 (6H)	2.0076
53^+	3.2 (4H), 2.6 (2H)	2.0088
54^+	2.55 (8H)	2.0086
58^+	3.45 (1H), 2.10 (2H), 1.05 (4H)	2.0082



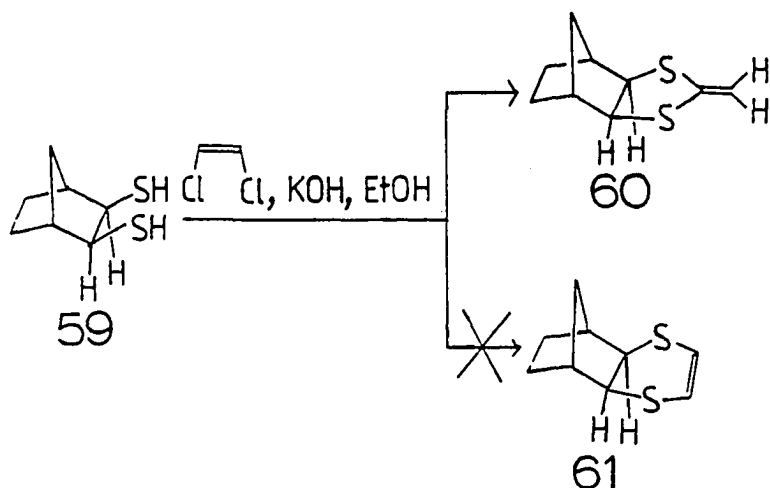
VIIIa



VIIIb

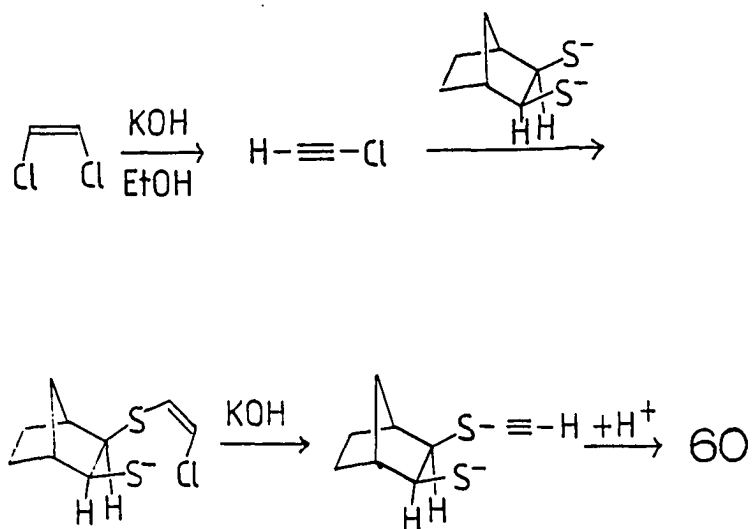
Both 52^+ and 58^+ have large doublet couplings which were assigned to the 7-*anti* hydrogens, and the a^H_{7-anti}/a^H_{exo} ratios are ~ 3 . These ratios indicate that both 1,4-dithiin and 1,4-benzodithiin radical cations have a symmetrical SOMO.

Reaction of *exo-cis*-bicyclo[2.2.1]heptane-2,3-dithiol **59** with *cis*-1,2-dichloroethylene under basic condition gave rise to a rather unexpected product **60** instead of the expected product **61**. The formation of **60** could be explained by a stepwise

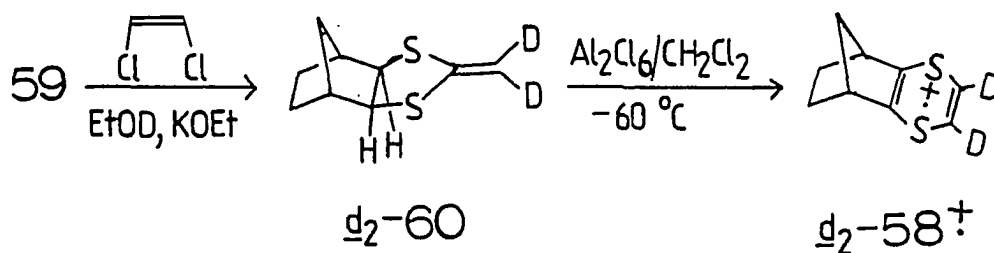


mechanism²⁸ (Scheme III). In the final step, owing to steric considerations, the sulfur anion may attach preferentially the *endo* position of the triple bond to form the five member ring product **60**.

Scheme III

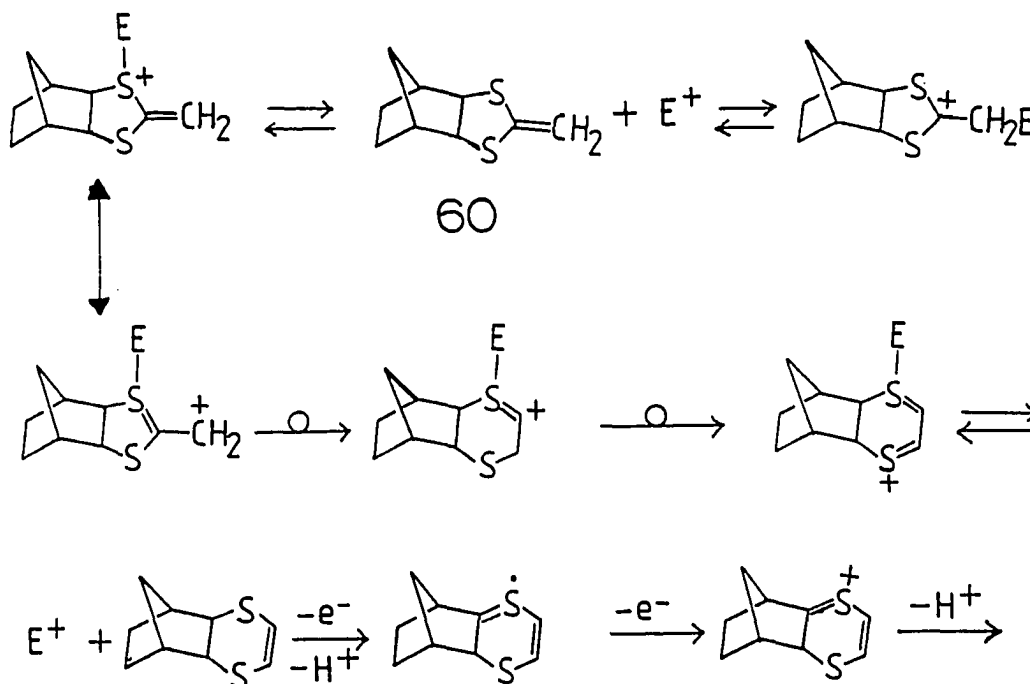


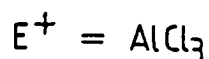
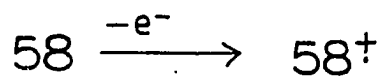
Treatment of **60** with $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$ at -60°C produced the rearrangement product **58⁺**. The di-deuterated compound d_2 -**60** was made, and was treated with $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$ at -60°C to give a broad doublet ESR spectrum. The hyperfine splitting pattern seems to



indicate that both of the deuterium atoms end up in the dithiin ring after the oxidative rearrangement (Figure 19). Scheme IV describes a proposed mechanism for the formation of **58⁺**.

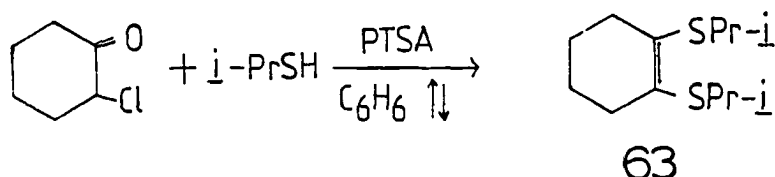
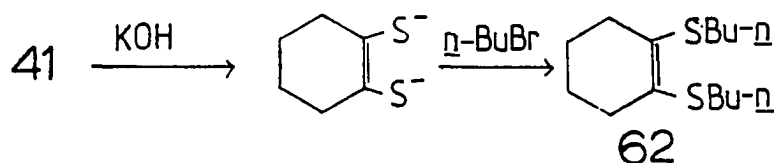
Scheme IV





1,2-Bis(alkylthio)cyclohexene radical cations

1,2-Bis(alkylthio)cyclohexene **62** was synthesized by reaction of 4,5-tetramethyl-1,3-dithiole-2-thione **41** with base followed by *n*-butyl bromide. 1,2-Bis(isopropylthio)cyclohexene **63** was synthesized by reacted isopropyl thiol with 2-chlorocyclohexanone.



Compounds **62** and **63** were oxidized by Al_2Cl_6/CH_2Cl_2 to form $62^{\cdot+}$ and $63^{\cdot+}$, respectively. Both $62^{\cdot+}$ and $63^{\cdot+}$ possessed the cyclohexene ring and were expected to display temperature dependent ESR spectra from the conformation equilibria involving the half-chair cyclohexene conformers.²⁷ Indeed, $62^{\cdot+}$ ($g = 2.0082$) gave a coalescence temperature of $-70\text{ }^\circ\text{C}$ and a frozen conformation at $-95\text{ }^\circ\text{C}$ with $a^H = 14.2$ (2H), 6.8 (2H), 5.8 (4H) G (Figure 20). The line broadening was measured in the fast exchange mode to

Figure 19. First derivative ESR spectrum of $\Delta^{2,7}, \Delta^{4,5}$ -4,5-dideutero-3,6-dithiatricyclo[6.2.1.0^{2,7}]undecadiene radical cation, d_2 -58⁺

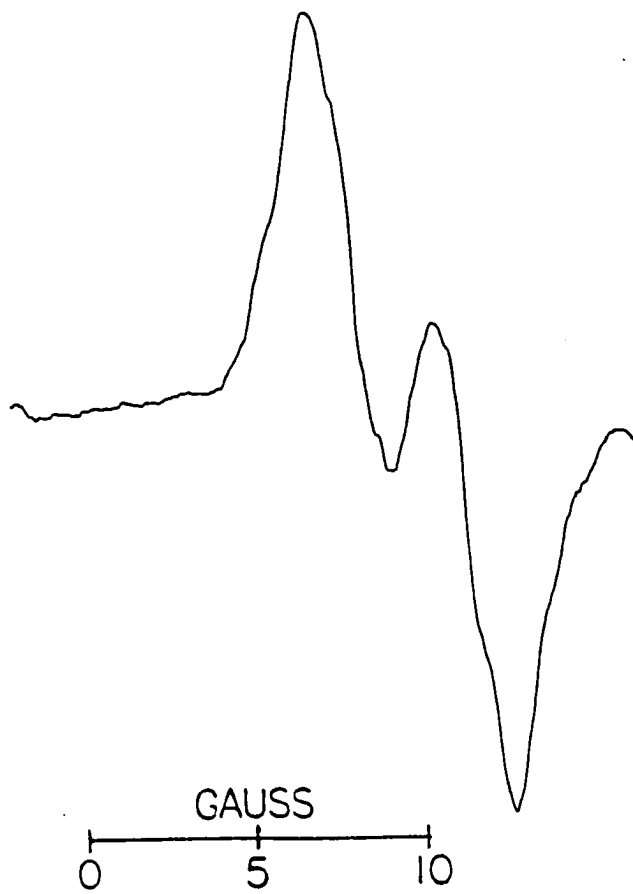


Figure 20. First derivative ESR spectra of 1,2-bis(*n*-butylthio)cyclohexene radical cation,

62⁺.

(a) At -95 °C in Al₂Cl₆/CH₂Cl₂

(b) At -70 °C in Al₂Cl₆/CH₂Cl₂

(c) At -20 °C in Al₂Cl₆/CH₂Cl₂



give $\Delta H^\ddagger = 5.6$ kcal/mol and $\Delta S^\ddagger = 3.5$ eu for 62^\ddagger (see Experimental section). The species 62^\ddagger ($g = 2.0080$) gave a time averaged spectrum at -20 °C with $a^H = 3.3$ (2H), 9.9 (4H) G (Figure 21), and showed selective line broadening below -20 °C. The line broadening was measured in the fast exchange mode. A much lower barrier ($\Delta H^\ddagger = 2.8$ kcal/mol, $\Delta S^\ddagger = -8.8$ eu) was calculated for 63^\ddagger (see Experimental section).

The size of the R group seems to affect the barrier of cyclohexene ring flip. For 1,2-bis(alkylthio)cyclohexene radical cation, there are three possible conformation, of which only IXa is relatively free of steric repulsion. Therefore, IXa should be the most stable conformer for 1,2-bis(alkylthio)cyclohexene. In the half-chair conformation IXa', the R groups interact with all four methylene hydrogens, while in the boat form transition state IXa'', the R groups interact with only two hydrogens. As a result of these interactions, the energy gap between the transition state and ground state is smaller for a bulky R group. Since the isopropyl group is more bulky than the *n*-butyl group, the steric interaction in the ground state of 63^\ddagger is larger than in 62^\ddagger . Therefore, the ΔH^\ddagger for ring flip of 63^\ddagger is smaller than the ΔH^\ddagger for ring flip of 62^\ddagger .

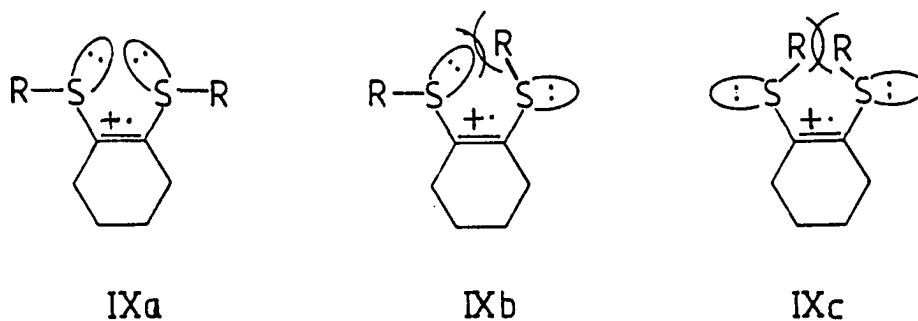
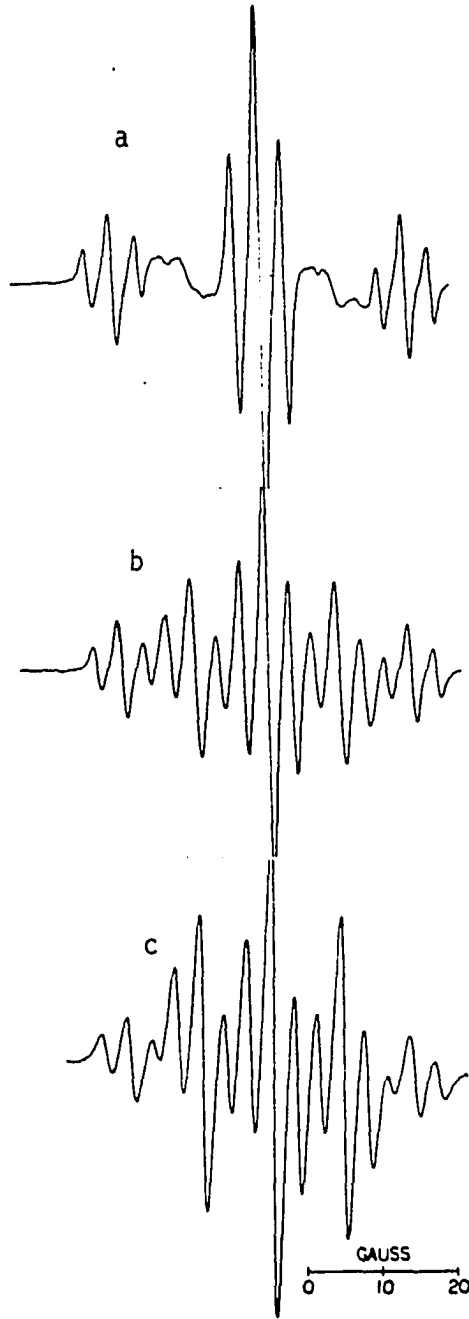


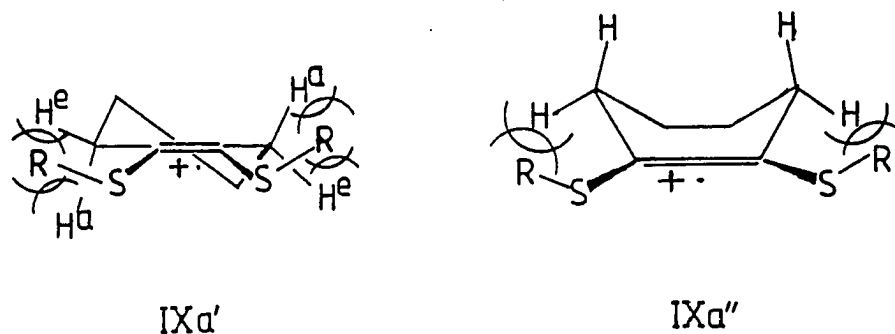
Figure 21. First derivative ESR spectra of 1,2-bis(isopropylthio)cyclohexene radical cation, **63⁺**.

(a) At -95 °C in $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$

(b) At -70 °C in $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$

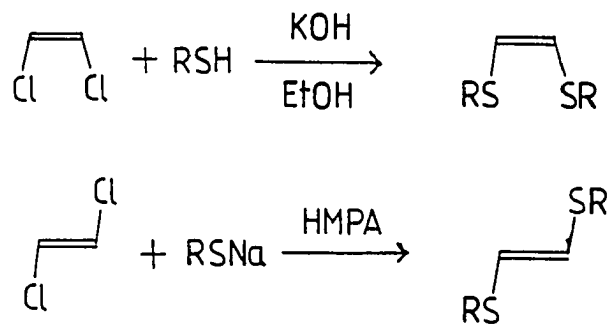
(c) At -20 °C in $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$





1,2-Bis(alkylthio)ethylene and 2,3-Bis(alkylthio)-2-butene radical cations

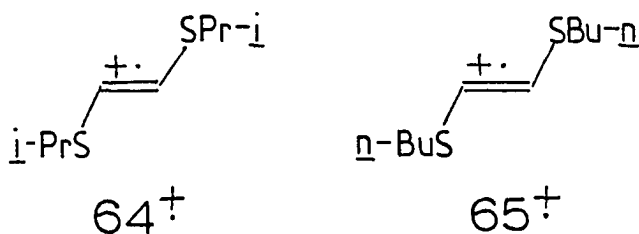
cis-1,2-Bis(alkylthio)ethylenes were synthesized by reaction of *cis*-1,2-dichloroethylene with alkylthiolates²⁸ in ethanol, while the *trans* isomers were made by reaction of *trans*-1,2-dichloroethylene with alkylthiolates in hexamethylphosphoric triamide (HMPA)²⁹.



When *cis*-1,2-bis(isopropylthio)ethylene was treated with Al_2Cl_6 in CH_2Cl_2 at -60°C no detectable ESR signal was observed, but when the mixture was warmed to 0°C , a weak pentet of 64^\ddagger ($a^{\text{H}} = 3.9 \text{ G}$, $g = 2.0099$) was observed. Treatment of *trans*-1,2-bis(isopropylthio)ethylene with Al_2Cl_6 in CH_2Cl_2 at below 0°C gave the same pentet ESR

signal but with a much stronger intensity. Treatment of *cis*-1,2-bis(*n*-butylthio)ethylene with Al_2Cl_6 in CH_2Cl_2 at below 0°C yielded a weak heptet of 65^\ddagger ($a^{\text{H}} = 4.4\text{ G}$) with $g = 2.0100$, while *trans*-1,2-bis(*n*-butylthio)ethylene gave the same but stronger signal under the reactions condition (Figure 22).

The above results seem to indicate that the signals observed were *trans*-1,2-bis(alkylthio)ethylene radical cations. Apparently, the *cis* isomers do not give stable radical cations in $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$. The *cis* isomers may first rearrange to the *trans* isomers and then be oxidized to form 64^\ddagger and 65^\ddagger , or they may be oxidized to form *cis* radical cations, which are not persistent and rearrange to the more stable *trans* radical cations.



There are three possible conformations for *trans*-1,2-bis(alkylthio)ethylene radical cation Xa-Xc. For relatively large R groups such as isopropyl or *n*-butyl, it seems that Xa is the most stable conformer, and our results provide no evidence for the existence of more than one isomer.

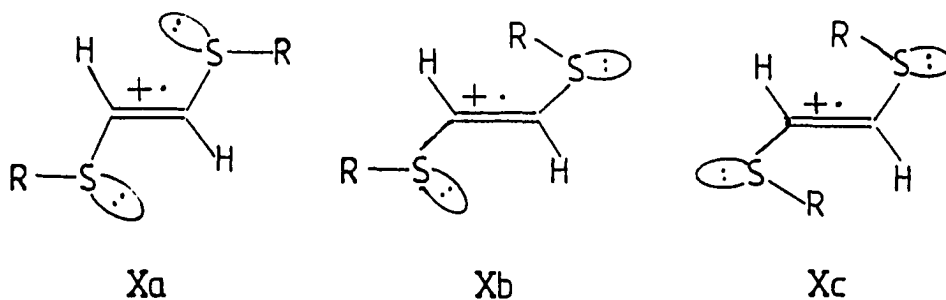
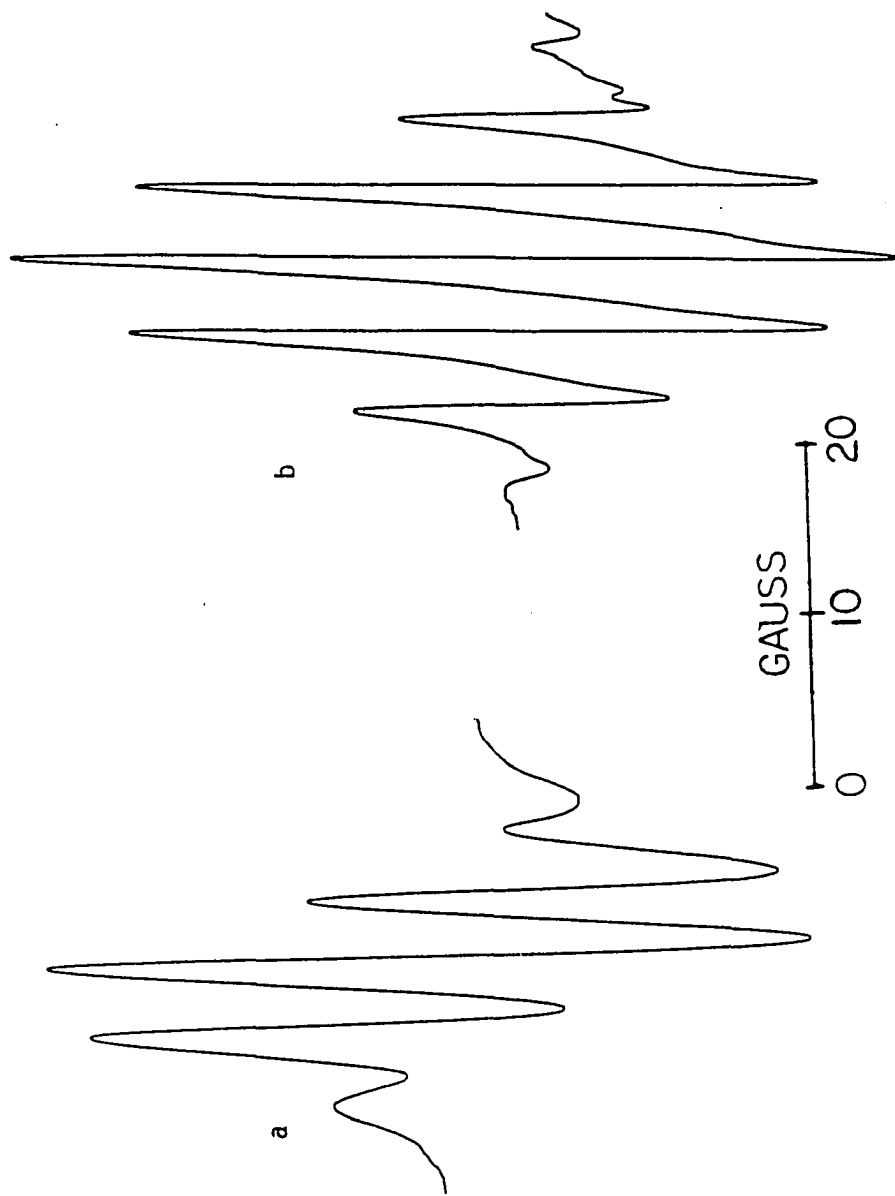


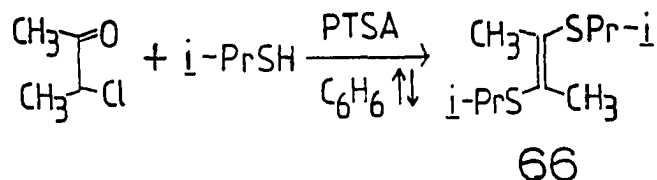
Figure 22. First derivative ESR spectra of

(a) *trans*-1,2-bis(isopropylthio)ethylene radical cation, 64⁺

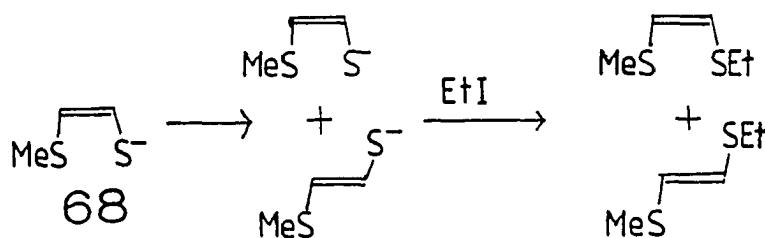
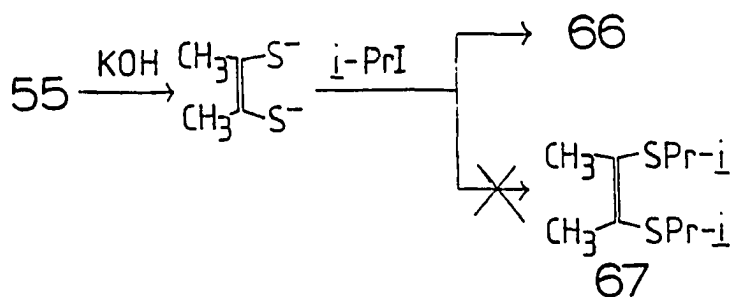
(b) *trans*-1,2-bis(*n*-butylthio)ethylene radical cation, 65⁺

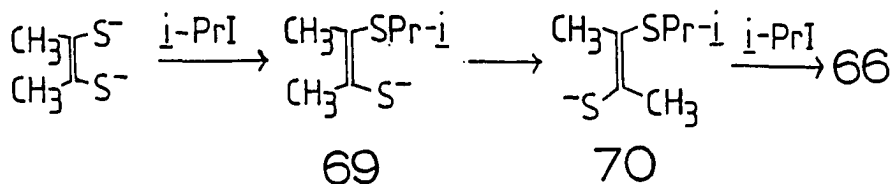


Reaction of 3-chlorobutanone with isopropyl thiol afforded a single isomer which was assigned as the thermodynamically most stable product, *trans*-2,3-bis(isopropylthio)-2-butene **66**. Compound **66** was oxidized by Al_2Cl_6 in CH_2Cl_2 to form $\mathbf{66}^+$ ($a^{\text{H}} = 5.1$ (6H),

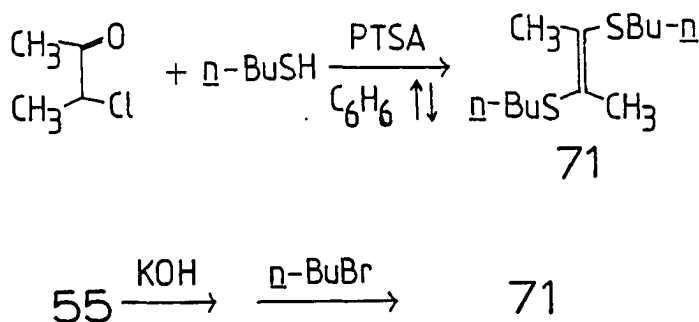


3.6 (2H) G, $g = 2.0085$). It was hoped that the *cis* isomer **67** could be synthesized and its oxidation could be carried out to see if it could give the *cis* radical cation $\mathbf{67}^+$. In this regard, **55** was reacted with base and then with isopropyl iodide. Unfortunately, the single isomer formed was identical with **66**. The *trans* product **66** was not really an unexpected product, since it is reported in the literature that²⁹ anions having structures such as **68** rearrange to the *trans* isomers. Therefore, it is logical to assume that the anion intermediate **69** rearranges to form **70** exclusively. As a result of this rearrangement, **66** was the only isomer formed.





Similarly, reaction of *n*-butyl thiol with 3-chlorobutanone yielded a single isomer which was assigned as *trans*-2,3-bis(*n*-butylthio)-2-butene, **71**. Compound **71** was oxidized by Al₂Cl₆ in CH₂Cl₂ at -60 °C to give **71**⁺ which had $a^{\text{H}} = 5.1$ (6H), 6.3 (4H) G and $g = 2.0088$ (Figure 23).



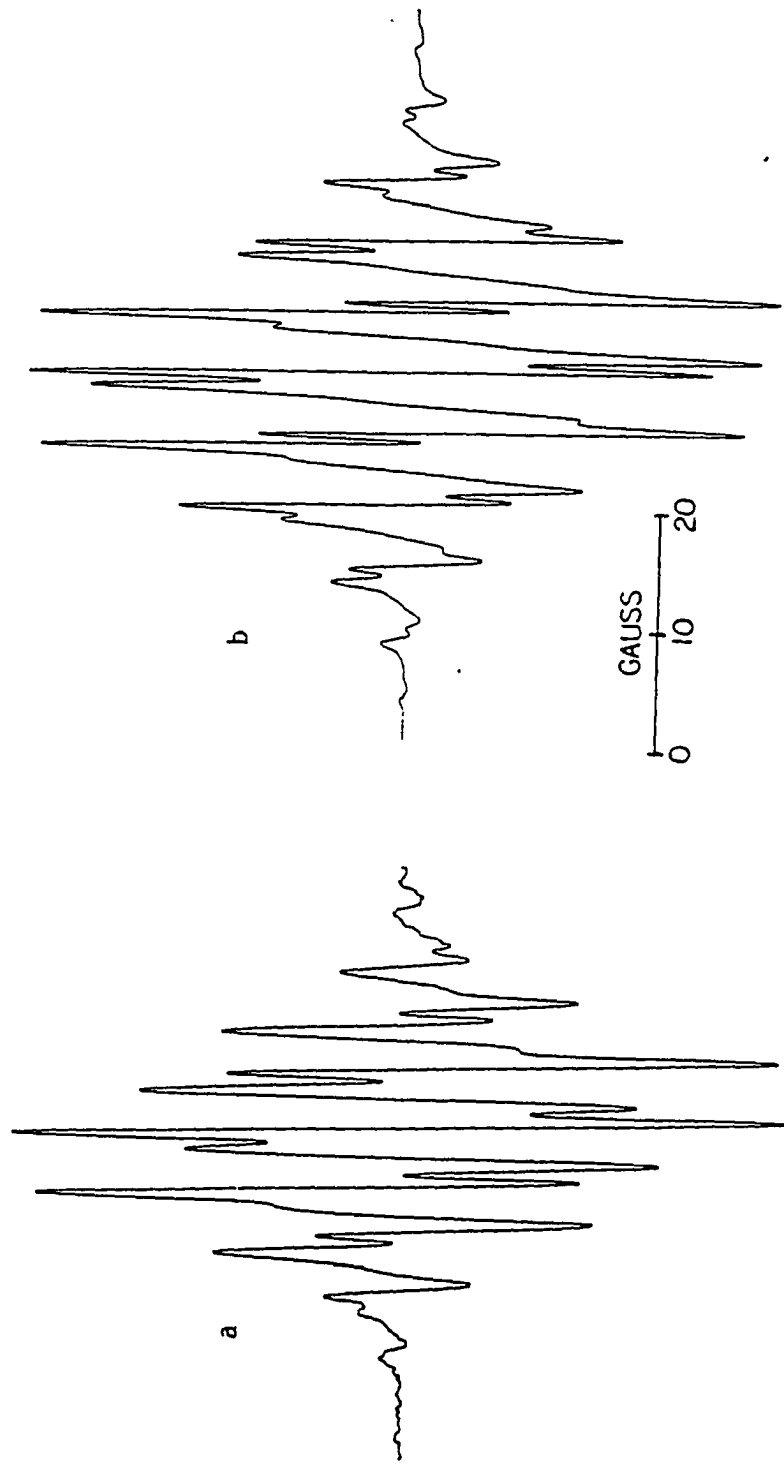
Formation of radical cations by rearrangement reactions

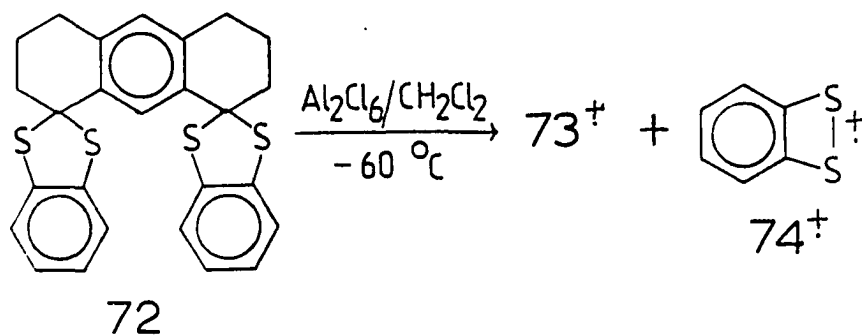
1,2-Dithioethylene derivatives Christopfel and Miller³⁰ recently reported the synthesis of **72**. X-ray crystallography showed that two benzodithiole rings in **72** were nearly parallel to each other. The previous success in generation of benzodithiole radical cations **27**⁺-**30**⁺ suggested that **72** could be a good system for studying intramolecular electron transfer between the two benzodithiole rings. When **72** was treated with Al₂Cl₆/CH₂Cl₂ at -70 °C, a doublet ESR signal due to **73**⁺ ($a^{\text{H}} = 5.7$ G, $g = 2.0077$) along with benzodithiete radical cation **74**⁺ were formed. Upon warming the sample to -30 °C, the signal assigned to **73**⁺ changed into a poorly resolved triplet ($a^{\text{H}} = 3.0$ G). The entire

Figure 23. First derivative ESR spectra of

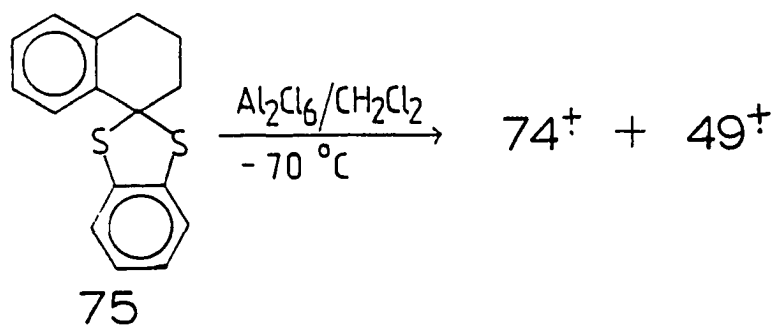
(a) *trans*-2,3-bis(isopropylthio)-2-butene radical cation, **66⁺**

(b) *trans*-2,3-bis(*n*-butylthio)-2-butene radical cation, **71⁺**





process was reversible (Figure 24). It was difficult to judge whether the temperature dependency of the ESR spectrum of **73⁺** was connected with conformation motion or intramolecular electron transfer between the two benzodithiophene rings. For comparison, **75** was synthesized and treated with $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$ at $-70\text{ }^\circ\text{C}$. The two known radical cations



74⁺ and **49⁺** were formed. There was no evidence that **75⁺** could be observed. The above result indicated that **75⁺** is not a persistent radical cation. Once formed, apparently **75⁺** decomposes and rearranges to form **74⁺** and **49⁺**. Assisted by this result, **73⁺** was assigned as the rearrangement product of **72** possessing a 1,4-benzodithiin unit.

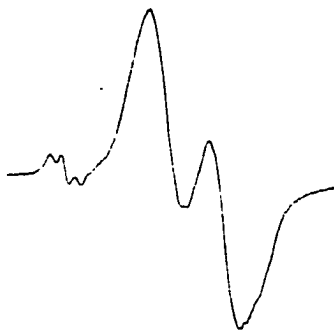
Figure 24. First derivative ESR spectra of radical cation **73⁺** (right) and benzodithiete radical cation **74⁺** (left), produced by treatment of compound **72** with $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$ below $-30\text{ }^\circ\text{C}$.

(a) At $-70\text{ }^\circ\text{C}$

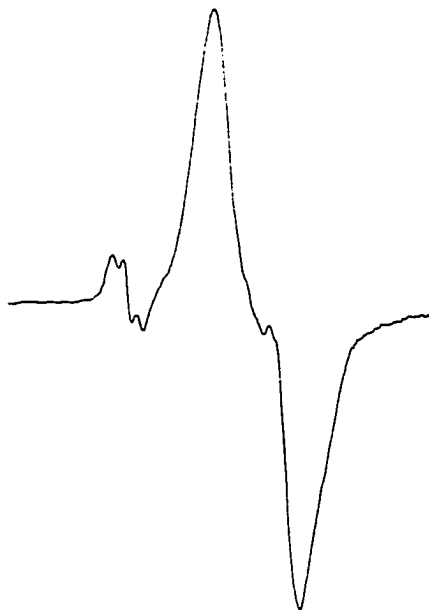
(b) At $-50\text{ }^\circ\text{C}$

(c) At $-30\text{ }^\circ\text{C}$

a

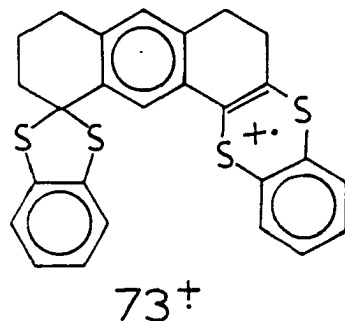


b



c





The discovery of the decomposition of **75** to **74⁺** and the rearrangement of **75** to **49** (observed as **49⁺**) raised the question whether this rearrangement was general and applicable to other systems. It turned out that this rearrangement is indeed a general rearrangement. When the benzodithiole derivative **76** was treated with $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$, **74⁺** and **50⁺** were formed. Treatment of **77** with $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$ produced **77⁺** along with **48⁺**, with **77⁺** as the predominant species. If the oxidation was carried out in concentrated H_2SO_4 **48⁺** and **74⁺** were formed with **48⁺** as the predominant species (Figure 25).

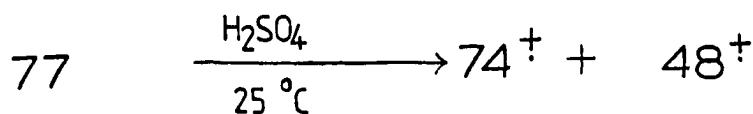
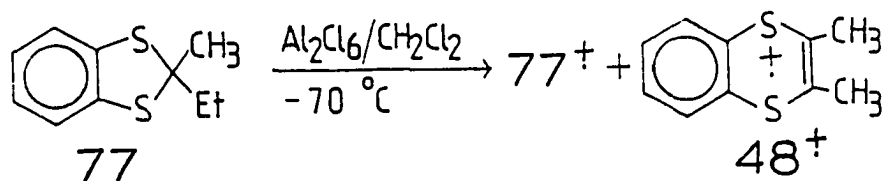
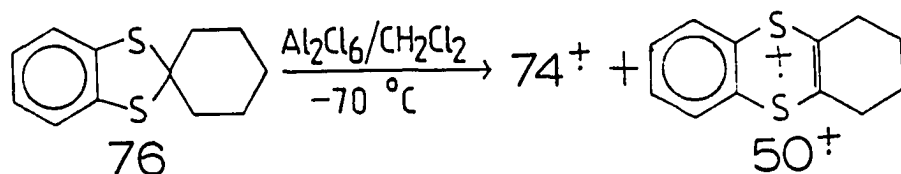
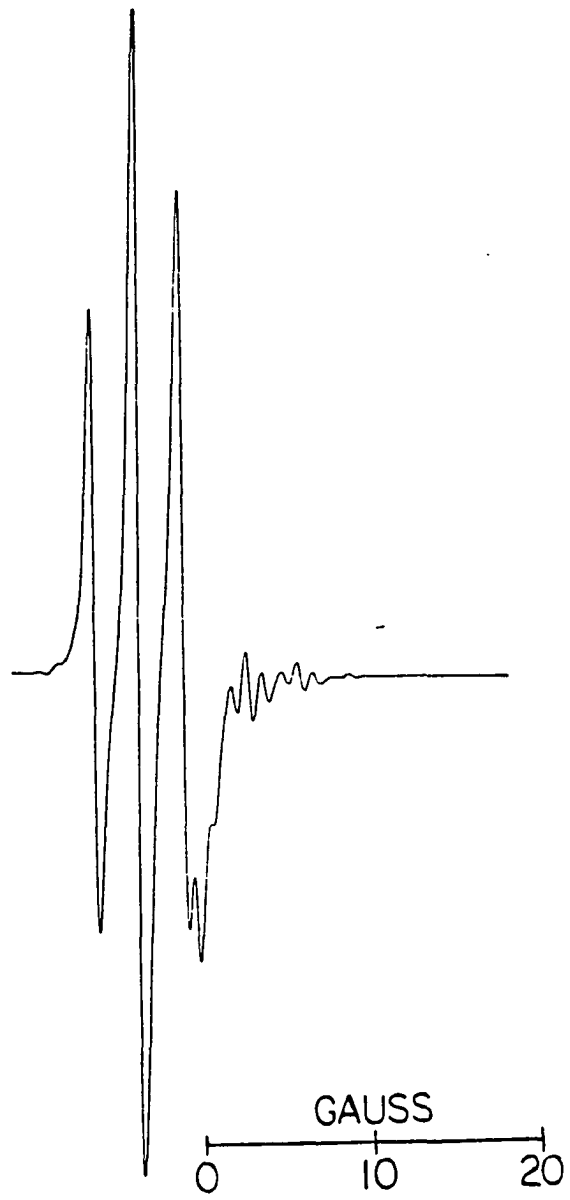
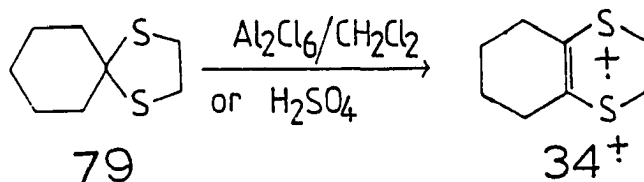
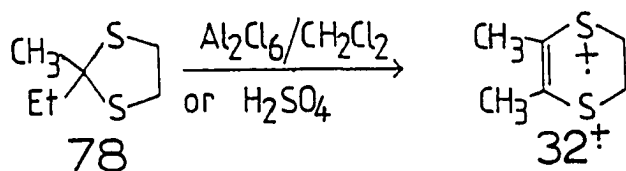


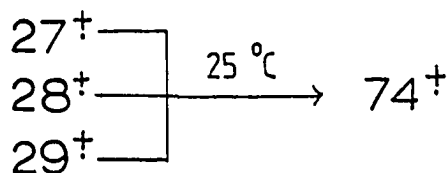
Figure 25. First derivative ESR spectrum of 2-methyl-2-ethyl-1,3-benzodithiole radical cation **77⁺** and 2,3-dimethyl-1,4-benzodithiin radical cation **48⁺**, produced by treatment of compound **77** with $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$ at $-70\text{ }^\circ\text{C}$



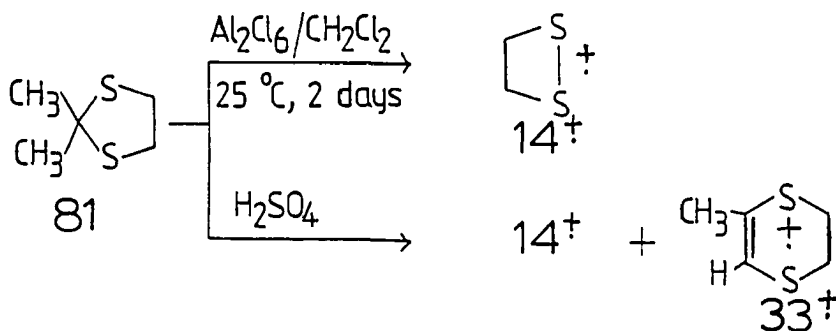
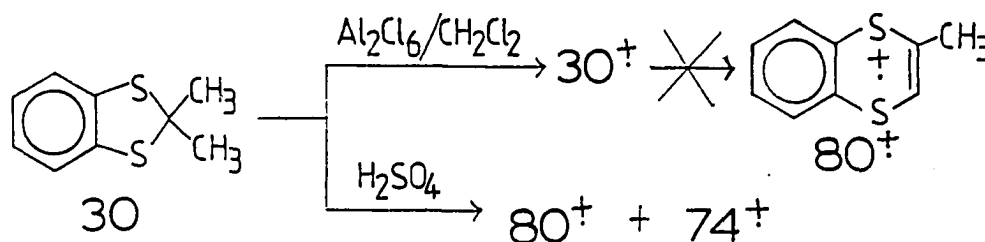
This oxidative rearrangement was not limited to 1,3-benzodithiole derivatives. When 2-methyl-2-ethyl-1,2-dithiolane **78** was treated with either $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$ or concentrated H_2SO_4 at room temperature, 32^\ddagger was produced as the only radical species. Under the same condition, compound **79** under went oxidative rearrangement to give 34^\ddagger .



The rearrangements from 1,3-dithiolanes to 2,3-dihydro-1,4-dithiin radical cations and 1,3-benzodithioles to 1,4-benzodithiin radical cations are only observed for 1,3-dithiolanes and 1,3-benzodithioles when their thioketal carbons are fully substituted with alkyl groups. If the thioketal carbons are not fully substituted, such rearrangements are not observed. For example, compounds **27**, **28**, and **29**, when treated with Al_2Cl_6 in CH_2Cl_2 at -60°C gave rise to 27^\ddagger , 28^\ddagger , 29^\ddagger . Upon warming the solution to room temperature, 1,4-benzodithiin radical cations were not formed, but instead, 74^\ddagger was formed in all cases.

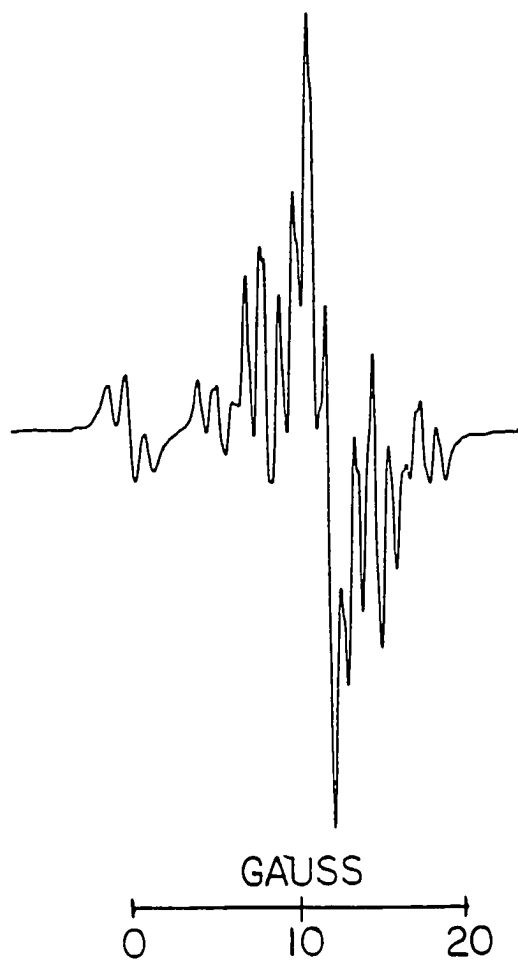


When $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$ was used as the oxidizing reagent, these rearrangements occur only when the compounds have at least one methylene group attached to the thioketal carbon. If the substituents at the thioketal carbon are methyl groups, the rearrangements from 1,3-

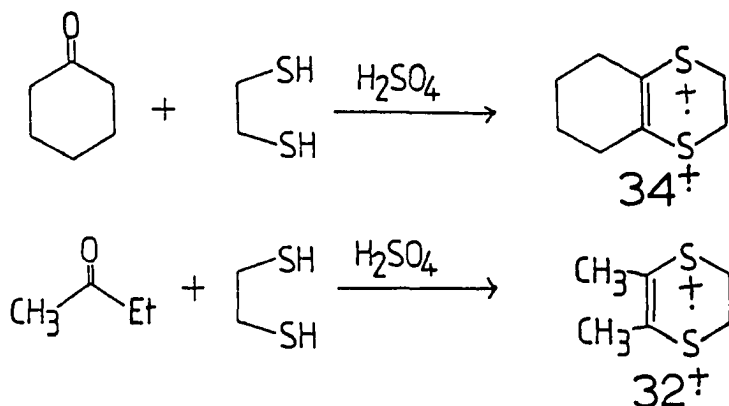


dithiolanes to 2,3-dihydro-1,4-dithiin radical cations and 1,3-benzodithioles to 1,4-benzodithiin radical cations were not observed. For example **30** gave 30^+ when treated with Al_2Cl_6 in CH_2Cl_2 at -70°C , and 80^+ was not formed even when the sample was warmed to room temperature for one hour. It seems that H_2SO_4 is a better reagent for the rearrangement than $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$. Thus, when compound **30** was treated with H_2SO_4 at room temperature, radical cation 80^+ ($a^{\text{H}} = 2.8$ (3H), 4.2 (1H), 1.1 (1H), 0.8 (1H) G, $g = 2.0081$) along with 74^+ were formed (Figure 26). Treatment of 2,2-dimethyl-1,3-dithiolane **81** with $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$ at room temperature initially didn't give an observable ESR signal but after two days, 1,2-dithietane radical cation 14^+ was formed. However, compound **81** dissolved in concentrated H_2SO_4 to give 33^+ along with 14^+ .

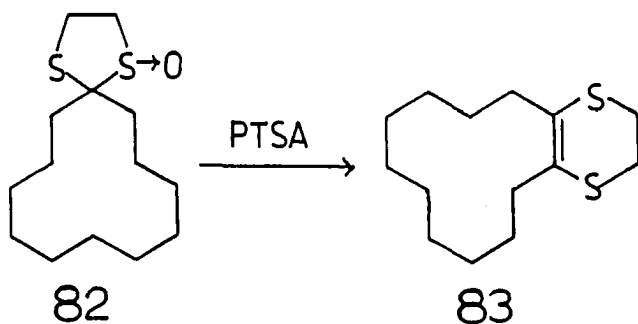
Figure 26. First derivative ESR spectrum of benzodithiete radical cation **74⁺** and 2-methyl-1,4-benzodithiin radical cation **80⁺**, produced by treatment of 2,2-dimethyl-1,3-benzodithiole **30** with H₂SO₄ at 25 °C



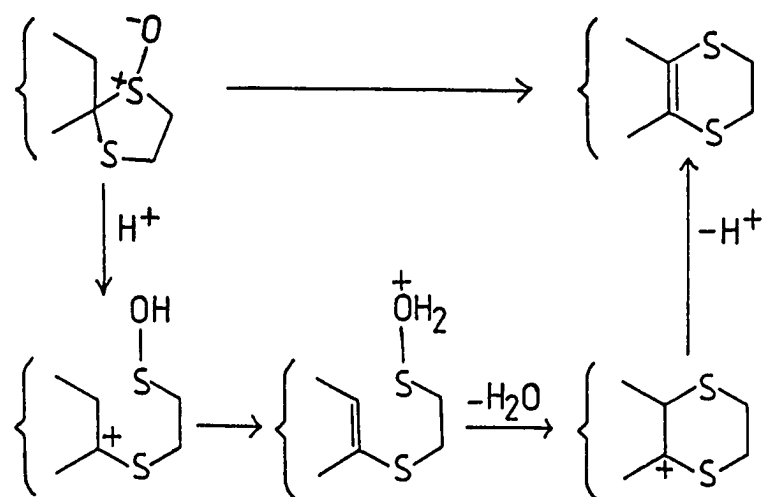
It was found that 2,3-dihydro-1,4-dithiin radical cation could be produced by simply dissolving a mixture of ketone and ethane-1,2-dithiol in concentrated H_2SO_4 . For example, dissolving a mixture of cyclohexanone and ethane-1,2-dithiol in H_2SO_4 produced $34^{\cdot+}$, while dissolving a mixture of butanone and ethane-1,2-dithiol in H_2SO_4 produced $32^{\cdot+}$.



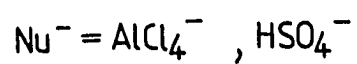
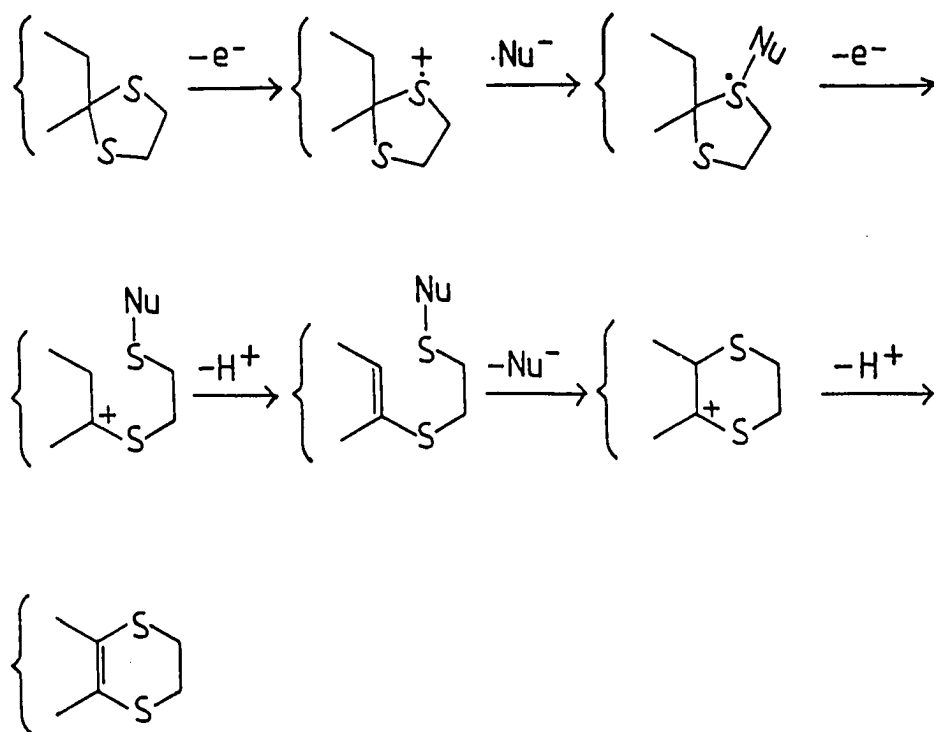
It was reported in the literature³¹ that PTSA catalyzed the rearrangement of 1,3-dithiolane-1-oxide **82** to 2,3-dihydro-1,4-dithiin **83**. The reaction was proposed to go through intermediates like those shown in Scheme V.^{31,32} It is logical to assume that the rearrangement from 1,2-dithiolanes to 2,3-dihydro-1,4-dithiin radical cations and 1,3-benzodithiole to 1,4-benzodithiin radical cations follow a similar reaction mechanism. Scheme VI provides a proposed mechanism for these rearrangements.



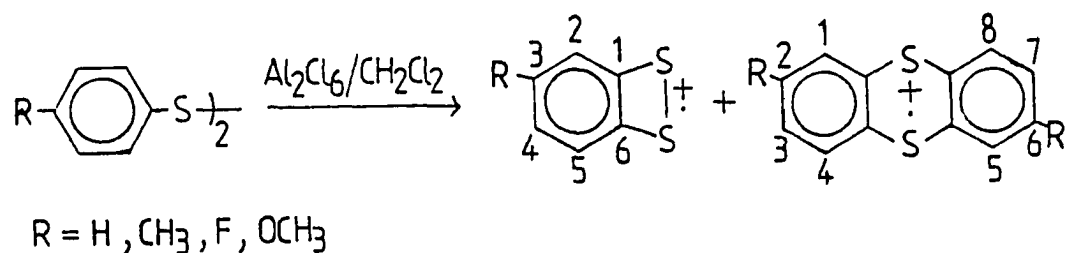
Scheme V



Scheme VI



Diaryl disulfides It was reported in the literature³ that *p*-substituted aryl disulfides, when treated with Al_2Cl_6 in CH_2Cl_2 , rearranged to form benzodithiete and thianthrene radical cations. However, neither 2-substituted benzodithiete nor 1,5-



disubstituted thianthrene radical cations were reported. The ideal precursors to these radical cations would be *m* or *o*-substituted aryl disulfides. When di-*m*-tolyl disulfide **84** was treated with $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$ at -60°C , 3-methylbenzodithiete and 2,6-dimethylthianthrene radical cations **85⁺** and **86⁺** were produced. When di-*o*-tolyl disulfide **87** was treated with Al_2Cl_6 in CH_2Cl_2 at -60°C a triplet signal $a^{\text{H}} = 1.15 \text{ G}$ with $g = 2.0150$ was observed along with a set of complicated signals (Figure 27). The triplet was assigned as 2-methylbenzodithiete radical cation **88⁺**, and the complicated signals were assigned as a mixture of

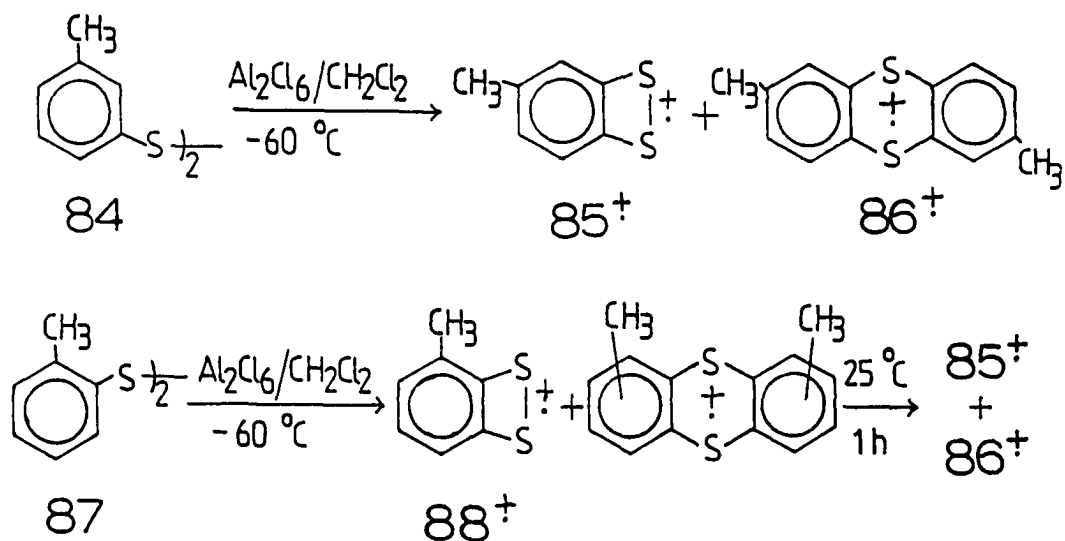
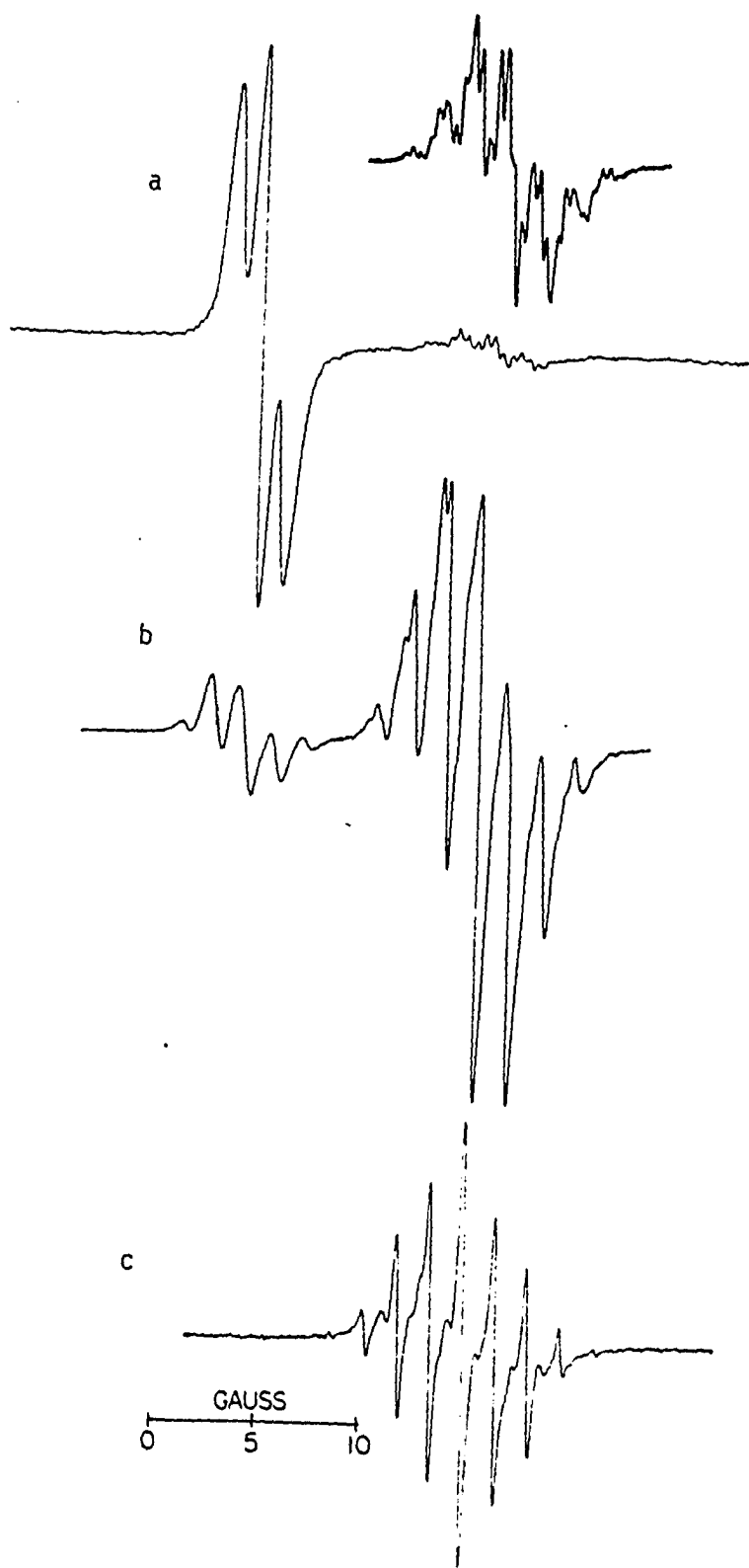


Figure 27. First derivative ESR spectra of radical cations produced by treatment of di-*o*-tolyl disulfide **87** with $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$

(a) At $-60\text{ }^\circ\text{C}$

(b) At $25\text{ }^\circ\text{C}$ for 1 h

(c) At $25\text{ }^\circ\text{C}$ for 1 week



isomeric dimethyl-substituted thianthrene radical cations. After the sample was warmed to room temperature for one hour, the triplet was replaced by a pentet ($a^H = 1.51$ G) with $g = 2.0150$, while the complicated signal changed into a rather simple nonet ($a^H = 1.68$ G) with $g = 2.0080$. These radical cations were identified as 85^+ and 86^+ , respectively. Apparently the reaction sequence $87 \rightarrow 88^+ \rightarrow 85^+$ is involved. This raised the question as to whether methyl migration or sulfur migration has occurred.

In order to gain more information about this rearrangement, the di-xylyl disulfides **89-91** were synthesized. When **89** was treated with Al_2Cl_6 in CH_2Cl_2 at -60 °C, two well-resolved ESR signals $a^H = 1.60$ (4H) G, $g = 2.0148$ and $a^H = 1.665$ (8H), 0.44 (8H) G, $g = 2.0080$ were observed. These signals were assigned as 2,4-dimethylbenzodithiete (92^+) and 1,3,5,7-tetramethylthianthrene (93^+) radical cations, respectively (Figure 28). The ESR spectra didn't change even after the sample was kept at room temperature for more than one week. The radical cation 92^+ was also generated by reacting *m*-xylene with either sulfur or S_2Cl_2 in Al_2Cl_6/CH_2Cl_2 .

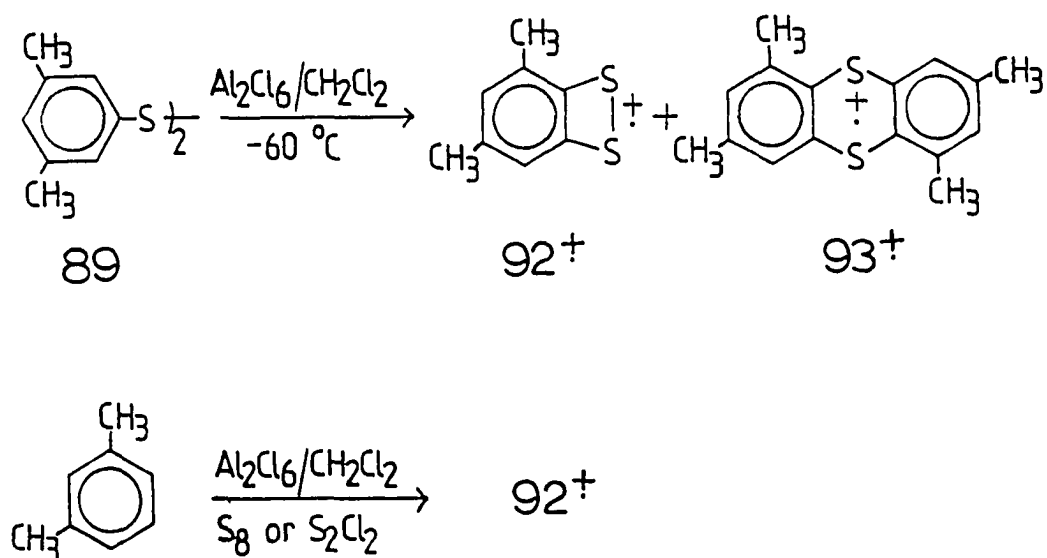
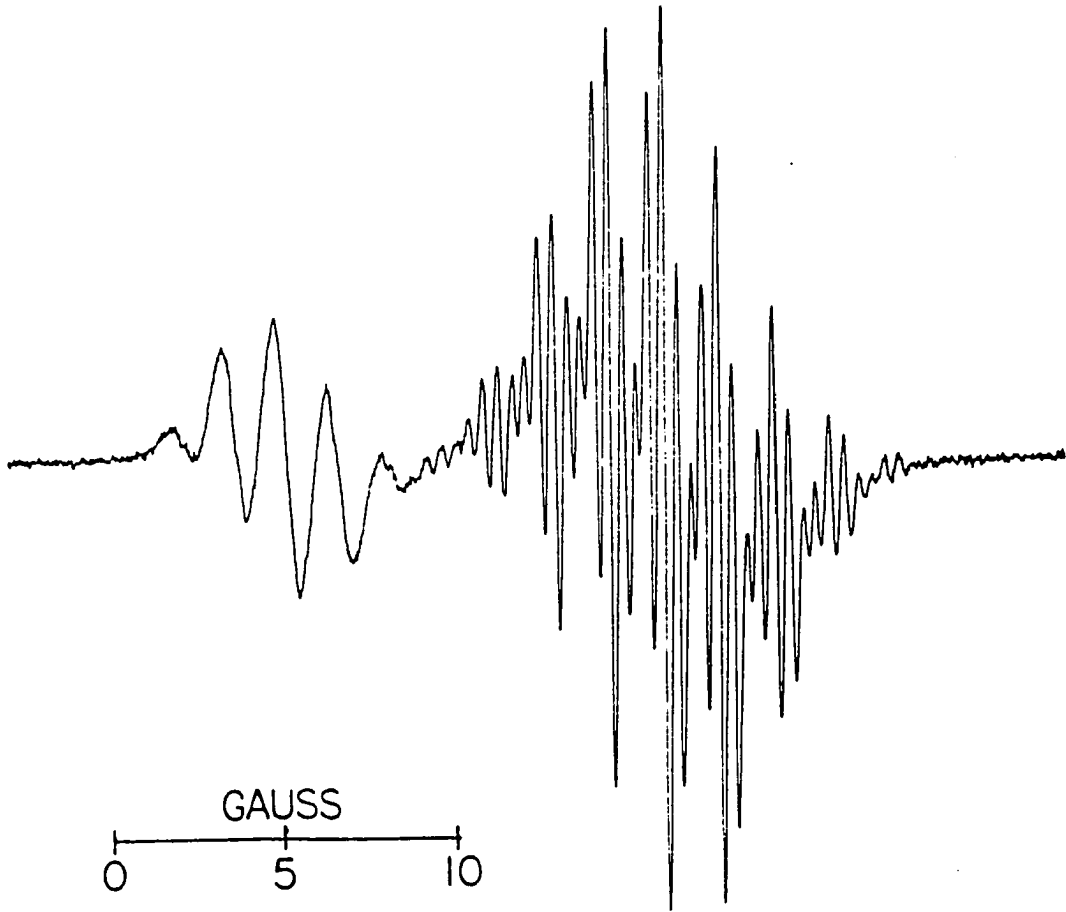
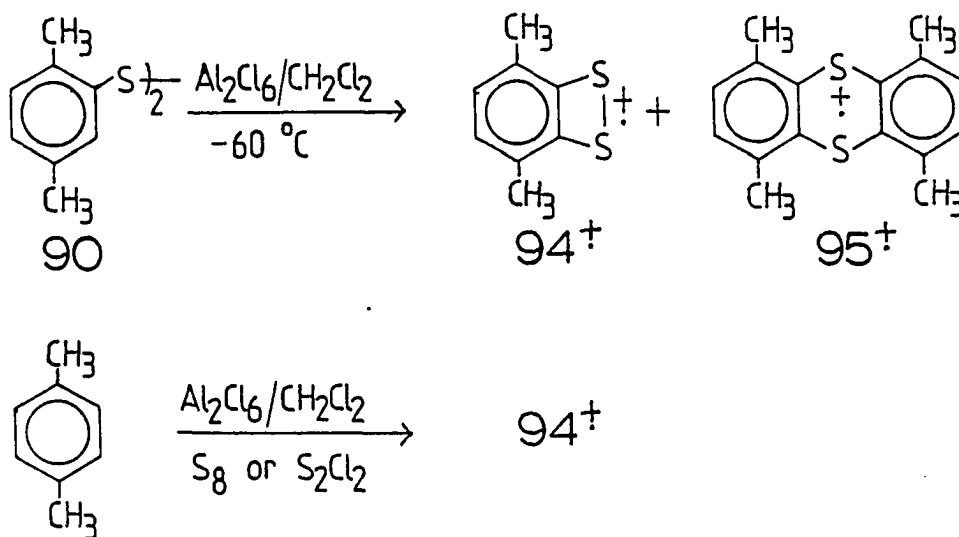


Figure 28. First derivative ESR spectrum of 2,4-dimethylbenzodithiete radical cation **92**⁺ (left) and 1,3,5,7-tetramethylthianthrene radical cation **93**⁺ (right), produced by treatment of disulfide **89** with Al₂Cl₆/CH₂Cl₂ at -60 °C

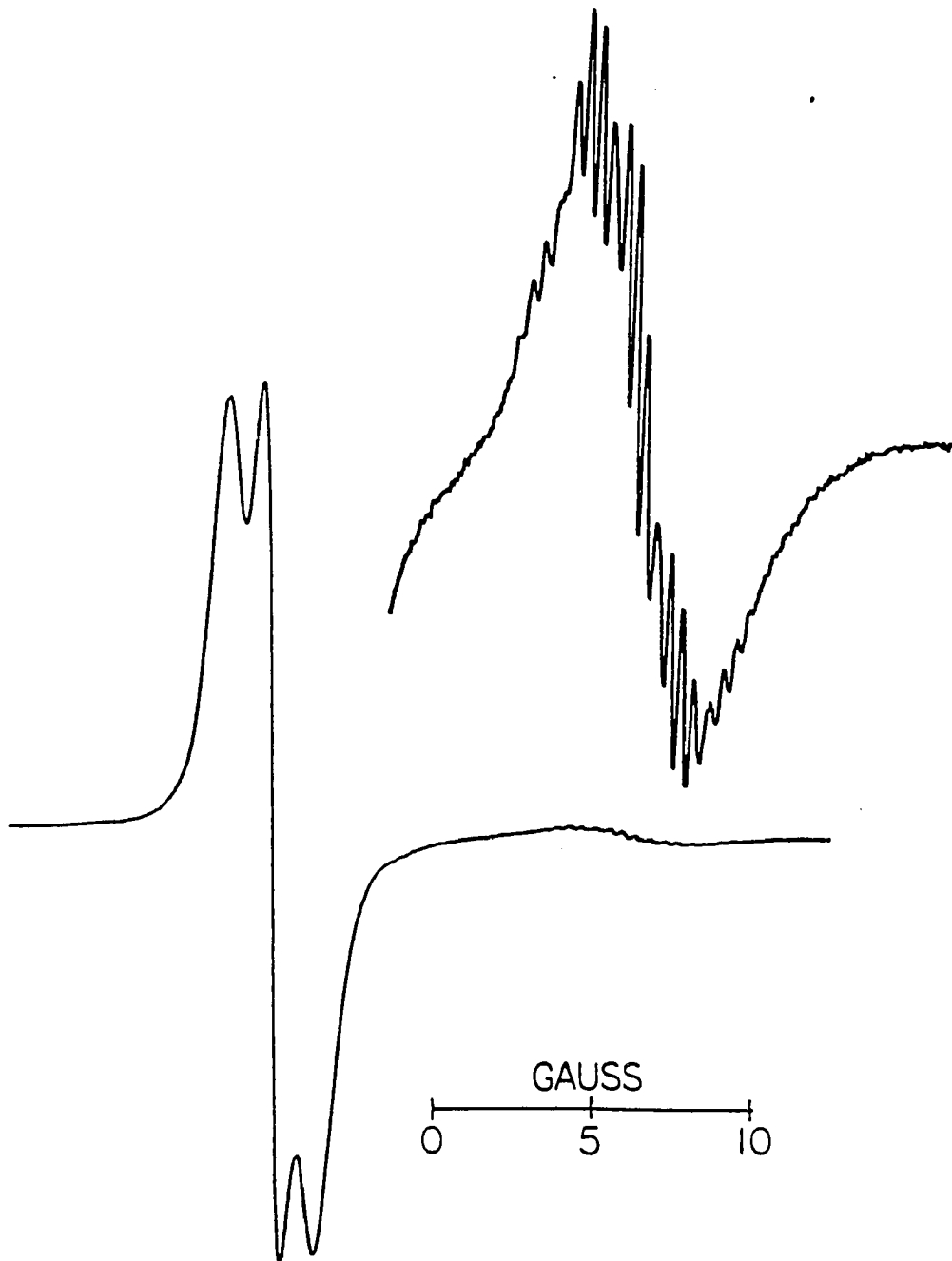


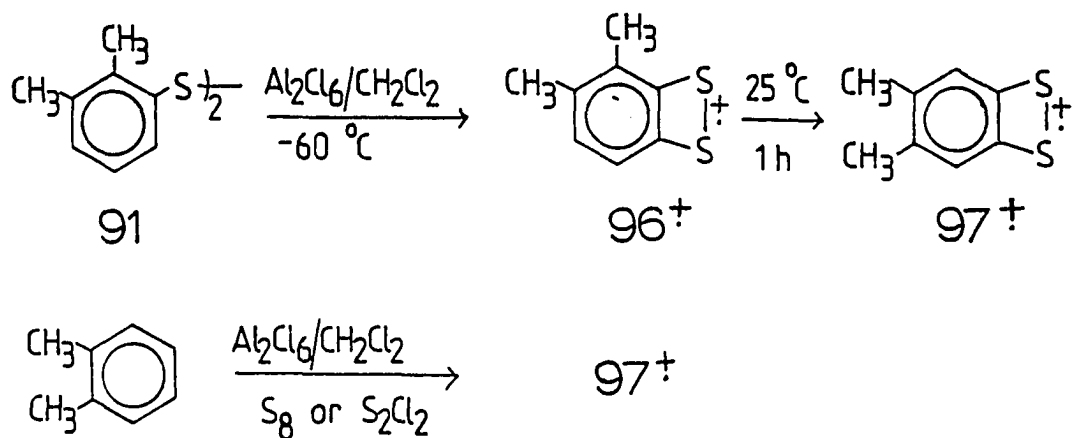
Treatment of **90** with Al_2Cl_6 in CH_2Cl_2 at -60°C gave rise to two long lived ESR signals which were assigned as 2,5-dimethylbenzodithiete and 1,4,5,8-tetramethylthianthrene radical cations **94⁺** ($a^{\text{H}} = 1.27$ (3H) G, $g = 2.0150$) and **95⁺** ($a^{\text{H}} = 1.405$ (4H), 0.40 (12H) G, $g = 2.0082$). Radical cations **94⁺** and **95⁺** were stable at room temperature for weeks (Figure 29). The radical cation **94⁺** was also generated by reaction of *p*-xylene with either sulfur or S_2Cl_2 in $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$.



Treatment of **91** with Al_2Cl_6 in CH_2Cl_2 at -60°C produced only a pentet ESR signal ($a^{\text{H}} = 1.635$ (4H) G, $g = 2.0148$) which was assigned as 2,3-dimethylbenzodithiete radical cation **96⁺**. Upon warming the sample to room temperature for one hour, the pentet was replaced by a heptet ($a^{\text{H}} = 1.62$ (6H) G, $g = 2.0148$) which was assigned as 3,4-dimethylbenzodithiete radical cation **97⁺** (Figure 30). The radical cation **97⁺** was also generated by reacting *o*-xylene with either sulfur or S_2Cl_2 in $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$.

Figure 29. First derivative ESR spectrum of 2,5-dimethylbenzodithiete radical cation **94⁺** (left) and 1,4,5,8-tetramethylthianthrene radical cation **95⁺** (right), produced by treatment of disulfide **90** with $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$ at $-60\text{ }^\circ\text{C}$





All the above results suggest that the rearrangement of 88⁺ to 85⁺ and 96⁺ to 97⁺ operate by a mechanism involving the migration of one or both of the sulfur atoms. Furthermore, the rearrangement occurs so that the resulting benzodithiete radical cation has the maximum number of methyl substituents in the 3,4-position of the aromatic ring. This phenomenon can be explained by the fact that in the unsubstituted benzodithiete radical cation 74⁺, the 3,4-positions of the aromatic ring have larger spin density than the 2,5-positions. Therefore, an electron donating substituent such as the methyl group would stabilize the benzodithiete radical cation more when it is in the 3,4-positions than in 2,5-positions.

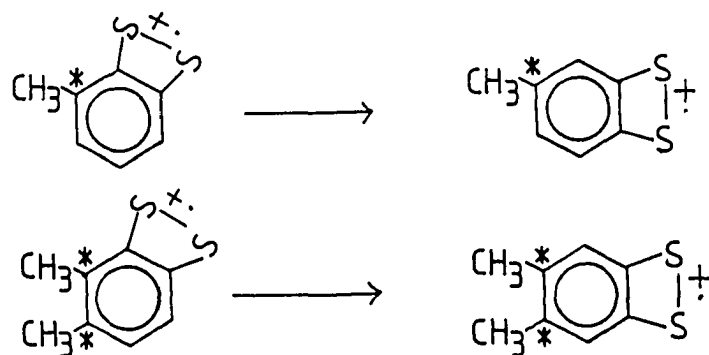


Figure 30. First derivative ESR spectra of

(a) 2,3-dimethylbenzodithiete radical cation **96[±]**, produced by treatment of disulfide **91** with $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$ at $-60\text{ }^\circ\text{C}$

(b) 3,4-dimethylbenzodithiete radical cation **97[±]**, produced by treatment of disulfide **91** with $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$ at $25\text{ }^\circ\text{C}$ for 1 h



It was found that benzodithiete and thianthrene radical cations could be generated by many routes. Among them were, (A) reaction of benzene derivatives with sulfur or S_2Cl_2 in the presence of Al_2Cl_6/CH_2Cl_2 ; (B) reaction of benzene derivatives with sulfur or S_2Cl_2 in H_2SO_4 ; (C) reaction of benzene derivatives with $Na_2S_2O_3$ or $Na_2S_2O_5$ in H_2SO_4 . Table 7 lists these results.

Table 7. A comparison of different methods of producing benzodithiete and thianthrene radical cations

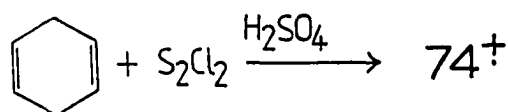
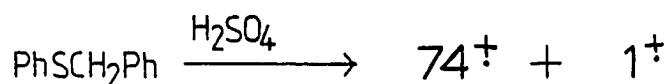
Benzene Derivative	Method ^a	Radical cation
benzene	A, B	74[†], 1[†]
toluene	A, B, C	85[†], 86[†]
<i>o</i> -xylene	A, B, C	97[†]
<i>m</i> -xylene	A, B, C	92[†]
<i>p</i> -xylene	A, B, C	94[†]
1,2,4-trimethylbenzene	A	98[†] b
durene	A	98[†] c

^aA, S_8 or S_2Cl_2 in Al_2Cl_6/CH_2Cl_2 ; B, S_8 or S_2Cl_2 in H_2SO_4 ; C, $Na_2S_2O_3$ or $Na_2S_2O_5$ in H_2SO_4 .

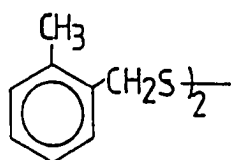
^b98[†] was assigned as 2,3,5-trimethylbenzodithiete radical cation ($a^H = 1.72$ (4H) G, $g = 2.0147$).

^cApparently a methyl group was lost during the reaction.

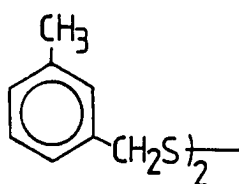
Benzodithiete and thianthrene radical cations could also be produced by dissolving benzyl phenyl sulfide in H_2SO_4 . 1,4-Cyclohexadiene reacted with S_2Cl_2 in H_2SO_4 to also give the benzodithiete radical cation 74^+ .



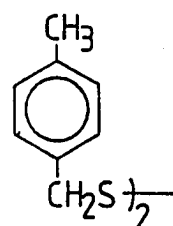
Dibenzyl disulfides Giordan and Bock³ reported that dibenzyl disulfide was oxidized by Al_2Cl_6 in CH_2Cl_2 to form its radical cation with a g -value of 2.0075 and $a^{\text{H}} = 1.4$ (4H) G. The result was very surprising because all the other known disulfide radical cations had g -values around 2.018-2.019 and significantly larger hfsc for a^{H}_{α} . In order to check their result, the ESR experiment was repeated. No detectable signal was observed even when the sample was kept at room temperature for several hours. However, a weak pentet ($a^{\text{H}} = 1.70$ G) with a g -value of 2.0149 appeared after 24 hours. This pentet appears to be the substituted benzodithiete radical cation. Based on the value of a^{H} , the radical cation formed could be either 92^+ or 98^+ . The mechanism of this transformation is rather intriguing. In this regard, the three methyl-substituted dibenzyl disulfides **99-101** were synthesized. All of them when treated with $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$ at room temperature provided ESR signals. For **101**, the first observed weak signal was that of 94^+ . However, all three compounds eventually gave the same ESR spectrum (after treatment with Al_2Cl_6 at room temperature for 2-10 hours) with two sets of signals. The high field signal was identified as 2,6-dimethylantracene radical cation 102^+ . The signal in the low field region consisted of



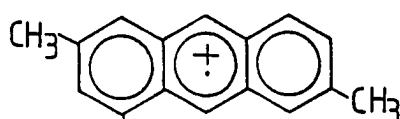
99



100



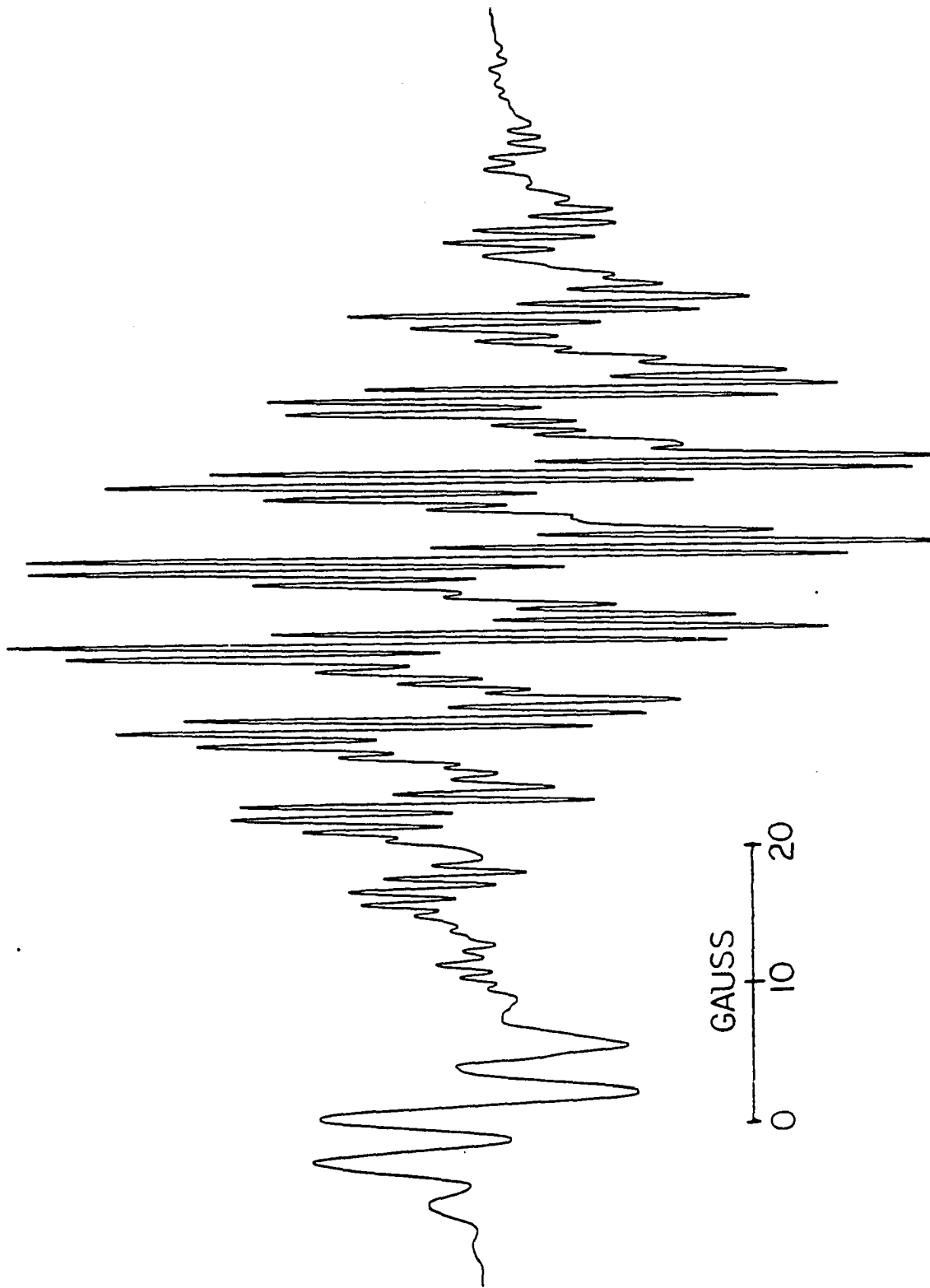
101

102⁺

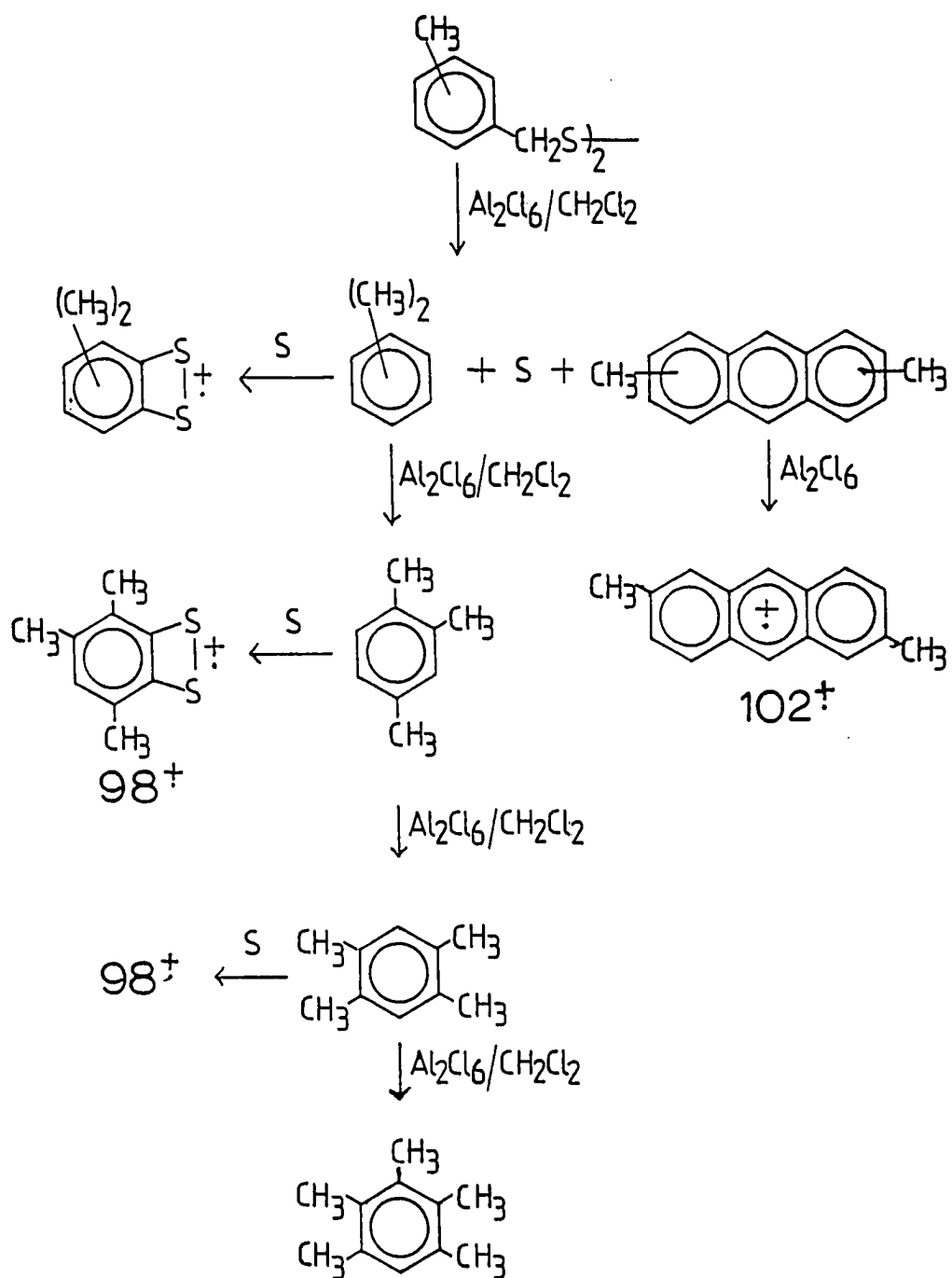
seven lines but didn't display the binominal intensity of a heptet arising from hfs of six equivalent hydrogen atoms. It is believed that this signal arises from a mixture of methylated benzodithiete radical cations (Figure 31). Treatment of 99-101 with Al_2Cl_6 in CH_2Cl_2 at room temperature for 24 hours yielded a mixture of products which were analysed by GCMS. All of the disulfides gave a mixture of dimethylantracenes and for 99 and 100, a small amount of pentamethylbenzene ($\sim 3\%$) were also formed.

The formation of essentially the same ESR spectrum from the different starting materials 99-101 can be explained by Scheme V. It is suggested that the disulfides react to form xylenes and dimethylantracenes. Dimethylantracenes can be oxidized to form radical cations, but since 2,6-dimethylantracene radical cation is the most stable isomer, only 102⁺ is seen in the ESR spectrum. The xylenes could be methylated by $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$ to form trimethylbenzenes, tetramethylbenzenes and pentamethylbenzene. Finally, the xylenes, trimethylbenzene and tetramethylbenzene can react with sulfur to form the polysubstituted benzodithiete radical cations observed.

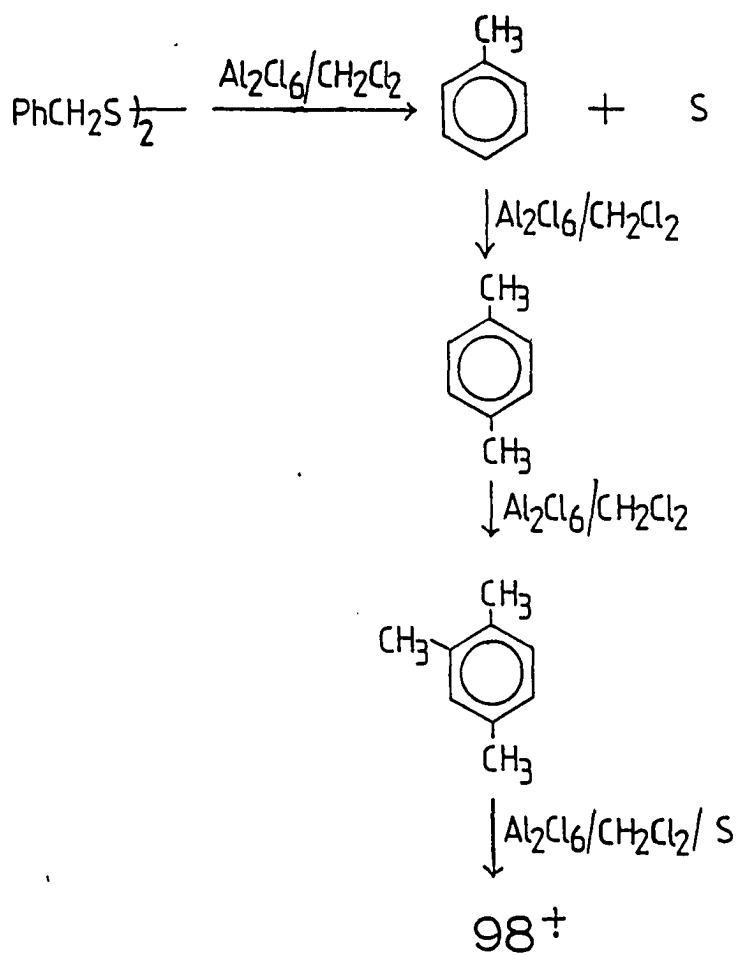
Figure 31. First derivative ESR spectrum of polymethylbenzodithiete radical cations (left) and 2,6-dimethylantracene radical cation (right), produced by treatment of disulfide **99** or **100** or **101** with $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$ at 25 °C for 10 h



Scheme V



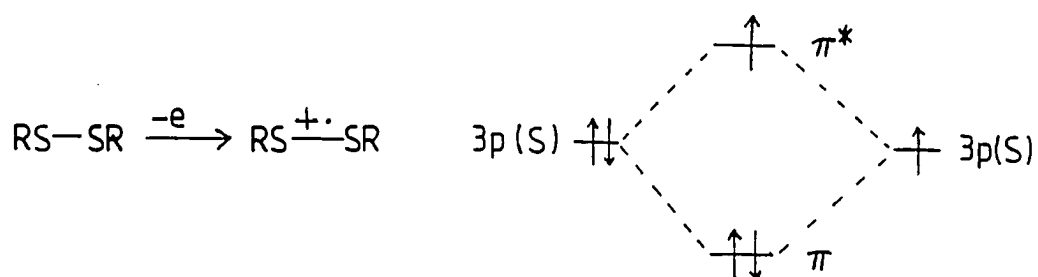
This general reaction pathway can also explain the formation of 98^+ by treatment of dibenzyl disulfide with Al_2Cl_6/CH_2Cl_2 . The dibenzyl disulfide can be decomposed to form toluene and the toluene then methylated twice by Al_2Cl_6/CH_2Cl_2 to form 1,2,4-trimethylbenzene which reacts with sulfur to form 98^+ . The explanation presented is probably not the only one possible and various other reaction scheme could be imagined. It will be quite difficult to establish experimentally that the ESR signal attributed by Giordan and Bock³ to $PhCH_2SSCH_2Ph^+$ is due to 98^+ alone and not to some mixture of methylated benzodithiete radical cations. However, the perplexing results reported by Giordan and Bock³ can now be understood at least in a general sense, and the dibenzyl disulfide radical cation excluded as a persistent species.



CHAPTER III. CYCLIC DISULFIDE RADICAL CATIONS

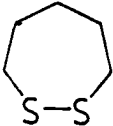
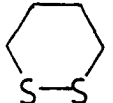
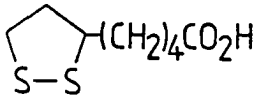
Introduction

Simple MO Theory shows that the unpaired electron of a disulfide radical cation is in a π^* orbital with antisymmetry. In the literature, acyclic disulfide radical cations have not

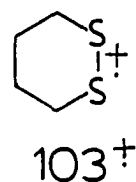
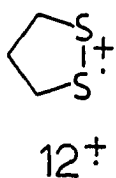
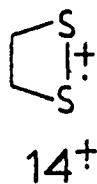


been reported in solution, but they have been generated in the solid state by UV irradiation.^{8,9} The nature of the disulfide linkage must be quite significantly altered by changes in the dihedral angle between the two carbon-sulfur bonds. As this angle is reduced from 90° to 0° the interaction between the two pairs of a 3p nonbonding electrons of the sulfur atoms becomes much stronger. Thus, cyclic disulfides with small dihedral angles absorb light at longer wavelengths in the UV and have lower ionization potentials than acyclic disulfides which possess larger dihedral angles. Table 6 lists the dihedral angles and ionization potentials of some disulfides.

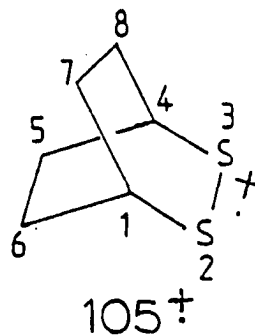
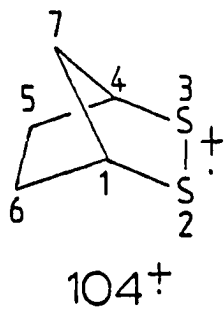
Table 6. Ionization potentials and dihedral angles for selected disulfides³³

	IE ₁ (eV)	Dihedral angle θ (deg)
H-S-S-H	10.01	90.5
CH ₃ SSCH ₃	8.98	84.7
	8.97	--
	8.36	60 (X-ray)
	8.02	35 (X-ray)

Small ring cyclic disulfides have low ionization potentials and one would therefore expect that they could be oxidized to form persistent radical cations. Indeed, there are reports⁴⁻⁶ on the successful generations of 1,2-dithietane ($a^H = 3.7$ (4H) G, $g = 2.0193$ (**14**⁺), 1,2-dithiolane (a^H (-95 °C) = 16.25 (2H), 3.9 (2H) G, a^H (25 °C) = 9.5 (4H) G, $g = 2.0183$) (**12**⁺), and 1,2-dithiane ($a^H = 9.5$ (4H), $g = 2.0183$) (**103**⁺) radical cations. Surprisingly, the radical cation **14**⁺ had much smaller hfsc than **12**⁺ and an explanation was advanced to rationalize this experimental result.⁴ Nevertheless, more examples of 1,2-dithietane and 1,2-dithiolane radical cations are needed to justify this explanation.



It is reported in literature that long range coupling phenomenon occurs for carbon, oxygen and nitrogen centered radical in conformational rigid frameworks and that the symmetry of the SOMO can have a dramatic effect on certain of these long range interactions. It is interesting to explore the possibility of a similar long range interaction occurring in sulfur-centered radical cations. In this regard, the bicyclic disulfide radical cations **104[†]** and **105[†]** were chosen as targets for the examination of this possibility.



Results and Discussion

1,2-Dithietane radical cations

When 1,2-dithietane radical cation 14^+ was generated in H_2SO_4 below room temperature, a selective line broadening effect was observed, with a coalescence temperature at $\sim -35^\circ C$. The species 14^+ was also generated by treatment of 2,2-dimethyl-1,2-dithiolane **81** with Al_2Cl_6/CH_2Cl_2 for two days at room temperature. In CH_2Cl_2 , 14^+ gave a triplet below $-50^\circ C$ with $a^H = 6.8$ G for two hydrogens with a^H less than 0.6 G for the other two hydrogens (Figure 32). Selective line broadening was also observed at above $-30^\circ C$ in CH_2Cl_2 for 14^+ . The temperature dependent ESR spectrum of 14^+ indicates that 14^+ has a nonplanar structure and involves the conformational equilibrium ($XIa \rightleftharpoons XIb$) which time-

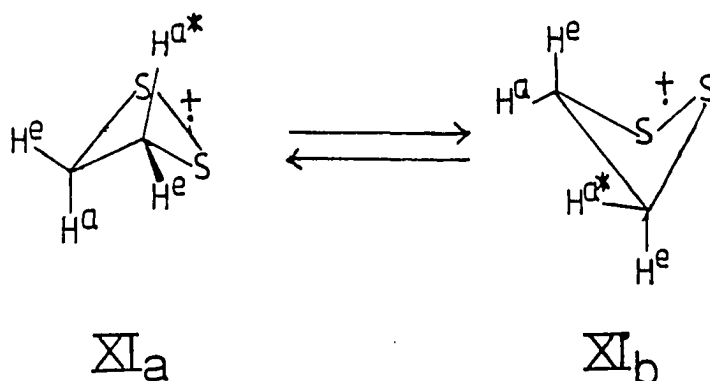
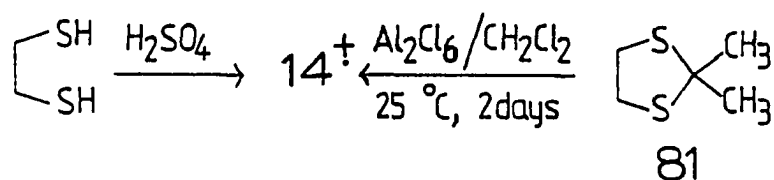
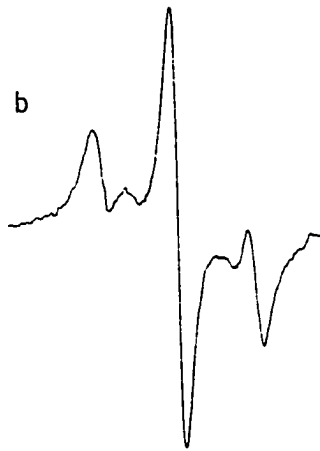
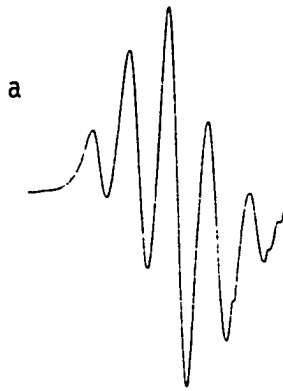


Figure 32. First derivative ESR spectra of 1,2-dithietane radical cation, 14^+ .

(a) At 25 °C in H_2SO_4

(b) At -35 °C in H_2SO_4

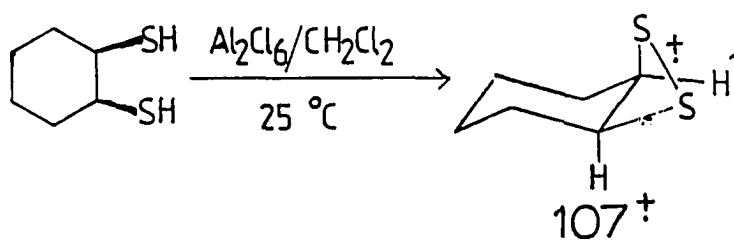
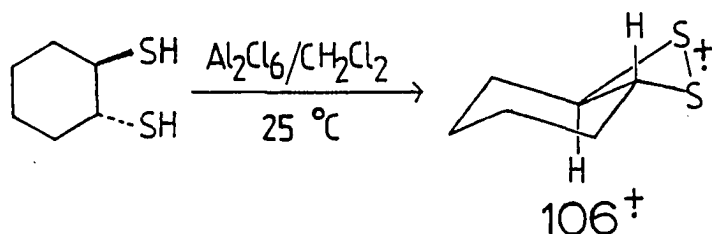
(c) At -90 °C in Al_2Cl_6/CH_2Cl_2



GAUSS
0 10 20

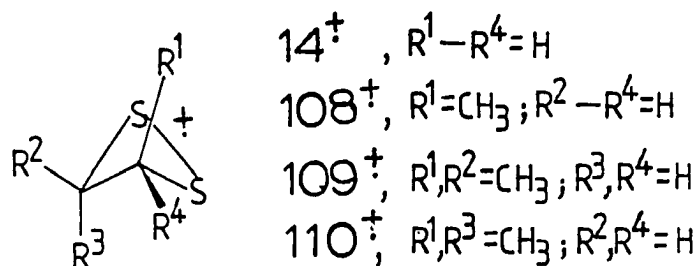
averages the hydrogen atoms of the methylene groups at above room temperature with an energy barrier for ring flip large enough that line broadening is observed at below room temperature. The line broadening was measured in the fast exchange mode and $\Delta H^\ddagger = 3.3$ kcal/mol and $\Delta S^\ddagger = -12$ eu were calculated for the conformational equilibrium (XIa \rightleftharpoons XIb).

It has been reported that ²⁶ many mono- or 1,2-disubstituted derivatives of HSCH₂CH₂SH underwent further oxidation upon treatment with H₂SO₄ to form the corresponding dithiete radical cations, and that additional examples of 1,2-dithietane radical cations could not be generated in H₂SO₄. In an attempt to generate the dithiete radical cation **21**⁺ in Al₂Cl₆/CH₂Cl₂ for variable temperature study by reaction of cyclohexene with S₂Cl₂, and unexpected radical cation **106**⁺ ($a^H = 6.3$ (2H) G, $g = 2.0190$) was formed. Since the g -value of **106**⁺ was nearly the same as other disulfide radical cations, this unexpected result suggested that substituted 1,2-dithietane radical cations could be generated in Al₂Cl₆/CH₂Cl₂. Indeed, *trans*-cyclohexane-1,2-dithiol gave **106**⁺ when treated with Al₂Cl₆ in CH₂Cl₂ at room temperature for one-half hour. Therefore, **106**⁺ was assigned as *trans*-7,8-dithiabicyclo[4.2.0]octane radical cation (Figure 33). *cis*-Cyclohexane-1,2-dithiol



was oxidized by Al_2Cl_6 at room temperature to form the corresponding cis dithietane radical cation 107^+ ($a^{\text{H}} = 7.6$ (1H) G, $g = 2.0187$). The ESR spectrum of 107^+ (Figure 33) clearly showed that the dithietane ring in 107^+ was not planar and that only one hydrogen atom in the dithietane ring gave a large hfsc. The ESR spectrum of 107^+ was independent of temperature between -70 to 25 °C, an observation which can be interpreted in terms of the population of only a single conformation.

Similarly, 1,2-propane-dithiol, *meso*-2,3-butanedithiol, and *d,l*-2,3-butanedithiol were oxidized to form 1,2-dithietane radical cations 108^+ , 109^+ and 110^+ , respectively. A consistent interpretation of the hfsc is that in 14^+ the quasi-axial hydrogens (^1H and ^3H) have a large hyperfine splitting (6.8 G) and that the quasi-equatorial hydrogens (^2H , ^4H)



have a small (<0.6 G) coupling. The magnitude of this interaction reflects the dihedral angle between the C-H bond and the sulfur orbital containing unpaired electron density with an added complication from a 1,3-interaction for the quasi-equatorial hydrogen atoms. Since the SOMO of $-\text{S}^+\text{S}-$ is antisymmetric, this homohyperconjugative interaction will in effect cancel some part of the 1,2-hyperconjugative interaction for the quasi-equatorial

Figure 33. First derivative ESR spectra of

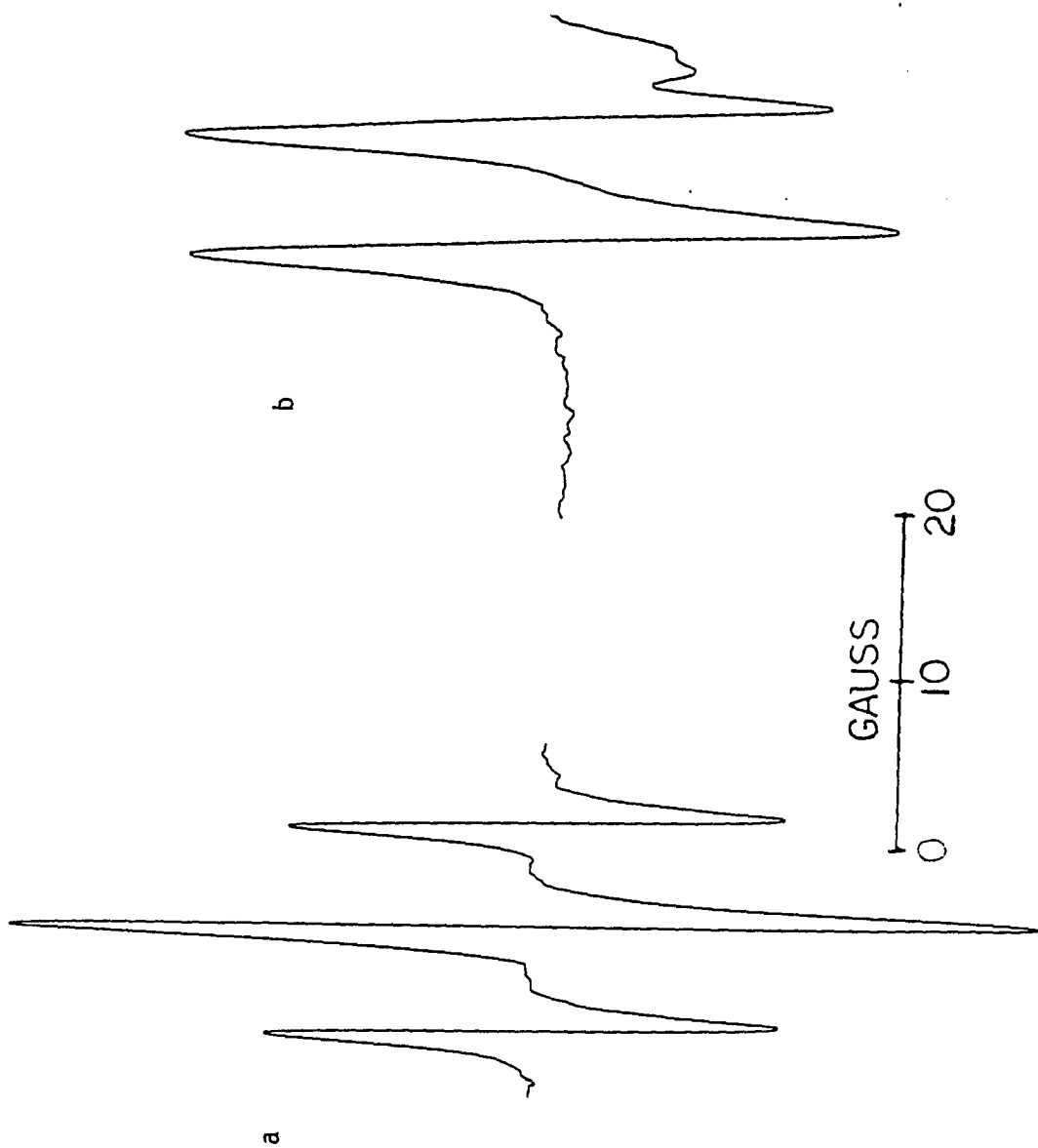
(a) *trans*-7,8-dithiabicyclo[4.2.0]octane radical cation, **106⁺**

(b) *cis*-7,8-dithiabicyclo[4.2.0]octane radical cation, **107⁺**

(c) 3-methyl-1,2-dithietane radical cation, **108⁺**

(d) *cis*-3,4-dimethyl-1,2-dithietane radical cation, **109⁺**

(e) *trans*-3,4-dimethyl-1,2-dithietane radical cation, **110⁺**



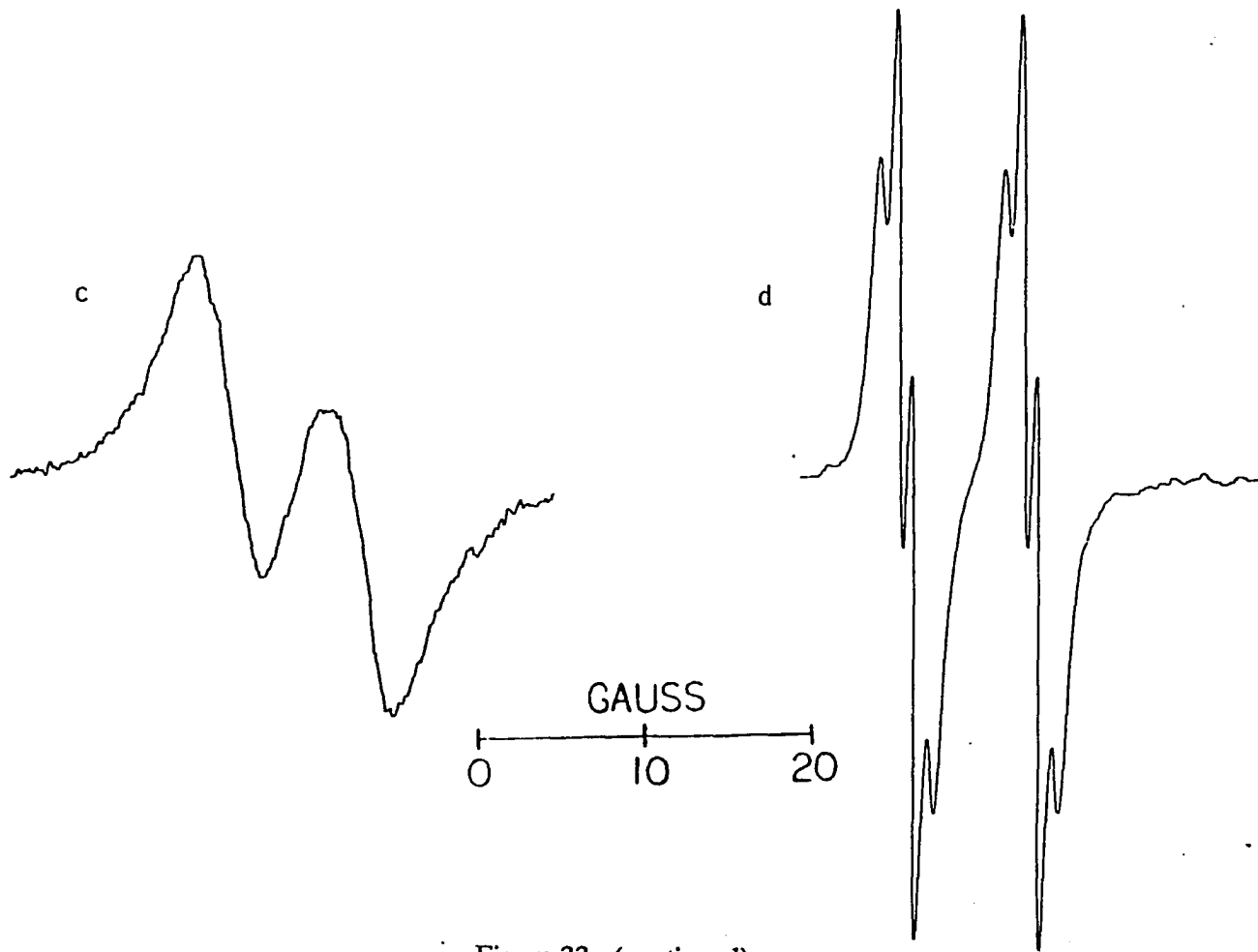


Figure 33. (continued)

e

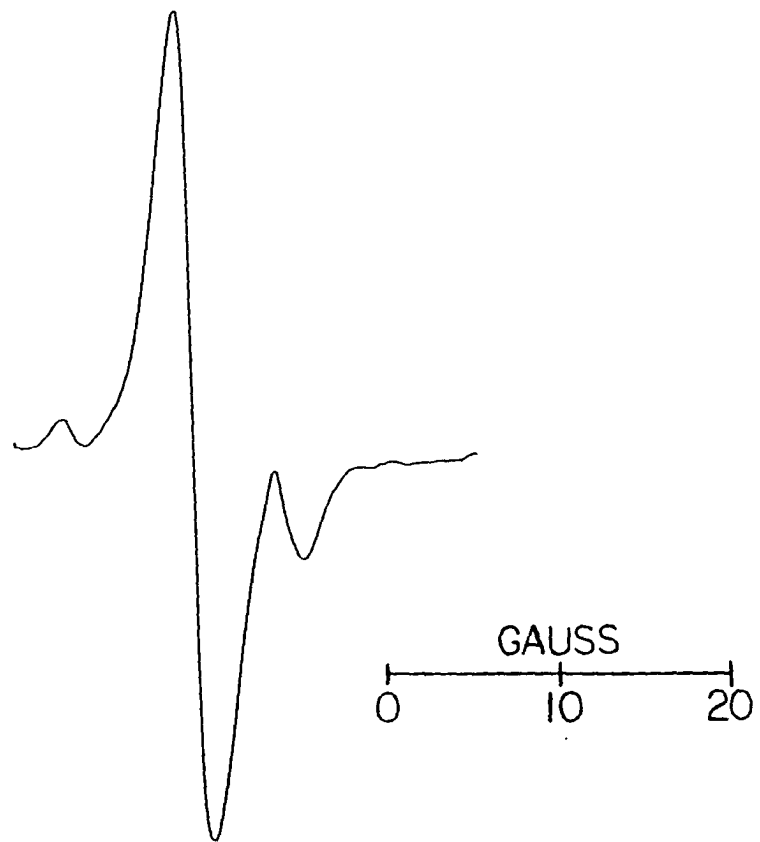
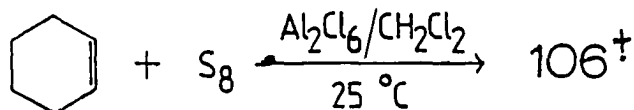


Figure 33. (continued)

hydrogen atoms. For the *cis*-dimethyl analogue **109**⁺, the ESR spectrum is a doublet with $a^H = 7.6$ G ($g = 2.0187$) for the quasi-axial hydrogen (³H) and <0.5 G for the quasi-equatorial hydrogen atom. The methyl group in the quasi-axial position shows a hfs with $a^H = 1.1$ G. Alkyl substituents prefer the quasi-axial position since the *trans*-dimethyl derivative **110**⁺ gives no hfs ($\Delta H_{1/2} = 2.5$ G, presumably from unresolved methyl hfs, $g = 2.0185$), and the mono-methyl derivative **108**⁺ has a resolved hfs for a single hydrogen only ($a^H = 8.5$ G, $g = 2.0184$). Dithietane radical cation **107**⁺ has a single quasi-axial hydrogen (relative to the dithietane ring), and the hfsc for ¹H is assigned as 7.6 G. On the other hand, the dithietane radical cation **106**⁺ derived from the *trans*-dithiol exists in a conformation with two quasi-axial hydrogen atoms (the only possible conformation with a chair cyclohexane ring) with $a^H = 6.30$ (2H) G. The species **106**⁺ is also detected by ESR in the reaction of cyclohexane with sulfur in the Al₂Cl₆/CH₂Cl₂ system.



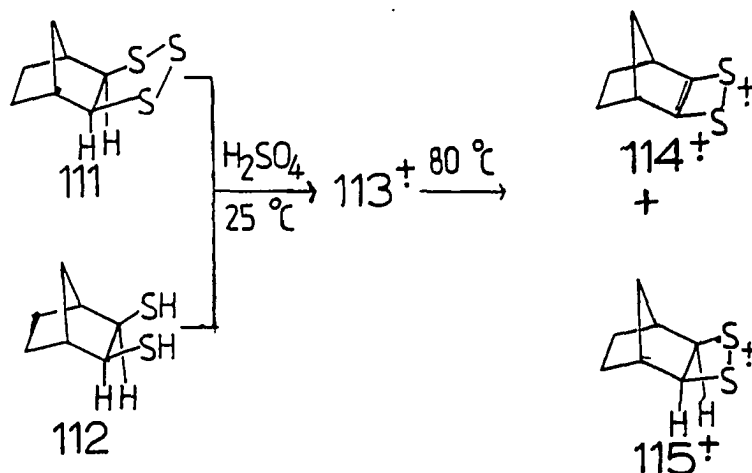
Treatment of *exo*-3,4,5-trithiatricyclo[5.2.1.0^{2,6}]decane **111** or *exo-cis*-bicyclo[2.2.1]heptane-2,3-dithiol **112** with H₂SO₄ at room temperature led to the formation of radical cation **113**⁺, which gave a doublet ESR signal ($a^H = 5.6$ (1H) G, $a^{33\text{S}} = 12.7$ G, $g = 2.0172$). When the sample was warmed to 80 °C, **113**⁺ disappeared, and two radical cations were formed (Figure 34). One of them was identified as the known dithiete radical cation **114**⁺ ($a^H = 2.75$ (1H), 0.90 (4H) G, $g = 2.0144$), while the other signal was a triplet ($a^H = 2.6$ (2H) G, $a^{33\text{S}} = 13.2$ G, $g = 2.0172$). Since the $a^{33\text{S}}$ of this species had the same value as the $a^{33\text{S}}$ of 1,2-dithiolane radical cation **12**⁺ ($a^{33\text{S}}$ was 13.3 G for **12**⁺), and the

Figure 34. First derivative ESR spectra of

(a) *exo*-3,4,5-trithiatricyclo[5.2.1.0^{2,6}]decane radical cation, **111**[†]

(b) *exo*-3,4-dithiatricyclo[4.2.1.0^{2,5}]nonane radical cation, **115**[†] and $\Delta^{2,5}$ -3,4-dithiatricyclo[4.2.1.0^{2,5}]nonene radical cation, **114**[†]





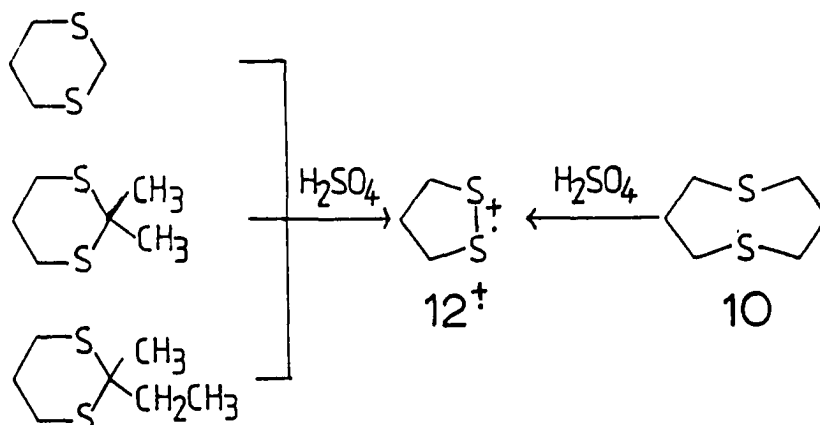
g -value and hfsc are reasonable for a dithietane radical cation, $\mathbf{115}^{\cdot+}$ was assigned as the structure. The rigidity of the bicyclic [2.2.1] ring system makes the dithietane ring planar in $\mathbf{115}^{\cdot+}$ and thus the two hydrogen atoms in the dithietane ring are equivalent. The radical cation $\mathbf{113}^{\cdot+}$ was assigned as the radical cation of $\mathbf{111}$. The assignment was based on the facts that $\mathbf{111}$ gave a large molecular ion peak in its mass spectrum, and the oxidation products of $\mathbf{112}$ always rearranged to form $\mathbf{111}$ under GC condition ($\sim 200\text{ }^\circ\text{C}$). Furthermore, the formation of $\mathbf{113}^{\cdot+}$ always preceded the formation of $\mathbf{115}^{\cdot+}$ under a variety of different ESR conditions.

1.2-Dithiolane radical cations

The 1,2-dithiolane radical cation $\mathbf{12}^{\cdot+}$ has been generated in both H_2SO_4^4 and $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$ ^{5,6} systems. In CH_2Cl_2 at low temperature, $\mathbf{12}^{\cdot+}$ shows selective line broadening from a ring inversion process. The activation energy for the ring inversion was reported to be 8 kJ/mol (1.9 kcal/mol). The activation enthalpy ΔH^\ddagger is calculated from the relationship $\Delta H^\ddagger = E_a - RT$ to be 1.5 kcal/mol (assumed $T = 200\text{ K}$). This small value of

ΔH^\ddagger seemed to be unreasonable since 1,2-dithietane radical cation **14**⁺ has a ΔH^\ddagger of 3.3 kcal/mol. Therefore, **12**⁺ was generated in CH_2Cl_2 by treatment of 1,2-dithiolane monosulfoxide with Al_2Cl_6 and the value of ΔH^\ddagger for the ring inversion process was measured. The line broadening was measured in the fast exchange mode as $\Delta H^\ddagger = 4.4$ kcal/mol and $\Delta S^\ddagger = -4.5$ eu. The new value seems to be a reasonable one since the 5-membered heterocyclic ring has relatively long S—S and C—S bonds. The envelope conformation of **12**⁺ should be relatively strain free compared to the envelope conformation of cyclopentene itself. Therefore, **12**⁺ has a sizable ΔH^\ddagger for the ring inversion compared to a very low (never measured) ΔH^\ddagger for cyclopentene.

The radical species generated by dissolving 1,5-dithiacyclooctane (DTCO) **10** in H_2SO_4 was first assigned as radical cation of DTCO.¹⁵ This experiment was repeated and it was found that the radical cation formed had a g -value of 2.018 instead of 2.012 reported previously. Apparently degradation occurred to form 1,2-dithiolane radical cation **12**⁺. It was also found that as a general reaction, 1,2-dithiolane radical cation **12**⁺ could be generated by dissolving thioketals of 1,3-propanedithiol in concentrated H_2SO_4 . Thus, 1,3-dithiane, 2,2-dimethyl-1,3-dithiane, and 2-methyl-2-ethyl-1,3-dithiane all gave the 1,2-dithiolane radical cation **12**⁺ when dissolved in concentrated H_2SO_4 .



4-Phenyl-1,2,3-trithiane **116** was synthesized by a four-step synthesis described in Scheme VI. Either compound **116** or **117** dissolved in concentrated H_2SO_4 to give 3-phenyl-1,2-dithiolane radical cation **118**⁺ ($a^{\text{H}} = 14.4$ (1H), 11.9 (1H), 4.7 (1H), 1.2 (1H) G, $g = 2.0172$) (Figure 35). The radical cations **118**⁺ contains two β hydrogen atoms with large hfsc and one with small hfsc. The ESR spectrum of **118**⁺ showed no effect of temperature from 0 to 60 °C. The results are interpreted in terms of the population of only a single conformation of which the phenyl group occupies the quasi-equatorial position.

Scheme VI.

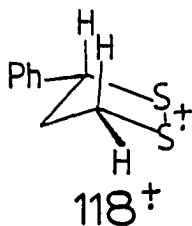
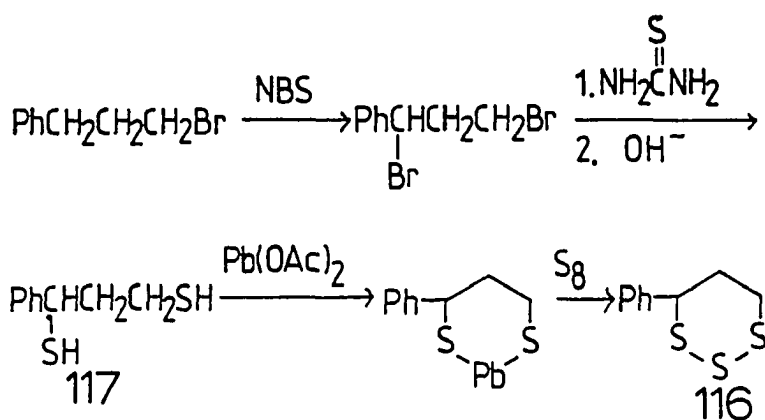
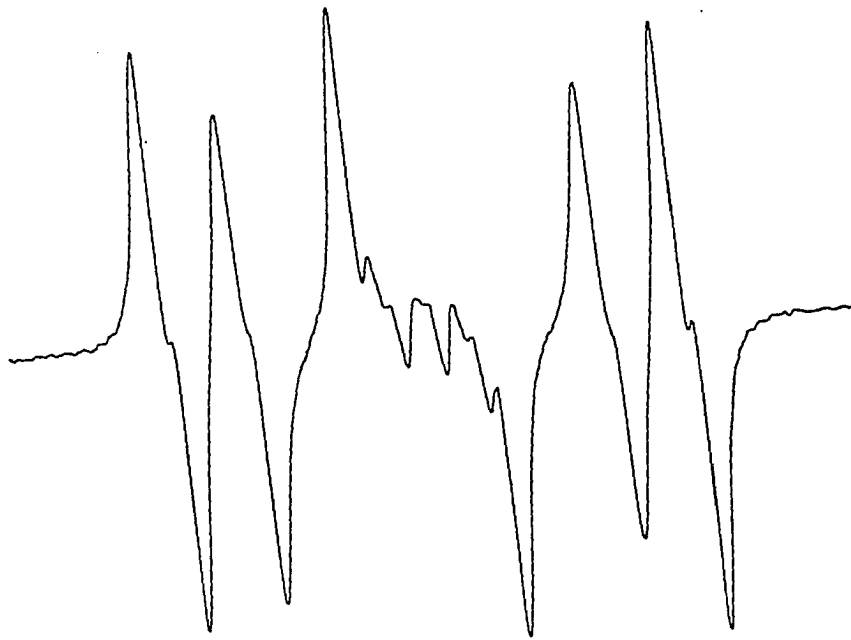


Figure 35. First derivative ESR spectrum of 3-phenyl-1,2-dithiolane radical cation, **118⁺**

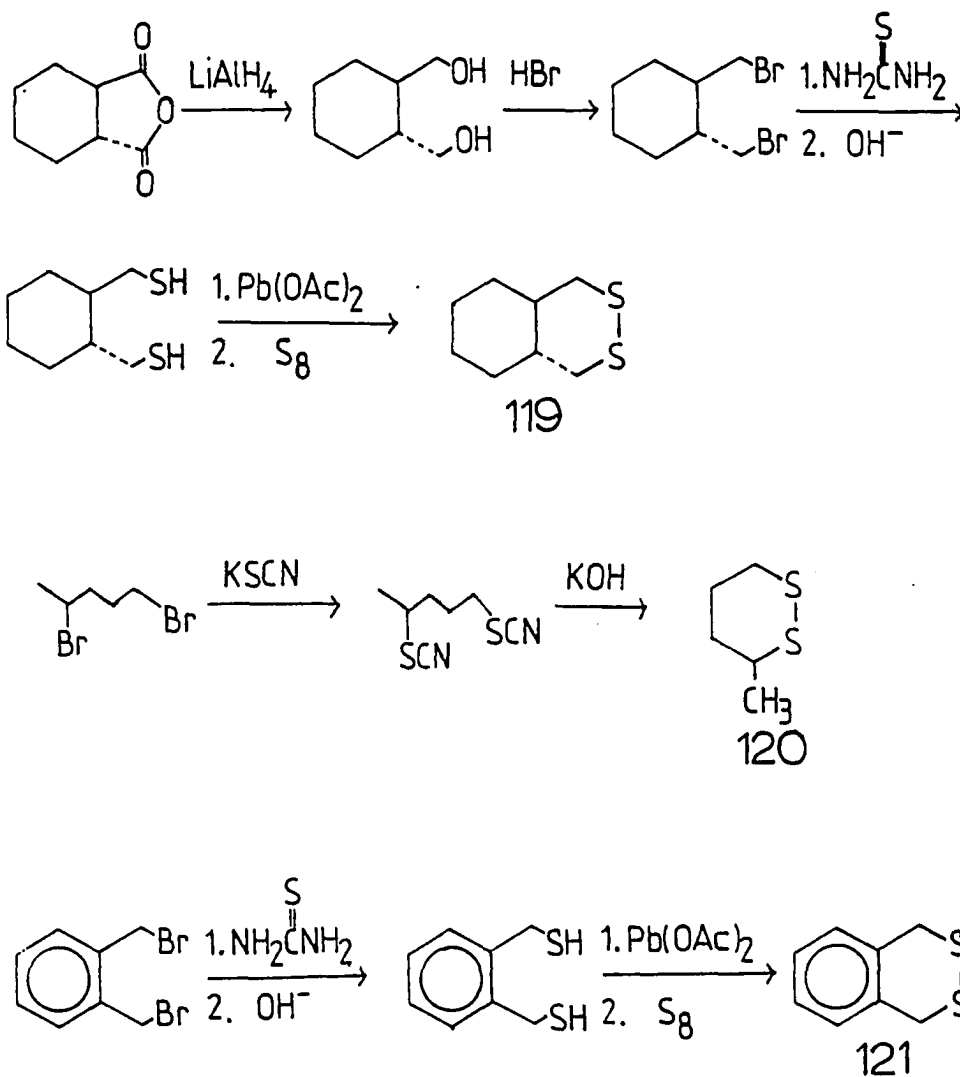


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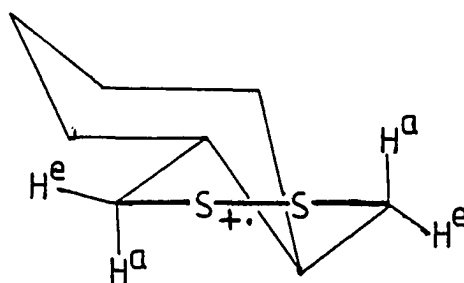
1.2-Dithiane radical cations

Four derivatives of 1,2-dithiane **119**³⁴, **120**³⁵, **121**³⁶, were synthesized by known procedures described by Scheme VII.

Scheme VII



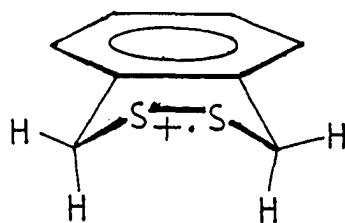
The compound **119** dissolved in H_2SO_4 to give $\mathbf{119}^+$ whose ESR spectrum was a triplet of triplets ($a^{\text{H}} = 17.5$ (2H), 4.3 (2H) G, $g = 2.0186$). The hyperfine splitting pattern of $\mathbf{119}^+$ clearly indicates that $\mathbf{119}^+$ is locked in a chair-halfchair conformation (XII) with the quasi-axial hydrogen atoms having a large hfsc (17.5 G) and the quasi-equatorial hydrogen atoms having a small hfsc (4.3 G).



XII

3-Methyl-1,2-dithiane **120** gave $\mathbf{120}^+$ in both H_2SO_4 and $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$. The three hydrogen atoms β to sulfur atoms have different hfsc and the hfsc change with temperature. At -70°C , $\mathbf{120}^+$ has $a^{\text{H}} = 4.0$ (1H), 12.5 (1H), 14.0 (1H) G, with $g = 2.0176$, while at 25°C $a^{\text{H}} = 8.0$ (1H), 9.9 (1H), 12.6 (1H) G. The temperature dependent ESR spectra of $\mathbf{120}^+$ suggest that $\mathbf{120}^+$ is not a planar system. At low temperature (-70°C) it has a frozen conformation with the methyl group in the quasi-equatorial position while at above room temperature ring inversion is fast enough that all three hydrogen atoms have comparable hfsc.

The compound **121** dissolved in H_2SO_4 to give $\mathbf{121}^+$. The ESR spectrum of $\mathbf{121}^+$ (Figure 36) is a triplet with large hfsc ($a^{\text{H}} = 15.8 \text{ G}$, $g = 2.0175$) and is independent of temperature from 0°C to 80°C . The hyperfine splitting pattern of $\mathbf{121}^+$ suggests that $\mathbf{121}^+$ is locked in a frozen boat conformation (XIII) with only the axial hydrogen atoms having large hfsc. Dideuterated **121** (d_2 -**121**) was made (Scheme VIII) to further explore the



XIII

Scheme VIII

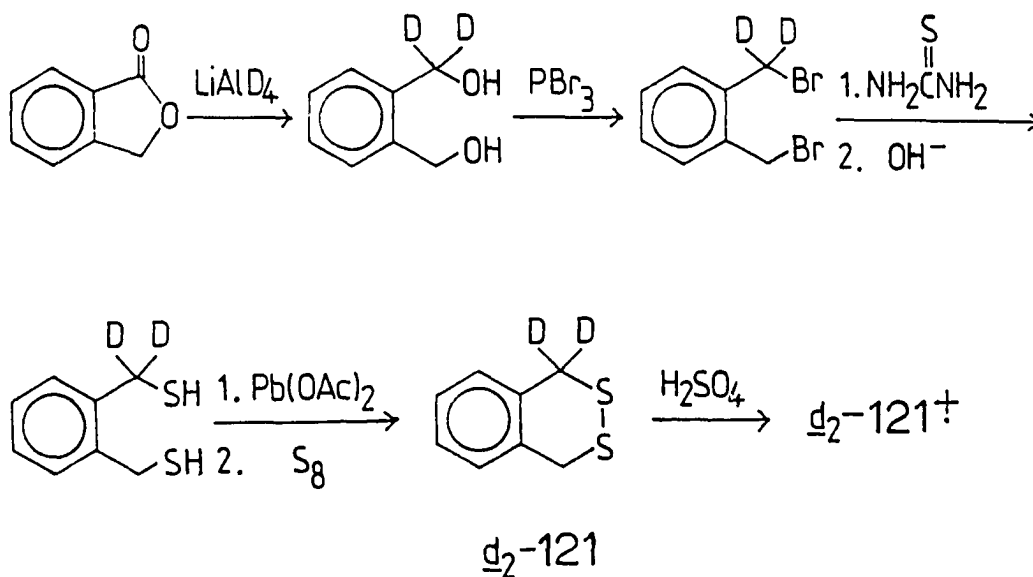


Figure 36. First derivative ESR spectra of

(a) *trans*-2,3-dithiadecalin radical cation, **119⁺**

(b)-(d) 3-methyl-1,2-dithiane radical cation, **120⁺**,

(b) at -70 °C in Al₂Cl₆/CH₂Cl₂

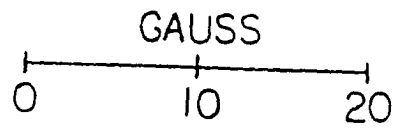
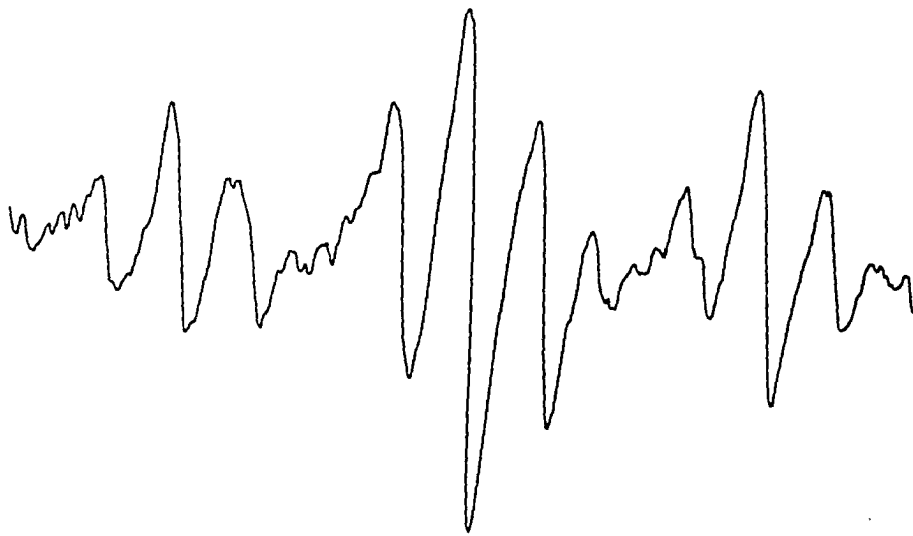
(c) at -20 °C in Al₂Cl₆/CH₂Cl₂

(d) at 25 °C in H₂SO₄

(e) 2,3-dithiatetralin radical cation, **121⁺**

(f) 1,1-dideutero-2,3-dithiatetralin radical cation, *d*₂-**121⁺**

a



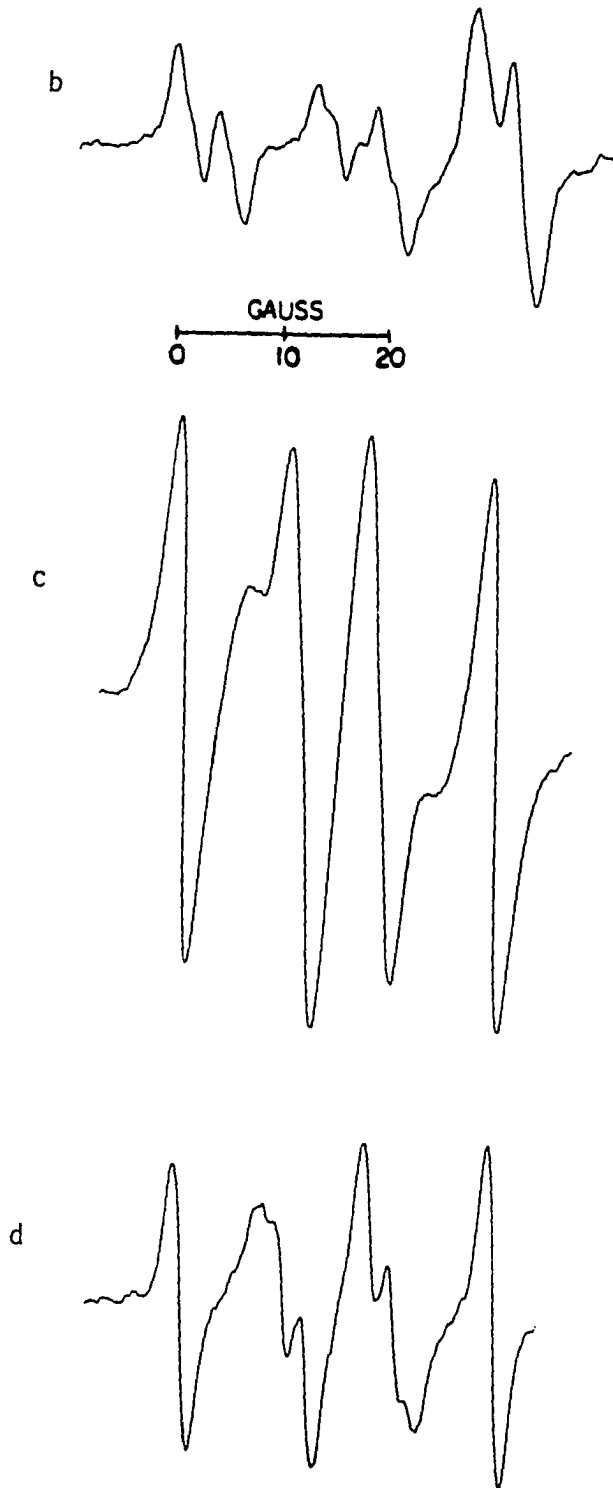


Figure 36. (continued)

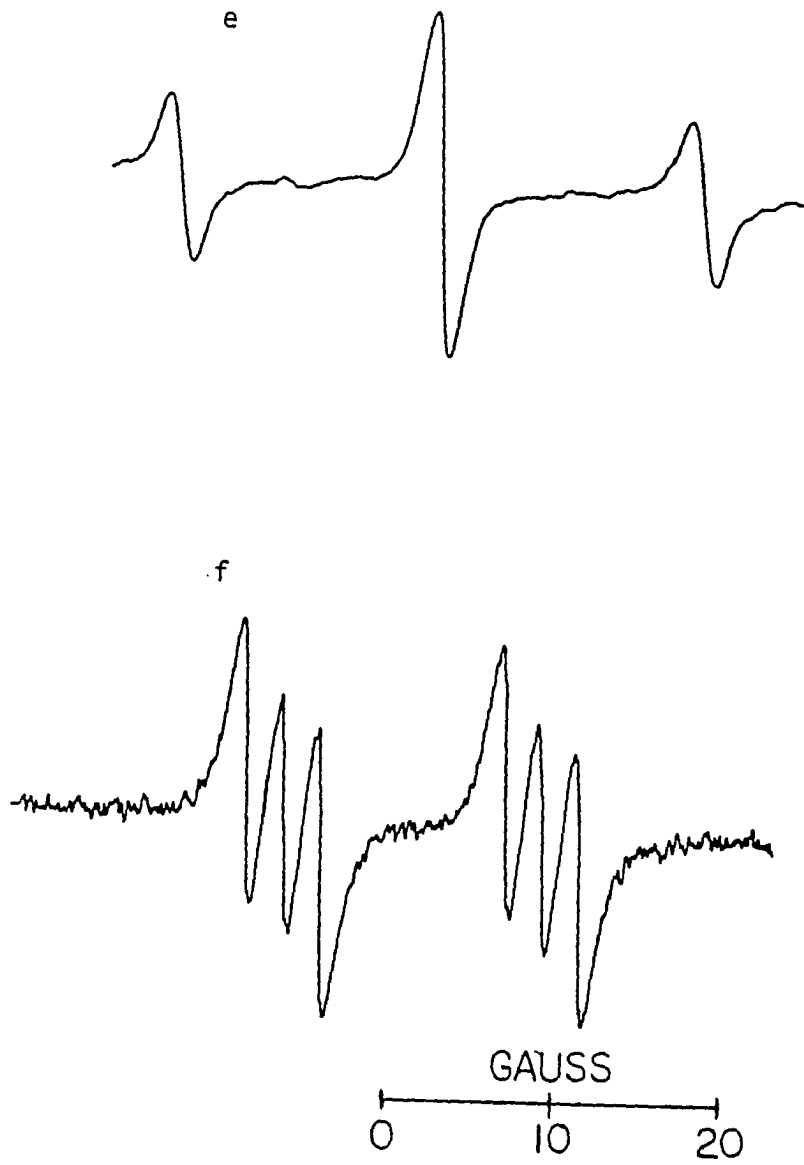


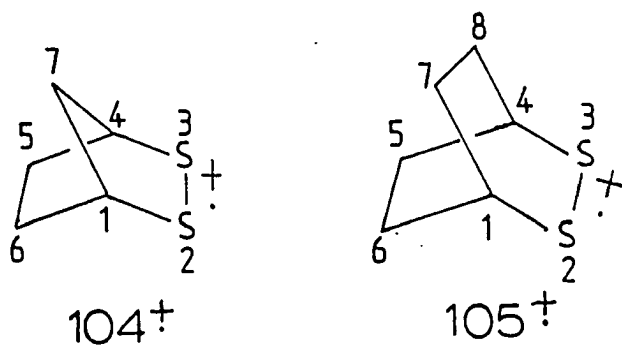
Figure 36. (continued)

structure of **121**⁺. The compound *d*₂-**121** was oxidized by H₂SO₄ to form *d*₂-**121**⁺ (*a*^H = 15.8 (1H) G, *a*^D = 2.42 (1D) G, *g* = 2.0175). This deuterium-labeled experiment proves that only one hydrogen of each methylene group leads to a large hyperfine splitting. The hyperfine splitting pattern of **121**⁺ also provides strong evidence that hyperfine splitting by hydrogen atoms β to a sulfur atom possessing unpaired spin density is mainly determined by an angle-dependent hyperconjugative interaction. The equatorial C—H bonds for the methylene groups α to the sulfur atoms are almost perpendicular to the p orbitals of the sulfur atoms and have very small (<1 G) hfsc.

Lüttringhaus, Kabuss, Maier, and Friebolin³⁷ reported that 4,4,5,5-tetradeuterodithiane (*d*₄-**103**) had a ΔH^\ddagger of 11.5 kcal/mol for the ring inversion process at -70 °C and compound **121** had a ΔG^\ddagger of 8.5 kcal/mol for the ring inversion process at -90 °C. Since *d*₄-**103** has a higher ΔH^\ddagger value than cyclohexane (10 kcal/mol), it is logical to assume that **103**⁺ and **120**⁺ should have higher ΔH^\ddagger values for the ring inversion process than cyclohexene (5.3 kcal/mol)^{38,39}. Since the ΔH^\ddagger values for the ring inversion process of **103**⁺ and **120**⁺ are not available, this assumption cannot be justified at this time. On the other hand, the high ΔG^\ddagger value for the ring inversion process of **121** is a positive support for the conformational rigidity of radical cation **121**⁺.

Bicyclic disulfide radical cations

In order to explore the symmetry of the SOMO of disulfide radical cations and the possibility of long range coupling of sulfur-centered radical cations, **104**⁺ and **105**⁺ were selected as the target radical cations. The approach toward **104**⁺ is described in Scheme IX. Although numerous attempts to synthesize the bicyclic disulfide **104** were unsuccessful, treatment of either *cis*-1,3-cyclopentanedithiolacetate **45** or *cis*-1,3-cyclopentanedithiol **122** produced **104**⁺ (*a*^H = 6.3 (2H) G, *g* = 2.018) (Figure 37). The triplet hfs was assigned to



Scheme IX

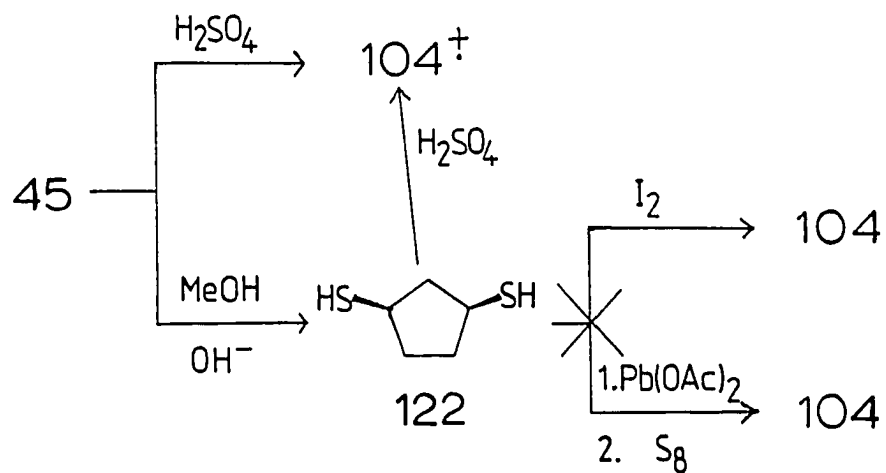
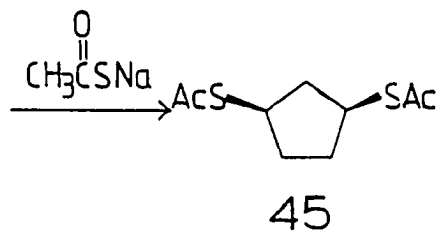
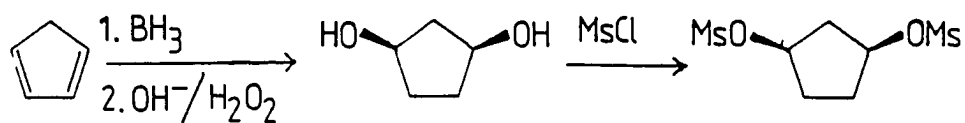
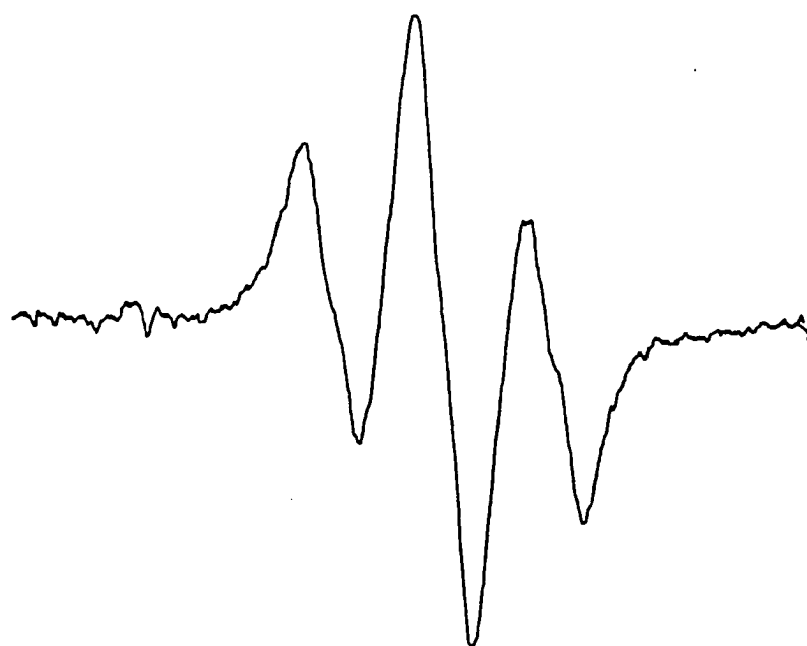


Figure 37. First derivative ESR spectrum of 2,3-dithiabicyclo[2.2.1]heptane radical cation,
104⁺



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the *exo* hydrogens at C-5,6. The absence of large hfs for the *anti*-hydrogen at C-7 is proof for the antisymmetric SOMO of $R-S^{\cdot+}S-R$ because the C-7 *anti*-hydrogen lies in the nodal plane of the spin probe.

cis-Cyclohexane-1,4-dithiol **123** which is reported in the literature,⁴⁰ was an ideal precursor for **105**⁺. The synthesis of **123** is described in Scheme X. Once again, attempts to synthesize the bicyclic disulfide **105** were unsuccessful. Nevertheless, the bicyclic disulfide radical cation **105**⁺ ($a^H = 3.8$ (4H) G, $g = 2.0186$) was generated by the reaction of dithiol **123** with concentrated H_2SO_4 . The pentet hyperfine splitting pattern of **105**⁺ was assigned to the four *exo*-hydrogens in C-5,6,7,8 positions. The dideuterated dithiol d_2 -**123** was also made (Scheme XI). The triplet hyperfine splitting pattern of the dideuterated cyclic disulfide radical cation d_2 -**105**⁺ ($a^H = 3.8$ (2H) G, $g = 2.0186$) further confirms this assignment.

Scheme X

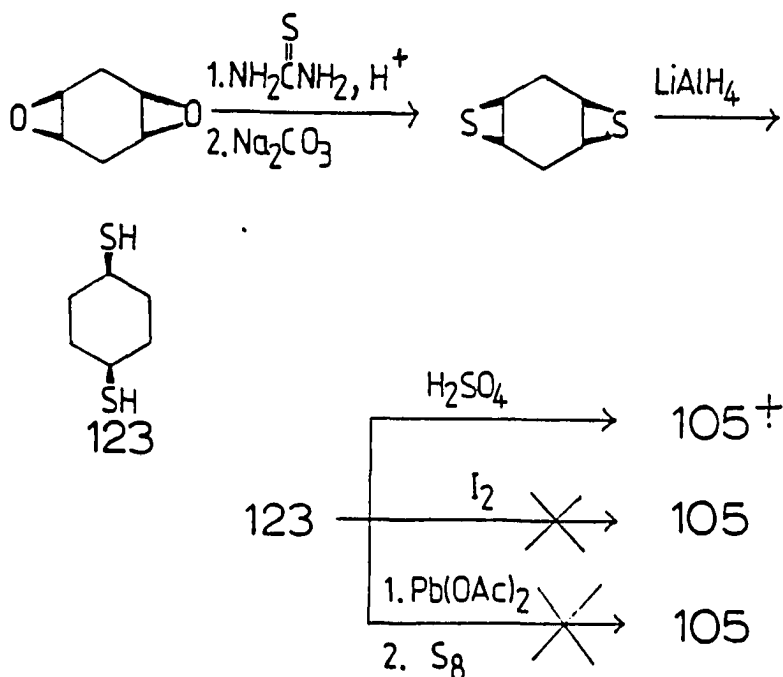
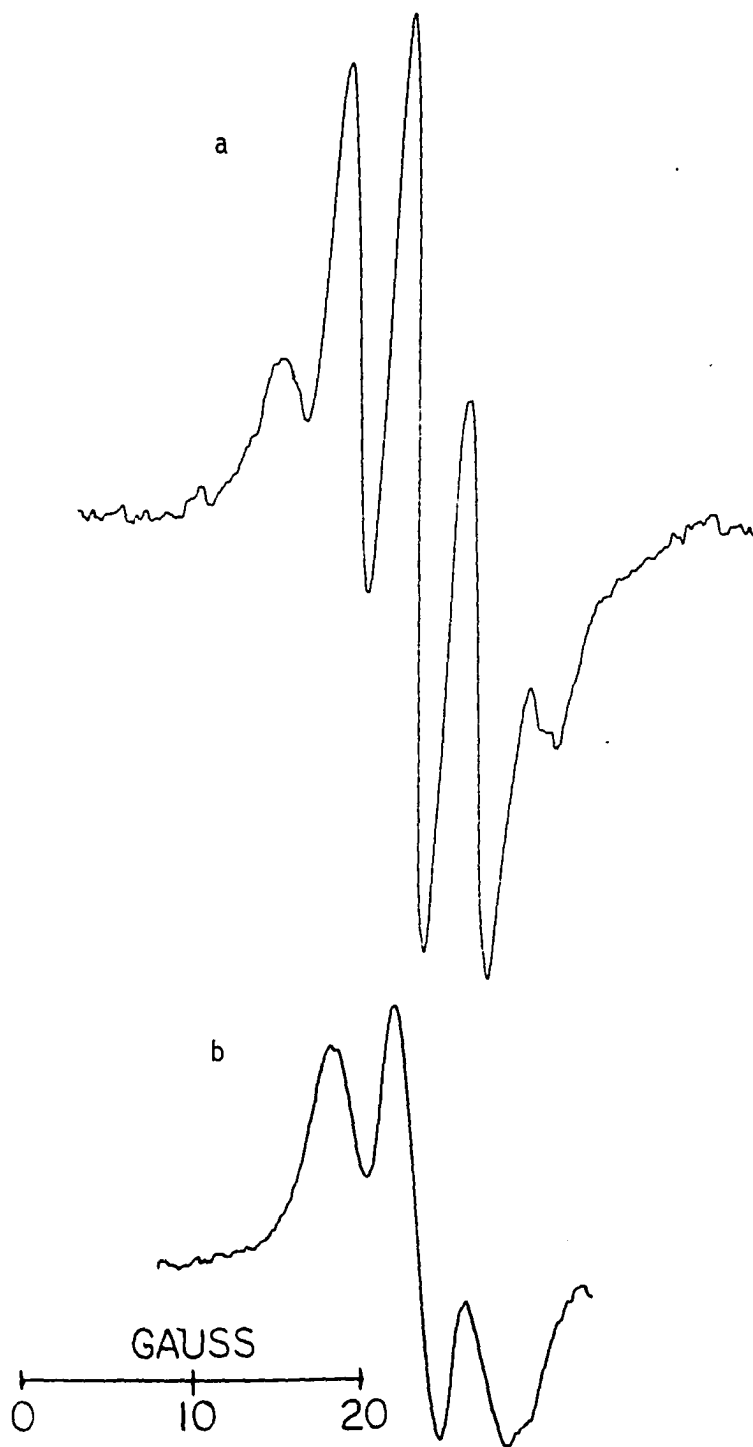


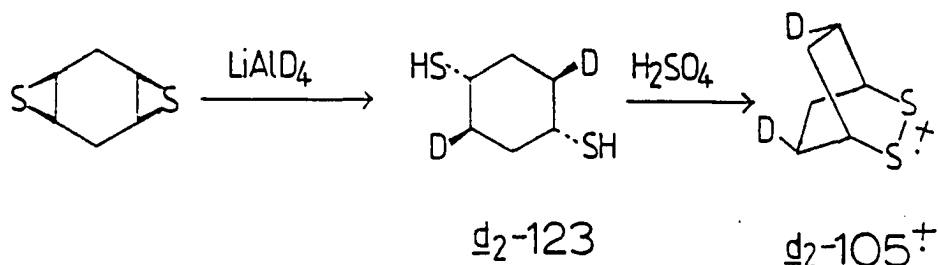
Figure 38. First derivative ESR spectra of

(a) 2,3-dithiabicyclo[2.2.2]octane radical cation, 105^\dagger

(b) *exo*-5,7-dideutero-2,3-dithiabicyclo[2.2.2]octane radical cation, d_2 - 105^\dagger



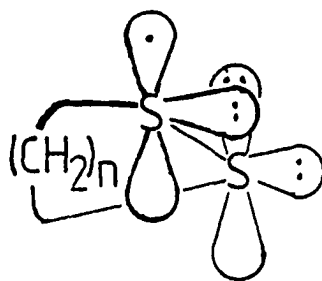
Scheme XI



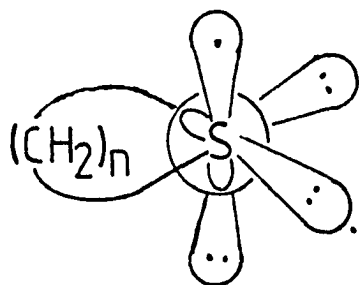
The ESR results of 104^+ , 105^+ , and d_2-105^+ confirm that the SOMO of $\text{R}-\text{S}^{\cdot+}-\text{S}-\text{R}$ is antisymmetrical. Furthermore, these results show that sulfur-centered radical cations are capable of delocalizing spin density through a long range (W plan) mechanism.

A comparison of all the ESR results obtained for different kinds of disulfide radical cations gives rise to some interesting questions. First of all, 1,2-dithiolane and 1,2-dithiane radical cations have similar hfsc for axial hydrogens (15-18 G), while 1,2-dithietane radical cations have significant smaller hfsc for axial hydrogens (6-9 G). Secondly, in contrast to the literature prediction, 1,2-dithietane radical cation 14^+ has a sizable energy barrier for ring inversion. Snyder and Carlsen³³ used a CNDO/B calculation to predict that 1,2-dithietane was a flat molecule and had very low energy barrier for the ring inversion process (~ 1 kcal/mol). 1,2-Dithietane radical cation 14^+ should have even shorter sulfur-sulfur bond and hence, smaller ring size than 1,2-dithietane **14**. If 14^+ has a three electron π bond and the two sulfur atoms are sp^2 hybridized, 14^+ should be a flat species with a very small energy barrier for the ring inversion.

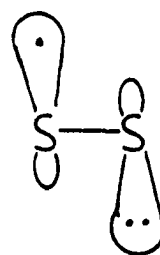
In order to explain this puzzle, two possible electronic structures (XIV and XV) are proposed. The first type (XIV) involves a normal three electron π bonding in which the sulfur atoms are sp^2 hybridized and the $C-S^+-S-C$ skeleton is completely planar. The second possible electronic structure is a bisected σ -delocalized structure where the geometry of the radical cation is essentially the same as the cyclic disulfide and the extent of overlap between the two bonding orbitals is smaller (XVa) than in XIV. Simple Huckel calculations with overlap integrals included predict⁴¹ that the three electron bond is significantly stabilizing only when the two levels initially are of equal or almost equal energy, and the overlap between the orbitals is not too large. For structure XIV, the two bonding p orbitals



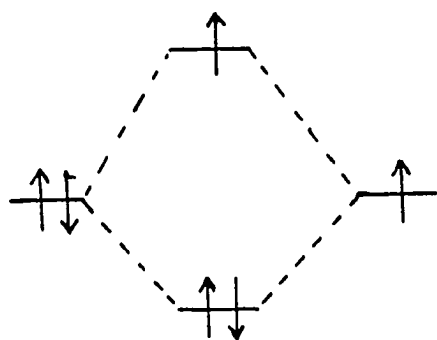
XIV



XV

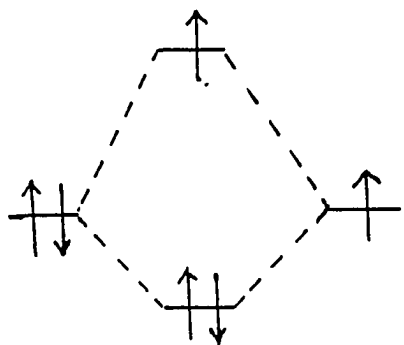


XVa



$$\begin{array}{c} \uparrow \\ \downarrow \\ \uparrow \\ \downarrow \end{array} \begin{array}{l} \frac{\beta - \alpha S}{1 - S} \\ \frac{\beta - \alpha S}{1 + S} \end{array}$$

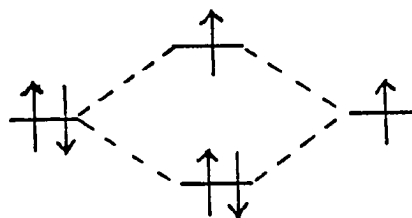
OVERLAP INCLUDED



XIV

$$\beta^{\text{XIV}} > \beta^{\text{XV}}$$

$$S_{1,2}^{\text{XIV}} > S_{1,2}^{\text{XV}}$$



XV

have better overlap and hence, a larger β , while the overlap between the two bonding orbitals in XV is smaller and hence electronic structure XV has a smaller β . When both β and $S_{1,2}$ are considered, the energy difference between electronic structure XIV and XV could be very small and the electronic structure which is adapted by a specific disulfide radical cation could be determined by other secondary interactions. For the bicyclic disulfide radical cations **104⁺** and **105⁺**, the steric rigidity makes XIV the only possible electronic structure for the three-electron bond. For dithietane radical cation, if it adapts the electronic state XIV, there will be significantly eclipsed interactions between the two methylene groups and between the two non-bonded lone pairs of electrons on the sulfur atoms. If the dithietane radical cation adapts the electronic state XV, the above non-bonded interactions are minimized. Thus, these secondary interactions make electronic state XV energetically more favorable than electronic state XIV. The dithietane radical cations (**14⁺**, **106⁺**-**110⁺**) thus adapt electronic state XV for their three electron bonds. The adaptation of electronic state XV for dithietane radical cations explains the sizable energy barrier for the ring inversion of **14⁺** and the conformational preference for **106⁺**-**110⁺**, since strong secondary interactions destabilize the planar transition state. For radical cation **115⁺** owing to the rigidity of the bicyclic[2.2.1] framework, the dithietane ring has to be planar, hence the three electron bond can only adapt the electronic state XIV. For 1,2-dithiolane and 1,2-dithiane radical cations, experimental results cannot determine which electronic state is adapted by these radical cations. CNDO calculation performed by Bock, Stein, and Semkow⁶ predicts that 1,2-dithiolane radical cations has the electronic state XIV with a completely planar C—S⁺—S—C skeleton. Therefore, based on this theoretical result, 1,2-dithiolane, 1,2-dithiane radical cations are assumed to possess normal three electron π bonding with a completely planar C—S⁺—S—C skeleton.

From the hyperfine splitting patterns of radical cations **119⁺** and **121⁺**, it is clear that hyperconjugation is the predominant mechanism operating in the hfs of hydrogen β to the sulfur atom which has spin density. In the case of **121⁺** equatorial hydrogens is too small to be resolved (<1 G). Hence one can assume that spin polarization is neglectable for disulfide radical cations. Based on this assumption, the hfsc for hydrogen atoms β to the sulfur atom are given by Equation 8,

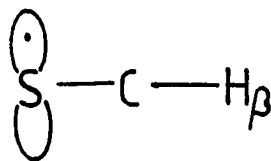
$$a^H = \rho_S B \langle \cos^2 \theta \rangle \quad (8)$$

where a^H is the hfsc for the β hydrogen, B is a constant, ρ_S is the spin density at the sulfur atom and θ is the angle between the orbital containing the unpaired electron and C—H bond. It follows that when Equation 9 is combined with Equation 10, that

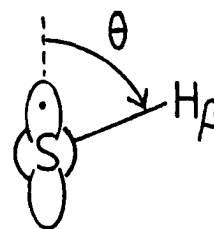
$$a^H_{\text{axial}}/a^H_{\text{equatorial}} = \langle \cos^2 \theta_{\text{axial}} \rangle / \langle \cos^2 \theta_{\text{equatorial}} \rangle \quad (9)$$

$$\theta_{\text{equatorial}} - \theta_{\text{axial}} = 120^\circ \quad (10)$$

θ_{axial} and $\theta_{\text{equatorial}}$ can be calculated. From the values of θ_{axial} and $\theta_{\text{equatorial}}$, the constant B can be calculated. Table 7 lists the calculated B values for radical cation **12⁺**, **119⁺**, and **121⁺**.



XVI



XVII

Table 7. Calculated B values for radical cations **12⁺**, **119⁺**, and **121⁺**

radical cations	a_{ax}^H (G)	a_{eq}^H (G)	ρ_s	$\langle \cos^2 \theta_a \rangle$	$\langle \cos^2 \theta_{eq} \rangle$	B(G)
12⁺ ^{5,6}	16.25	3.9	0.5	1	0.25	33
119⁺	17.5	4.3	0.5	1	0.25	35
121⁺	15.8	1 ^a	0.5	0.88	0.03	36

^aEstimated value.

For all three radical cations **12⁺**, **119⁺**, **121⁺**, the B values are essentially the same (the average value is ~ 35 G). Zweig and Hodgson²⁰ investigated the cation radicals of 1,4-bis(methylthio)benzene and 1,2,4,5-tetrakis(methylthio)benzene and suggested that the coupling constants of the methyl hydrogens β to sulfur were related to ρ_s by the expression (Equation 1) where $Q_{CH_3}^H = 21$ G. In a reexamination of Zweig's work,

$$a^H = Q_{SCH_3}^H \cdot \rho_s \quad (1)$$

Sullivan and Forbes²¹ suggested a value of $Q_{SCH_3}^H = 18.5$ G. Comparing Equation 1 with Equation 8, the relationship of Equation 11 is obtained. For a freely rotating methyl group, $\langle \cos^2 \theta \rangle = 0.5$

$$Q_{SCH_3}^H = B \langle \cos^2 \theta \rangle \quad (11)$$

and $B = 2 Q_{SCH_3}^H$. So for Zweig and Hodgson's case, $B = 42$ G, while for Sullivan and Forbe's case, $B = 37$ G. The B values obtained from their results are in good agreement with the B values obtained in this work. It is therefore concluded that for π -type sulfur-centered radical cations, the hfsc of the hydrogen atom β to sulfur atom which has spin density, are predominantly determined from an angle-dependent hyperconjugative model,

and the constant B is shown to be about 35 G. This B value for sulfur is in the same order as the B value (40-80 G) obtained for carbon-centered radicals. It is important to point out that although the 3p orbital of sulfur has significant higher energy than the 2p orbital of carbon, the ability of the sulfur atom to delocalize its spin density to the β hydrogen through hyperconjugation is comparable to the carbon atom.

CHAPTER IV. SUMMARY AND CONCLUSIONS

A series of new radical cations in 1,4-dithiin, 1,4-benzodithiin, 2,3-dihydro-1,4-dithiin, 1,4-dithiepin, 1,2-dithietane, 1,2-dithiolane, 1,2-dithiane series were prepared. An experimental technique is described for determining the symmetry of a SOMO for radical cations or anions fused into the bicyclo[2.2.1]heptane ring system. The SOMO of 1,4-dithiin, 1,4-benzodithiin, 2,3-dihydro-1,4-dithiin radical cations were found to be symmetrical while the SOMO of cyclic saturated 1,2-disulfide radical cations were found to be antisymmetrical. 2,3-Dihydro-1,4-dithiin and 1,4-dithiepin radical cations were found to have conformational preference at low temperature and the activation parameters for the ring inversion processes were obtained. For 1,2-bis(isopropylthio)cyclohexene radical cation (63^+), the unusually low value of ΔH^\ddagger for the cyclohexene ring inversion were explained by secondary interactions between the isopropyl groups and the α methylene groups. The unexpectedly high values of ΔH^\ddagger for cyclohexadiene ring inversion of radical cation 26^+ and 49^+ were explained by secondary steric interaction between the lone pair of one sulfur atom and one of the hydrogens in the dihydronaphthalene ring. Sulfur-centered radical cations were found to be capable of showing sizable long range couplings in the radical cations of 2,5-dithiabicyclo[4.2.1]non-3-ene (44^+), 2,3-dithiabicyclo[2.2.1]heptane (104^+), 2,3-dithiabicyclo[2.2.2]octane (105^+). It is established from all the ESR results that the hfs of a hydrogen β to a sulfur atom with spin density arises predominantly from angle-dependent hyperconjugation. For disulfide radical cations (not including 1,2-dithietane radical cations), a value of 35 G was calculated for the constant B which is a measure of the magnitude of this interaction. For 1,2-dithietane radical cations, a σ -delocalized electronic structure for the three-electron bond is proposed to explain the unusual conformational preference and the unusually low values of a^H .

Sulfur-centered radical cations were generated by oxidative rearrangement. Thus, 2,3,-dialkyl-1,2-dithiolanes rearranged to form 2,3-dihydro-1,4-dithiin radical cations when treated with either H_2SO_4 or $\text{Al}_2\text{Cl}_6/\text{CH}_2\text{Cl}_2$. Similarly, 2,2-dialkyl-1,3-benzodithioles rearranged to form the 1,4-benzodithiin radical cations. Diaryl disulfides underwent oxidative rearrangement to form benzodithiete and thianthrene radical cations. Methylbenzyl disulfides underwent oxidative rearrangement to form polymethylbenzodithiete and 2,6-dimethylantracene radical cations.

CHAPTER V. EXPERIMENTAL

Reagents

Common solvents and chemicals were obtained from commercial sources and were used without purification. If purification was required, it is so stated where pertinent. Ether and tetrahydrofuran were freshly distilled from lithium aluminum hydride. The methylene chloride used for ESR experiment was freshly distilled from calcium hydride. Aluminum chloride was sublimed under vacuum.⁴²

Preparation of Solutions of Radical Cations

Radical cation in H_2SO_4 solution was generated by addition of concentrated sulfuric acid to the precursor to give a 0.05-1.0 M solution. The solution was then transferred into a flat fused-silica cell for ESR study.

Radical cations in CH_2Cl_2 were generated by the following procedure.⁴³⁻⁴⁶ Sublimed Al_2Cl_6 (5-10 mg) was placed in a round glass tube. The tube was capped with a rubber septum and evacuated through a hypodermic needle which was connected to a vacuum pump. The tube was then cooled with liquid N_2 . A solution of 5-10 mg of the precursor in ~ 0.3 ml of CH_2Cl_2 was introduced into the tube by a syringe, and the tube was sealed under vacuum. The methylene chloride was allowed to melt and the mixture shaken immediately before the tube was placed in a pre-cooled cavity of the ESR spectrometer.

Recording and Simulation of ESR Spectra

ESR spectra were recorded using a Bruker ER 200D-SRC spectrometer with a 10-inch magnet and 100 KHz field modulation. g -Values were measured with a Systron Donner Frequency Counter Model 6245A set at 100 Hz resolution and which had been calibrated to better than one part in ten million. Used in conjunction with the frequency

counter was an ER035 NMR Gaussmeter with an auto-lock self-tracking proton NMR field measuring device providing direct 6-digit readout. Prior to each g -value determination, the gaussmeter was calibrated for the difference in absolute field between the sample and the probehead. A solid sample of diphenylpicrylhydrazyl (DPPH) with $g = 2.0036^{47}$ was used as a standard, and characteristic shifts ranged from 10 to 100 mG. NMR lock was maintained during the course of a single experiment to ensure a constant correction factor. Simulation of ESR spectra was executed on an Aspect 2000 computer with an ERRSC .015 software package.

Characterization of Compounds

^1H NMR spectra were recorded at room temperature on either a Varian EM 360 (A,L) or a JOEL FX-90Q spectrometer. ^{13}C NMR spectra were recorded at room temperature on a FX-90Q spectrometer. Chemical shifts are reported in parts per million (δ) from tetramethylsilane (TMS). Coupling constants (J) are reported in Hertz. Infrared spectra were measured on a Beckman IR-4250 or Beckman Acculab 2 Double Beam Spectrometer. Mass spectra were recorded on an Kratos MS-50 spectrometer.

Preparation of Compounds

4,5-Tetramethylene-1,3-dithiole(20)

The procedure used was that of Zaleta.⁴⁸ To 0.7 g of lithium aluminum hydride stirred at 0 °C in 20 mL of dry ether under nitrogen was added 2.5 g of 4,5-tetramethylene-1,3-dithiole-2-thione⁴⁸ (41) in 100 mL of ether. Addition took 10 minutes. The mixture was stirred over night at 0 °C, poured into sat. NH_4Cl solution, acidified with 10% H_2SO_4 , and separated. The ether layer was washed with water, dried over MgSO_4 , and evaporated, leaving an oil which was chromatographed on silica gel with hexane as eluent to give 1.05 g

(50%) of **20** as a yellowish liquid⁴⁹ : $^1\text{H NMR}$ (CDCl_3) δ 4.30 (s,2H), 2.16(m,4H), 1.72(m,4H).

Methanedithiol

To a solution of 0.1 mole potassium thiolacetate (from 7.7 g thiolacetic acid and 7.3 g KOH) in 50 mL MeOH was added slowly 8 g of dibromomethane.⁵⁰ The mixture was then refluxed for 0.5 h, poured into ice-water and extracted with ether. The extract was washed with H_2O and dried over MgSO_4 , the ether was removed by vacuum to give the crude methanedithiol diacetate which was used without purification. The crude methanedithiol diacetate was dissolved in 35 mL 2% methanolic hydrogen chloride and allowed to stand for 6 h.⁵¹ The mixture was then poured on to ice-water and extracted with benzene. The extract was washed with water and dried over Na_2SO_4 . Owing to the smell of methanedithiol, the crude methanedithiol in benzene solution was used directly for other reactions. The yield was estimated to be ~ 30% (based on dibromomethane).

4.5-Dimethyl-1,3-dithiole (25)

To a solution of ~ 0.8 g of methanedithiol in 20 mL of benzene was added 0.86 g of 3-chlorobutanone and small amount of *p*-toluenesulfonic acid. The mixture was refluxed for 24 h after which time the mixture was cooled to room temperature, washed with 5% NaOH, water, and the organic layer dried over Na_2SO_4 . Evaporation of the solvent and chromatography of the residue on silica gel with hexane as eluent gave 470 mg (40%) of **25** as a yellowish liquid: $^1\text{H NMR}$ (CDCl_3) δ 4.25(s, 2H), 1.85(s, 6H); IR(neat) 2945, 2895, 1440, 1360, 1250, 1155 cm^{-1} ; HRMS calculated for $\text{C}_5\text{H}_8\text{S}_2$ 132.00675, measured 132.00688.

4.5-Dihydronaphtho-[1,2-d]-1,3-dithiole (26)

The method used for the synthesis of **25** was followed. Reaction of ~ 0.7 g of methanedithiol with 1.5 g of 2-bromo- α -tetralone gave 0.39 g (28%) of **26**: $^1\text{H NMR}$ (CDCl_3) δ 7.0-7.6 (m, 4H), 4.46 (s, 2H), 2.25-3.10 (m, 4H); IR(neat) 3050, 3010, 2910, 1590, 1555, 1480, 1440, 1260 cm^{-1} ; HRMS calculated for $\text{C}_{11}\text{H}_{10}\text{S}_2$ 206.02240, measured 206.02176.

General procedure for synthesis of 1,3-benzodithioles 27-29

A solution of 12 mmol of $\text{RCH}(\text{OMe})_2$ in 8 mL of CHCl_3 was slowly added to a refluxing mixture of 10 mmol of 1,2-benzenedithiol, 3 mL of $\text{BF}_3\cdot\text{Et}_2\text{O}$, 4 mL of HOAc, and 6 mL of CHCl_3 ⁵². The resulted mixture was refluxed for 4 h, cooled, extracted twice with water followed by 5% Na_2CO_3 and again with water. The organic layer was dried over MgSO_4 . Evaporation of the solvent gave a residue which was chromatographed on silica gel with hexane as eluent to give the 1,3-benzodithiole.

1,3-Benzodithiole (27)

The above general procedure was used to produce **27** in 34 % yield⁵³: $^1\text{H NMR}$ (CDCl_3) δ 7.3-6.9 (m, 4H), 4.43(s, 2H).

2-Methyl-1,3-benzodithiole (28)

The general procedure was used to produce **28** in 62% yield⁵⁴: $^1\text{H NMR}(\text{CDCl}_3)$ δ 7.36-6.95 (m, 4H), 5.00 (q, 1H, $J = 6.5$ Hz), 1.70(d, 3H, $J = 6.5$ Hz).

2-Phenyl-1,3-benzodithiole (29)

The general procedure was used to produced **29** in 73% yield⁵⁴: $^1\text{H NMR}(\text{CDCl}_3)$ δ 7.6-6.9(m, 9H), 6.15(s, 1H).

2.2-Dimethyl-1,3-benzodithiole (30)

A solution of 220 mg of 1,2-benzenedithiol, 1 mL of acetone, and 1 mL of chlorotrimethylsilane in 5 mL of CHCl_3 was stirred at room temperature for 3 h. The mixture was then washed with 5% NaOH, water, and dried with Na_2SO_4 . Evaporation of the solvent left a residue which was chromatographed on silica gel with hexane as eluent to give 0.25 g (89%) of **30**: $^1\text{H NMR}(\text{CDCl}_3)$ δ 7.38-6.97 (m, 4H), 1.90 (s, 6H); HRMS calculated for $\text{C}_9\text{H}_{10}\text{S}_2$ 182.02240, measured 182.0221.

General procedure for synthesis of 2,3-dihydro-1,4-dithiin 31-36

The procedure of Mursakulov, Kerimov, Kasumov, Ramazanov, and Zefirov⁵⁵ was used. The α -chloro ketone (10 mmol) and 1,2-dithiol (11 mmol) were stirred with a small amount of *p*-toluenesulfonic acid in 10 mL of refluxing benzene for 24 h. The mixture was washed with 10% NaOH, water, and dried with MgSO_4 . The solvent was evaporated and the residue was either distilled under vacuum or chromatographed on silica gel with hexane as eluent to give the 2,3-dihydro-1,4-dithiin.

2,3-Dihydro-1,4-dithiin (31)

The above procedure was employed with chloroacetaldehyde diethyl acetal. The crude product was distilled to give **31** as a colorless liquid in 39% yield: bp 100 °C (10 torr) [lit.⁵⁶ bp 101 °C(29 torr)]; $^1\text{H NMR}(\text{CDCl}_3)$ δ 6.1(s, 2H), 3.2(s, 4H).

5,6-Dimethyl-2,3-dihydro-1,4-dithiin (32)

The general procedure was used and the crude product was distilled to give **32** as a colorless liquid in 34% yield: bp 90-92 °C (10 torr) [lit.⁵⁷ bp 113-114 °C(25 torr)]; $^1\text{H NMR}(\text{CDCl}_3)$ δ 3.17(s, 4H), 1.86(s, 4H).

5-Methyl-2,3-dihydro-1,4-dithiin (33)

The general procedure was used and the crude product was distilled to give 33 as a colorless liquid in 33% yield⁵⁵: bp 62 °C (1.7 torr); ¹H NMR(CDCl₃) δ 5.83(s, 1H), 3.55(s, 4H), 1.93(s, 3H).

5,6-Tetramethylene-2,3-dihydro-1,4-dithiin (34)

The general procedure was used and the crude product was chromatographed on silica gel with hexane as eluent to give 34 as a colorless liquid in 83% yield⁵⁵: ¹H NMR (CDCl₃) δ 3.16(s, 4H), 2.10(m, 4H), 1.65(m, 4H).

Δ^{3,8}-*trans*-2,9-Dithiatricyclo[8.4.0.0^{3,8}]tetradecene (35)

The general procedure was used and the crude product was chromatographed on silica gel with hexane as eluent to give 35 as a white solid in 83% yield: mp 74-75 °C (from EtOH), ¹H NMR(CDCl₃) δ 3.03(m, 2H), 2.2-1.1(m, 16H); ¹³C NMR (CDCl₃) δ 120.1 (s), 45.7 (d), 32.0 (t), 31.2 (t), 26.1 (t), 23.3 (t); IR (CCl₄) 2910, 2850, 1615, 1440, 1330 cm⁻¹; HRMS calculated for C₁₂H₁₈S₂ 226.0850, measured 226.0848.

Δ^{3,8}-*cis*-2,9-Dithiatricyclo[8.4.0.0^{3,8}]tetradecene (36)

The general procedure was used and the crude product was chromatographed on silica gel with hexane as eluent to give 36 as a semi-solid in 79% yield: ¹H NMR(CDCl₃) δ 3.36 (m, 2H), 2.25-1.20 (m, 16H); ¹³C NMR(CDCl₃) δ 118.34 (s), 42.66 (d), 31.61 (t), 31.05 (t), 23.43 (t), 23.32 (t); IR(neat) 2920, 1462, 1321, 1253 cm⁻¹; HRMS calculated for C₁₂H₁₈S₂ 226.0850, measured 226.0853.

Δ^{2,7}-3,6-dithiatricyclo[6.2.1.0^{2,7}]undecene (38)

3-*exo*-Chloro-2-norbornanone (0.89 g) was extracted with 0.8 mL of 1,2-ethanedithiol in the presence of a small amount of *p*-toluenesulfonic acid in 35 mL of

refluxing toluene for 12 h. The mixture was washed with aqueous NaOH, water, and the toluene was removed by vacuum distillation. The residue was chromatographed on silica gel with EtOAc/hexane (3 : 97) as eluent to give 1.12 g (92%) of the dithiolane derivative **37**: $^1\text{H NMR}(\text{CDCl}_3)$ δ 4.1 (d, 1H, $J = 2$ Hz), 3.25 (d, 4H), 1.3-2.8 (m, 8H); IR(neat) 2950, 1450, 1270 cm^{-1} ; HRMS calculated for $\text{C}_9\text{H}_{13}\text{ClS}_2$ 220.01472, measured 220.01529.

Treatment of 0.31 g of **37** with 0.25 g of Al_2Cl_6 in 10 mL of CH_2Cl_2 at 0 °C under N_2 for 30 minutes gave, after washing with aqueous NaOH and water, vacuum distillation of the CH_2Cl_2 , and chromatography on silica gel with hexane as eluent, a 93% yield (240 mg) of **26** as a colorless oil: $^1\text{H NMR}(\text{CDCl}_3)$ δ 3.3-2.7 (m, 6H), 1.9-0.9 (m, 6H); $^{13}\text{C NMR}(\text{CDCl}_3)$ δ 126.85 (s), 48.08 (d), 43.64 (t), 27.7 (t), 27.27 (t); IR (neat) 2960, 1550, 1440, 1410, 1285 cm^{-1} ; HRMS calculated for $\text{C}_9\text{H}_{12}\text{S}_2$ 184.03804, measured 184.0386.

$\Delta^{4,2}$ -cis-exo-3,10-Dithiatetracyclo[10.2.1.0.2-110^{4,2}]pentadecene (39)

2-Chlorocyclohexanone (0.49 g) and *exo-cis*-bicyclo[2.2.1]heptane-2,3-dithiol (**112**) (0.59 g) were stirred with a small amount of *p*-toluenesulfonic acid in 100 mL of refluxing benzene for 4 h. The mixture was washed with 5% NaOH, water, and dried with MgSO_4 . The benzene was removed under vacuum to give a mixture of **39** and the 1,3-dithiolane derivative **40**. The mixture was treated with 0.50 g of Al_2Cl_6 in CH_2Cl_2 at 0 °C for 30 minutes. After washing with aqueous NaOH and water, vacuum removal of the CH_2Cl_2 , and chromatography on silica gel with hexane an eluent, a 74% yield (0.65 g) of **39** was obtained as a colorless oil: $^1\text{H NMR}(\text{CDCl}_3)$ δ 3.25 (d, 2H, $J = 2$ Hz), 2.3 (br s, 6H), 1.9-1.0 (m, 10H); $^{13}\text{C NMR}(\text{CDCl}_3)$ δ 134.54 (s), 57.34 (d), 49.72 (d), 34.91 (t), 33.34 (t), 29.44 (t), 23.59 (t); IR (neat) 2920, 1445, 1300, 1200 cm^{-1} ; HRMS calculated for $\text{C}_{13}\text{H}_{18}\text{S}_2$ 238.0850, measured 238.0843.

2,3-Tetramethylene-1,4-dithiepin (42)

A solution of 0.5 g of 4,5-tetramethylene-1,3-dithiole-2-thione (**41**) and 1.22 g of KOH in 50 mL of EtOH was refluxed for 2 h. The mixture was cooled to room temperature, and to this mixture was added dropwise over 20 minutes a solution of 0.55 g of 1,3-dibromopropane in 10 mL of EtOH. The mixture was then refluxed for 2 h, poured on to ice-water, and extracted with ether. The ether extract was washed with water twice, dried over MgSO₄, and evaporated, leaving an oil which was chromatographed on silica gel with hexane as eluent to give 170 mg (34%) of **42** as a colorless liquid: ¹H NMR(CDCl₃) δ 3.26 (t, 4H), 2.12 (m, 4H), 1.66 (m, 2H); ¹³C NMR(CDCl₃) δ 127.98 (s), 34.32 (t), 31.55 (t), 30.63 (t), 23.16 (t); IR (neat) 2935, 1605, 1405, 1300 cm⁻¹; HRMS calculated for C₉H₁₄S₂ 186.05370, measured 186.05390.

2,3-Dimethyl-1,4-dithiepin (43)

The procedure used was that of Corey and Seebach.^{58,59} To a solution of 1.0 g 1,3-dithiane in 30 mL dry tetrahydrofuran was added 1.05 equivalent of *n*-BuLi (2.2M solution in hexane) at -30 °C. The solution was stirred for 2 h at this temperature and after cooling to -70 °C, 1.18 g iodomethane was added. The mixture was stirred at 0 °C overnight, then cooled to -30 °C and 1.05 equivalent of *n*-BuLi added. The solution was stirred for another 2 h, and 0.44 g of acetaldehyde was added. The mixture, after being warmed to room temperature was acidified with diluted HCl and extracted with ether. The ether extract was washed with water, dried over MgSO₄ and evaporated, to leave a residue which was stirred with a small amount of *p*-toluenesulfonic acid in 30 mL of refluxing benzene overnight. The mixture was washed with water, dried over MgSO₄ and evaporated. The residue was chromatographed on silica gel with hexane as eluent to give 440 mg (33%) of **43** as a colorless liquid: ¹H NMR(CDCl₃) δ 2.98 (t, 4H), 2.3-1.9 (m, 2H), 1.87 (s, 6H); ¹³C

NMR(CDCl₃) δ 124.6 (s), 31.8 (t), 30.0 (t), 23.2 (q); IR (neat) 2930, 1598, 1440, 1412, 1375, 1300, 1275, 1140 cm⁻¹; HRMS calculated for C₇H₁₂S₂ 160.0381, measured 160.0384.

cis-1,3-Cyclopentanediy l dithioacetate (45)

cis-1,3-Cyclopentane diol dimesylate^{60,61} from 5.3 g of *cis*-1,3-cyclopentane diol was treated with 0.19 mol of CH₃C(O)S⁻ Na⁺ in 300 mL of Me₂SO/DMF (1:1) at 60 °C for 10 h. The mixture was poured on to ice-water and extracted with CH₂Cl₂. The CH₂Cl₂ extract was washed with water for three times, dried over MgSO₄, and evaporated to give a residue which was chromatographed on silica gel using hexane/ethyl acetate (9:1) as eluent to yield 8 g of **45** (71%) as a yellow liquid : ¹H NMR(CDCl₃) δ 3.78 (m, 2H), 2.30 (s, 6H), 2.55-1.2 (m, 6H); IR(neat) 2970, 1680, 1430, 1350, 1240, 1105, 935, cm⁻¹; GCMS (relative intensity), *m/z* 218 (M⁺ 3.8), 175 (68), 133 (100), 99 (63), 67 (96); HRMS calculated for C₉H₁₄O₂S₂ 218.0432, measured 218.0436.

2,5-Dithiabicyclo[4.2.1]non-3-ene (44)

A solution of 1 g of **45** was treated with 2.4 g of KOH in 45 mL of EtOH for 1 h at 30 °C. The mixture was heated to reflux, and 0.44 g of *cis*-1,2-dichloroethylene in 3 mL of EtOH was added. After 6 h of reflux, the EtOH was removed under vacuum, the residue was hydrolyzed, and extracted with CH₂Cl₂. The extract was dried over MgSO₄ and the CH₂Cl₂ was removed under vacuum to give **44** as an oil which showed only one peak in GLC: ¹H NMR(CDCl₃) δ 6.2 (s, 2H), 3.4-3.1 (m, 2H), 2.4-1.3 (m, 6H); ¹³C NMR(CDCl₃) δ 123.2 (d), 44.9 (d), 41.4 (t), 32.7 (t); GCIR 3024, 3001, 2950, 2920, 1539, 1454, 1438, 1276 cm⁻¹; HRMS calculated for C₇H₁₀S₂ 158.0224, measured 158.0222.

General procedure for synthesis of 1,4-benzodithiins 48-50

The α -halo ketone (1 mmol) and 1,2-benzenedithiol (1 mmol) were stirred with a small amount of *p*-toluenesulfonic acid in 10 mL of refluxing benzene for 24 h. The mixture was washed with 10% NaOH, water and dried with Na₂SO₄. The solvent was evaporated and the residue was chromatographed on silica gel with hexane as eluent to give the 1,4-benzodithiin.

2,3-Dimethyl-1,4-benzodithiin (48)

The above procedure was used to give 71% yield of **48** as a white solid, mp 59-60 °C (from EtOH); ¹H NMR(CDCl₃) δ 7.5-7.1 (m, 4H), 2.08 (s, 6H); IR(CCl₄) 3040, 2970, 2915, 2850, 1608, 1515, 1440, 1425 cm⁻¹; HRMS calculated for C₁₀H₁₀S₂ 194.02240, measured 194.02230.

4,5-Dihydronaphtho-[1,2-d]-1,4-benzodithiin (49)

The general procedure was used to give 83% yield of **49** as a yellowish semi-solid : ¹H NMR(CDCl₃) δ 8.0-7.0 (m, 8H), 3.1-2.3 (m, 4H); IR(CCl₄) 3060, 2930, 1580, 1530, 1475, 1445, 1425, 1240, 1105 cm⁻¹; HRMS calculated for C₁₆H₁₂S₂ 268.03805, measured 268.03778.

2,3-Tetramethylene-1,4-benzodithiin (50)

The general procedure was used to give 80% yield of **50** as a white solid, mp 61-62 °C (from EtOH); ¹H NMR(CDCl₃) δ 7.4-7.0 (m, 4H), 2.35 (m, 4H), 1.7 (m, 4H); IR(CCl₄) 3050, 2922, 1670, 1615, 1442, 1320, 1235, 1105 cm⁻¹; HRMS calculated for C₁₂H₁₂S₂ 220.0380, measured 220.0380.

2,3-(1,3-Cyclopentanediy)-1,4-benzodithiin (52)

A mixture of 1.05 g 1,2-benzenedithiol and 0.89 g of 2-chloronornonanone was stirred with a small amount of *p*-toluenesulfonic acid in 15 mL of refluxing toluene for 24 h. TLC showed that a large amount of starting material still remained. The mixture was washed with aqueous NaOH, water, and dried over MgSO₄. The solvent was evaporated to give a residue which was chromatographed on silica gel with hexane as eluent to give 300 mg of the benzodithiole derivative **51**. Treatment of **51** with 0.25 g Al₂Cl₆ in 10 mL CH₂Cl₂ at 0 °C under N₂ for 30 minutes gave, after washing with aqueous NaOH and water, vacuum distillation of the CH₂Cl₂ and chromatography on silica gel with hexane/EtOAc (98 : 2) as eluent, a 58% yield (150 mg) of **52** as a white solid: ¹H NMR(CDCl₃) δ 7.15 (br s, 2H); 3.00 (br s, 2H), 1.85-0.8 (m, 6H); ¹³C NMR(CDCl₃) δ 136.44 (s), 133.29 (s), 127.77 (d), 127.01 (d), 48.40 (d), 46.13 (t), 26.41 (t); IR(CCl₄) 3050, 2940, 1525, 1440, 1290 cm⁻¹; HRMS calculated for C₁₃H₁₂S₂ 232.03805, measured 232.03804.

2,3-Tetramethylene-1,4-dithiin (53)

A mixture of 0.8 g of **41** and 2.3 g of KOH were stirred in 30 mL of refluxing EtOH for 1.5 h; 0.49 g *cis*-1,2-dichloroethylene was then added and the resulted mixture was refluxed for another 5 h. The EtOH was removed under vacuum and the residue was hydrolyzed and extracted with ether. The ether extract was washed with water twice, dried over MgSO₄, and the ether was removed under vacuum to give a residue which was chromatographed on silica gel to give a 65% yield (0.46 g) of **53** as a colorless liquid : ¹H NMR(CDCl₃) δ 6.45(s, 2H), 2.35 (m, 4H), 1.70 (m, 4H); IR(neat) 3025, 2925, 1535, 1442, 1428, 1320 cm⁻¹; HRMS calculated for C₈H₁₀S₂ 170.0224, measured 170.0226.

4.5-Dimethyl-1,3-dithiole-2-thione (55)

The procedure used was that of Haley and Fichtner.⁶² 3-Chlorobutanone (0.01 mol) was added to a solution of *t*-butyl thiol (0.01 mol), CS₂ (0.011 mol), and KOH(0.011 mol) in 25 mL of EtOH at 10 °C. The mixture was stirred at room temperature for 2 h, and then 100 mL of water was added. The resulting mixture was extracted twice with ether, dried over MgSO₄, and the solvent evaporated to give the crude 2-(3-oxobutyl)*tert*-butyl trithiocarbonate which was dissolved in a mixture of trifluoroacetic acid (10 mL), acetic acid (10 mL), and *p*-toluenesulfonic acid (0.1 g). The solution was warmed on steam bath for 30 minutes and then refluxed for 30 minutes. Upon cooling, a yellow solid crystallized from the solution. The yellow solid was collected by filtration and recrystallized to give **55** in 74% yield, mp 93.-94 °C (from MeOH) [lit.⁶³ mp 96 °C].

2,3-Dimethyl-1,4-dithiin (54)

A mixture of 1.5 g of **55** and 5 g of KOH were stirred in 30 mL of refluxing EtOH for 2 h after which 0.99 g of *cis*-1,2-dichloroethylene in 5 mL of EtOH was added. After 5 h of reflux, the EtOH was removed under vacuum and the residue was hydrolyzed and extracted with ether. The ether extract was washed twice with water, dried over MgSO₄, and the ether removed under vacuum to give a residue which chromatographed on silica gel with hexane as eluent to give a 23% yield (0.31 g) of **54** as a colorless liquid: ¹H NMR(CDCl₃) δ 6.32 (s, 2H), 2.00 (s, 6H); IR(neat) 3020, 2960, 2910, 1550, 1515, 1425, 1365 cm⁻¹; HRMS calculated for C₆H₈S₂ 144.00675, measured 144.00691.

Δ^{2,7}Δ^{4,5}-3,6-Dithiatricyclo[6.2.1.0^{2,7}]undecadiene (58)

A mixture of 0.4 g of **38** and 0.54 g of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone was stirred in 10 mL of refluxing xylene for 16 h. The mixture was filtered, washed with dilute aqueous KOH, water, and dried over MgSO₄. The solvent was removed under

vacuum and the residue was chromatographed on silica gel with hexane as eluent to give 0.11 g of **58** (28%) as a pale yellow oil: $^1\text{H NMR}(\text{CDCl}_3)$ δ 5.95 (s, 2H), 2.82 (m, 2H), 1.0-2.3 (m, 6H); $^{13}\text{C NMR}(\text{CDCl}_3)$ δ 132.8 (s), 119.4 (d), 48.1 (d), 46.9 (t), 26.4 (t); IR(neat) 3015, 2970, 1525, 1290 cm^{-1} ; HRMS calculated for $\text{C}_9\text{H}_{10}\text{S}$ 182.02240, measured 182.02245.

exo-cis-Bicyclo[2.2.1]heptane-2,3-dithiol (59)⁶⁴

A solution of 20 g of *exo*-3,4,5-trithiatricyclo[5.2.1.0^{2,6}]decane (**111**) in 50 mL ether was added to a suspension of 6 g of LiAlH_4 in 100 mL ether. The mixture was refluxed for 2 h and acidified carefully with diluted HCl. The ether layer was separated, washed with water, dried over MgSO_4 , and the ether was removed under vacuum to give 14.3 g (85%) of **59** as a yellowish oil with only a single peak in GLC.

4-Methylene-3,5-dithia-exo-cis-tricyclo[5.2.1.0^{2,6}]decane (60)

To a solution of 1 g of **59** and 3 g of KOH in 35 mL of refluxing EtOH was added a solution of 0.64 g of *cis*-1,2-dichloroethylene in 3 mL of EtOH dropwise. After refluxing for 4 h, the EtOH was removed under vacuum and the residue was hydrolyzed and extracted with ether. The ether extract was washed with water twice, dried over MgSO_4 , and the ether was removed under vacuum to give a residue which was purified by chromatography on Al_2O_3 using hexane/EtOAc (95 : 5) as eluent to yield 0.80 g (70%) of **60**, mp 50.0-51.5 °C; $^1\text{H NMR}(\text{CDCl}_3)$ δ 5.00 (s, 2H), 3.85 (d, 2H, $J = 1.8$ Hz), 2.30 (br s, 2H), 2.0-1.0 (m, 6H); $^{13}\text{C NMR}(\text{CDCl}_3)$ δ 146.7 (s), 100.0 (t), 61.8 (d), 45.4 (d), 32.3 (t), 27.8 (t); IR(CCl_4) 2950, 1668, 1565, 1445 cm^{-1} ; HRMS calculated for $\text{C}_9\text{H}_{12}\text{S}_2$ 184.03805, measured 184.03810.

4-Dideuteromethylene-3,5-dithia-exo-cis-tricyclo[5.2.1.0^{2,6}]decane(*d*₂-60)

To a solution of 0.25 g **59** in 12.5 mL of ethyl alcohol-*d* was added 0.4 g potassium. The solution was heated to reflux, and 0.15 g of *cis*-1,2-dichloroethylene was added. The reflux was continued for 5 h, after which time the alcohol was removed by vacuum to leave a residue which was hydrolyzed, and extracted twice with ether. The ether extract was washed with water, dried over MgSO₄ and evaporated to give 0.21 g (72%) of *d*₂-**60** as a white solid : ¹H NMR(CDCl₃) 3.85(d, 2H, *J*= 1.8 Hz), 2.30(br s, 2H), 2.0-1.0 (m, 6H).

1,2-Bis(*n*-butylthio)cyclohexene (62**)**

A mixture of 0.8 g of **41** and 1.5 g of KOH was stirred in 20 mL of refluxing EtOH for 2 h after which 1.75 g of *n*-butyl bromide was added. The mixture was refluxed for another 1.5 h and the EtOH was removed under vacuum. The residue was hydrolyzed and extracted with ether. The ether extract was washed twice with water and dried over MgSO₄. Removal of the solvent under vacuum gave a residue which was chromatographed on silica gel with hexane as eluent to yield 0.87 g (79%) of **62** as a colorless liquid: ¹H NMR(CDCl₃) δ 2.66 (q, 4H, *J* = 6 Hz), 2.30 (m, 4H), 1.8-1.3 (m, 8H), 0.90 (t, 6H, *J* = 6 Hz); ¹³C NMR(CDCl₃) δ 130.53, 32.04, 31.28, 30.85, 23.37, 22.02, 13.68; IR(neat) 2920, 1450 cm⁻¹; HRMS calculated for C₁₄H₂₆S₂ 258.1478, measured 258.1474.

1,2-Bis(isopropylthio)cyclohexene (63**)**

A mixture of 1.5 g of 2-chlorocyclohexanone and 2.58 g of isopropyl thiol was stirred with a small amount of *p*-toluenesulfonic acid in 20 mL of refluxing benzene for 24 h. The mixture was washed with aqueous NaOH, water, and dried over MgSO₄. Removal of the solvent gave a residue which was chromatographed on silica gel with hexane/EtOAc (97 : 3) as eluent to give 1.32 g (51%) of **63** as a colorless liquid: ¹H NMR(CDCl₃) δ 3.4 (spt,

2H, $J = 7$ Hz), 2.50 (m, 4H), 1.68 (m, 4H), 1.23 (d, 12H, $J = 7$ Hz); ^{13}C NMR(CDCl_3) δ 132.86 (s), 34.91 (d), 33.37 (t), 23.97 (t), 23.43 (q); IR (neat) 2945, 2905, 2850, 1432, 1370, 1355, 1310, 1228, 1140 cm^{-1} ; HRMS calculated for $\text{C}_{12}\text{H}_{22}\text{S}_2$ 230.11630, measured 230.11657.

cis-1,2-Bis(isopropylthio)ethylene²⁸

To a solution of 1.32 g of isopropyl thiol and 4.5 g of KOH in 30 mL of refluxing EtOH was added dropwise a solution of 0.8 g *cis*-1,2-dichloroethylene in 3 mL of EtOH. After refluxing for 5 h, the EtOH was removed under vacuum and the residue was hydrolyzed and extracted with ether. The ether extract was washed twice with water, dried over MgSO_4 , and the ether removed under vacuum to give 1.17g (81%) of *cis*-1,2-bis(isopropylthio)ethylene as a yellowish liquid: ^1H NMR(CDCl_3) δ 6.2 (s, 2H), 3.15(spt, 2H), 1.33 (d, 6H); ^{13}C NMR(CDCl_3) δ 122.35, 37.68, 23.59.

cis-1,2-Bis(*n*-butylthio)ethylene

Reaction of 1.5 g of *n*-butyl thiol with 0.89 g of *cis*-1,2-dichloroethylene and 5.5 g of KOH following the same procedure used for the synthesis of *cis*-1,2-bis(isopropylthio)ethylene gave 1.34 g (79%) of *cis*-1,2-bis(*n*-butylthio)ethylene as a yellowish liquid: ^1H NMR(CDCl_3) δ 6.07 (s, 2H), 2.73 (t, 4H), 1.80-1.25(m, 8H), 0.90(t, 6H); ^{13}C NMR(CDCl_3) δ 123.43, 33.94, 32.31, 21.69, 13.57.

trans-1,2-Bis(isopropylthio)ethylene

The procedure used was that of Tiecco, Testaferri, Tingoli, Chianelli, and Montanucci.²⁹ A solution of 0.01 mol of *trans*-1,2-dichloroethylene and 0.03 mol of *i*-PrSNa in HMPA (25 mL) was stirred under nitrogen at room temperature for 1 h. The reaction mixture was poured on water and extracted with ether; the ether was washed with

water, dried over MgSO_4 , and evaporated. Purification was achieved by column chromatography on silica gel with hexane as eluent to give *trans*-1,2-bis(isopropylthio)ethylene: $^1\text{H NMR}(\text{CDCl}_3)$ δ 6.25 (s, 2H), 3.05 (spt, 2H), 1.3 (d, 12H).

***trans*-2,3-Bis(isopropylthio)-2-butene (66)**

A mixture of 0.5 g of 3-chlorobutanone and 1.07 g of isopropyl thiol was stirred with a small amount of *p*-toluenesulfonic acid in 20 mL of refluxing benzene for 5 h. The mixture was washed with aqueous NaOH, water, and dried over MgSO_4 . Evaporation of the benzene gave a residue which was chromatographed on silica gel with hexane/EtOAc (98 : 2) as eluent to give 0.26 g (27%) of **66** as a colorless liquid: $^1\text{H NMR}(\text{CDCl}_3)$ δ 3.3 (spt, 2H), 2.23 (s, 6H), 1.22 (d, 12H); $^{13}\text{C NMR}(\text{CDCl}_3)$ δ 131.6 (s), 36.0 (d), 23.4 (q), 22.1 (q); IR (neat) 2982, 2940, 1440, 1382, 1365, 1238, 1150, 1045 cm^{-1} ; HRMS calculated for $\text{C}_{10}\text{H}_{20}\text{S}_2$ 204.1007, measured 204.1011.

***trans*-2,3-bis(*n*-butylthio)-2-butene (71)**

Reaction of 1.0 g of 3-chlorobutanone and 1.80 g of *n*-butyl thiol following the procedure used for the synthesis of **66** gave 0.48 g (22%) of **77** as a colorless liquid: $^1\text{H NMR}(\text{CDCl}_3)$ δ 2.9-2.5 (4H), 2.18 (s, 6H), 1.7-1.1 (m, 8H), 0.89 (t, 6H); IR (neat) 2940, 2910, 1440, 1360 cm^{-1} ; HRMS calculated for $\text{C}_{12}\text{H}_{24}\text{S}_2$ 232.13195, measured 232.13138.

2',3',4',5',6',7'-Hexahydrodispiro[1,3-benzodithiole-2,1'-anthracene-8',2"-[1,3]-benzodithiole](72)

This compound was synthesized according to the procedure of Christopf and Miller³⁰: $^1\text{H NMR}(\text{CDCl}_3)$ δ 9.7 (s, 1H), 7.05 (m, 8H), 6.80 (s, 1H), 2.78 (t, 4H), 2.60 (m, 4H), 2.0 (m, 4H).

General procedure for synthesis of 1,3-benzodithioles and 1,3-dithiolanes⁶⁵

A solution of 0.01 mol of 1,2-benzenedithiol or 1,2-ethanedithiol, 0.011 mol of ketone, and 1 mL of chlorotrimethylsilane in 5 mL of CHCl_3 was stirred at room temperature for 2 h after which 20 mL of CH_2Cl_2 was added. The organic layer was washed with aqueous NaOH, water, dried over MgSO_4 , and evaporated to give a residue which was chromatographed on silica gel with hexane as eluent to give 1,3-benzodithiole or 1,3-dithiolane. The yield was normally higher than 80%.

Spiro[1,3-benzodithiole-2,1'-tetralin] (75)

The general procedure was used to produce a 94% yield of **75** as a semi-solid: ^1H NMR(CDCl_3) δ 8.42 (m, 1H), 7.10 (m, 7H), 3.00-2.50 (m, 4H), 2.05 (m, 2H); HRMS calculated for $\text{C}_{16}\text{H}_{14}\text{S}_2$ 270.05370, measured 270.0536.

Spiro[1,3-benzodithiole-2,1'-cyclohexane] (76)

The general procedure was used to give an 88% yield of **76** as a yellowish oil: ^1H NMR(CDCl_3) δ 7.10 (m, 4H), 2.20 (m, 4H), 1.60 (m, 6H); HRMS calculated for $\text{C}_{12}\text{H}_{14}\text{S}_2$ 222.05370, measured 222.0536.

2-Methyl-2-ethyl-1,3-benzodithiole (77)

The general procedure was used to give an 82% yield of **77** as a yellowish oil: ^1H NMR(CDCl_3) δ 7.2-6.8 (m, 4H), 2.29-1.90 (q, 2H, $J = 7$ Hz), 1.85 (s, 3H), 1.22-0.95 (t, 3H, $J = 7$ Hz); HRMS calculated for $\text{C}_{10}\text{H}_{12}\text{S}_2$ 196.03805, measured 196.0380.

2-Methyl-2-ethyl-1,3-dithiolane (78)

The general procedure was used to give an 82% yield of **78** as a colorless liquid⁶⁶: ^1H NMR(CDCl_3) δ 3.33 (s, 4H), 1.89 (q, 2H, $J = 7$ Hz), 1.64 (s, 3H), 0.95 (t, 3H, $J = 7$ Hz).

1,4-Dithiaspiro[4.5]decane (79)

The general procedure was used to give a 90% yield of **79** as a colorless liquid⁶⁷:
¹H NMR(CDCl₃) δ 3.31 (s, 4H), 2.05-1.85 (m, 4H), 1.85-1.45 (m, 6H).

2,2-Dimethyl-1,3-dithiolane (81)

The general procedure was used to give an 81% yield of **81** as a colorless liquid⁶⁸:
¹H NMR(CDCl₃) 3.40 (s, 4H), 1.82 (s, 6H).

General procedure for synthesis of diaryl disulfides⁶⁹⁻⁷²

A solution of 0.02 mol of aryl bromide was treated with 0.024 mol magnesium in 30 mL of refluxing ether for 2 h. The mixture was cooled to 0 °C and 0.02 mol of sulfur was added after which the mixture was refluxed for 0.5 h and acidified carefully with diluted HCl. The organic layer was separated, washed with water, and extracted twice with 10% NaOH. To the NaOH extract was added 0.02 mol of I₂. The mixture was stirred at room temperature overnight and extracted with ether. The ether extract was washed with water, dried over MgSO₄, and evaporated to give the crude diaryl disulfide which was purified by recrystallization or column chromatography.

Di-*m*-tolyl disulfide (84)

The general procedure was used to give a 32% yield of **84** as a pale yellow oil⁷³: ¹H NMR(CDCl₃) δ 7.35-6.90 (m, 8H), 2.31 (s, 6H).

Di-*o*-tolyl disulfide (87)

The general procedure was used to give a 34% yield of **87** as a white solid, mp, 37-38.5 °C (from EtOH)[lit. 38 °C⁷³, 39 °C⁷⁴]; ¹H NMR(CDCl₃) δ 7.50 (m, 2H), 7.13 (m, 6H), 2.43 (s, 6H).

5-*m*-Dixylyl disulfide (89)

The general procedure was used to give a 37% yield of **89** as a yellow oil: ^1H NMR(CDCl_3) δ 7.15-6.9 (m, 6H), 2.28 (s, 12H); HRMS calculated for $\text{C}_{16}\text{H}_{18}\text{S}_2$ 274.08500, measured 274.0848.

***p*-Dixylyl disulfide (90)**

The general procedure was used to give a 36% yield of **90** as a white solid, mp 46-47 °C (from EtOH) [lit.⁷⁴ 47 °C]; ^1H NMR(CDCl_3) δ 7.38 (br s, 2H), 7.02 (br s, 4H), 2.38 (s, 6H), 2.26 (s, 6H).

3-*o*-Dixylyl disulfide (91)

The general procedure was used to give a 45% yield of **91** as a white solid, mp 97-98 °C (from EtOH); ^1H NMR(CDCl_3) δ 7.5-6.95 (m, 6H), 2.34 (s, 6H), 2.27 (s, 6H); HRMS calculated for $\text{C}_{16}\text{H}_{18}\text{S}_2$ 274.08500, measured 274.0849.

General procedure for synthesis of substituted benzyl disulfides 99-101

A mixture of 0.01 mol of α -bromoxylene and 0.02 mol thiourea was heated in 20 mL refluxing EtOH for 20 minutes,⁷⁵ a solution of 0.05 mol KOH in 20 mL H_2O was added, and the solution refluxed for another 2 h. After cooling to room temperature, a solution of 0.022 mol I_2 in 30 mL of EtOH was added and the mixture was stirred at room temperature overnight and extracted with ether twice. The ether extract was washed with water, dried over MgSO_4 , evaporated to give the crude disulfide which was purified by recrystallization (hexane) or chromatography.

Di-*o*-methylbenzyl disulfide (99)

The general procedure was used to give a 60% yield of **99** as a white solid, mp 84-85 °C [lit^{76,77} 83-85 °C]; ^1H NMR(CDCl_3) δ 7.08 (s, 8H), 3.63 (s, 4H), 2.33 (s, 6H).

Di-*m*-methylbenzyl disulfide (100)

The general procedure was used to give a 53% yield of **100** as a pale yellow oil: ^1H NMR(CDCl_3) δ 7.05 (br s, 8H), 3.59 (s, 4H), 2.33 (s, 6H).

Di-*p*-methylbenzyl disulfide (101)

The general procedure was used to give a 73% yield of **101** as a white solid, mp 41-42 °C [lit.^{76,77} 46 °C]; ^1H NMR(CDCl_3) δ 7.07 (s, 8H), 3.59 (s, 4H), 2.31 (s, 6H).

Cyclohexene trithiocarbonate

The procedure used was that of Culvenor, Davies, and Pansacker.⁷³ A solution of 10.5 g of KOH in MeOH (46 mL) containing CS_2 (18 g) was treated at room temperature with cyclohexene oxide (7.5 g). The mixture was stored overnight after which water was added and the product heated on the water-bath until the CS_2 had evaporated. Filtration gave 13.1 g (90%) of cyclohexene trithiocarbonate as a yellow crystals, mp 167-168 °C [lit.⁷⁸, 169 °C].

***trans*-Cyclohexane-1,2-dithiol**

The procedure used was that of Iqbal and Owen.⁷⁹ Cyclohexene trithiocarbonate (13.1 g) in THF (100 mL) was reduced with lithium aluminum hydride (3.8 g) in ether (100 mL) to give *trans*-cyclohexane-1,2-dithiol (8.5 g, 83%).

***cis*-Cyclohexane-1,2-dithiol**

The procedure used was that of Böhme and Müller⁵⁰. A mixture of 40 g of cyclohexene and 5.5 g of sulfur were heated in a sealed-tube at 140 °C for 5 h. The mixture was then diluted with 50 mL of THF, added to a solution of 4 g of LiAlH_4 in 100 mL of THF, and refluxed for 4 h. The reaction mixture was acidified by diluted HCl and extracted twice with ether. The ether extract was washed with water, dried over MgSO_4 , and

evaporated to give a residue which was distilled to give 1.5 g of *cis*-cyclohexane-1,2-dithiol, bp 110 °C (1.5 torr) [lit.⁵⁰ 99-100 °C/0.9 torr].

trans-4,5-Dimethyl-1,3-dithiolane-2-thione

The procedure used was that of Iqbal and Owen.⁷⁹ *cis*-2,3-Epoxybutane (5.9 g) was slowly added (15 minutes) with shaking to a solution of KOH (11.7 g) and carbon disulfide (19 g) in MeOH (50 mL). The mixture was then set aside for 5 days. The solid which had gradually formed was collected and washed with water. Recrystallization from hexane gave the *trans*-4,5-dimethyl-1,3-dithiolane-2-thione (3.8 g, 28%) as yellow crystals, mp 35-36°C [lit.⁸⁰ 40-41 °C]; ¹H NMR (CDCl₃) δ 4.10 (m, 2H), 1.58 (d, 6H); ¹³C NMR(CDCl₃) δ 61.26, 18.47.

d,l-2,3-Butanedithiol

The procedure of Iqbal and Owen was used.⁷⁹ *trans*-4,5-Dimethyl-1,3-dithiolane-2-thione (0.69 g) in ether (10 mL) was reduced with lithium aluminum hydride (0.5 g) in ether (20 mL) to give *d, l*-2,3-butanedithiol (330 mg, 64%) as a colorless liquid.

cis-4,5-Dimethyl-1,3-dithiolane-2-thione

trans-2,3-Epoxybutane (5 g) was reacted with 10 g KOH and 16 g of CS₂ followed the same procedure for the synthesis of the *trans* isomer to give *cis*-4,5-dimethyl-1,3-dithiolane-2-thione (3.52 g, 31%) as yellow crystals, mp 35-38 °C [lit.⁸⁰ 40-41 °C]; ¹H NMR(CDCl₃) δ 4.40 (m, 2H), 1.48 (d, 6H); ¹³C NMR(CDCl₃) δ 58.32, 14.38.

meso-2,3-Butanedithiol

cis-4,5-Dimethyl-1,3-dithiolane-2-thione (3.8 g) was reduced by lithium aluminum hydride (2.5 g) followed the procedure for synthesis of the *d, l* isomer to give *meso*-2,3-butanedithiol (1.58 g, 56%) as a colorless liquid.

exo-3.4.5-Trithiatricyclo[5.2.1.0^{2,6}]decane (111)

The procedure of Shields and Kurtz⁶⁴ was used. Sulfur powder (10 g) slurried in 170 mL of DMF was treated by bubbling a stream of ammonia gas at 35 °C. Bicyclo[2.2.1]hept-2-ene (20 g) was added and the mixture was stirred for 2 h at 110 °C. After quenching with ice water and extracting with ether, vacuum removal of the ether afforded 25.8 g (64%) of essentially pure **111** (with a single peak in GLC) as a yellowish oil which could be further purified by chromatography on silica gel with hexane as eluent: ¹H NMR(CS₂) δ 3.6 (d, 2H, *J* = 2 Hz), 2.4 (m, 2H), 2.3-0.8 (m, 6H); ¹³C NMR(CDCl₃) 69.85, 40.82, 32.51, 27.65.

1-Phenyl-1,3-propanedithiol (117)

A mixture of 1-phenyl-1,2-dibromopropane⁸¹ (3.0 g) and thiourea (3.2 g) was heated in 20 mL of refluxing EtOH for 1.5 h. A solution of 5.7 g KOH in water was then added. The mixture was refluxed for 1 h, acidified with diluted HCl and extracted twice with ether. The ether extract was washed twice with water, dried over MgSO₄ and evaporated to give 1.65 g (83%) of **117** as a yellow liquid: ¹H NMR(CDCl₃) δ 7.36 (br s, 5H), 4.18 (m, 1H), 2.8-2.1 (m, 4H), 1.92 (d, 1H, *J* = 6Hz), 1.35 (t, 1H, *J* = 7 Hz).

4-Phenyl-1,2,3-trithiane (116)

The crude dithiol **117** (1.65 g) was treated with 3.8 g of Pb(OAc)·3H₂O in 20 mL of water⁸² to afford the corresponding lead dithiolate (yellow solid) which was isolated by filtration. The lead dithiolate was stirred with 0.28 g sulfur powder in 20 mL of benzene. After a few minutes the yellow mixture turned black, and the lead sulfide was filtered after another 30 minutes of reaction. Removal of the solvent gave a residue which was chromatographed on silica gel with hexane as eluent to give 880 mg (31%) of **116** as a yellowish solid: ¹H NMR(CDCl₃) δ 7.35 (br s, 5H), 4.5-4.2 (m, 1H), 3.5-3.1 (m, 2H),

2.6-2.2 (m, 2H), ^{13}C NMR (CDCl_3) δ 141.05, 128.80, 128.15, 127.33, 52.58, 36.70, 32.74; IR(CCl_4) 3050, 3022, 2930, 2890, 1485, 1445, 1400 cm^{-1} ; HRMS calculated for $\text{C}_9\text{H}_{10}\text{S}_3$ 213.99447. measured 213.99423.

trans-2,3-Dithiadecalin (119)

The procedure of Bass and Evans³⁴ was used with modification. A solution of 5 g of *trans*-1,2-cyclohexanedicarboxylic anhydride was treated with 2.3 g of lithium aluminum hydride in 35 mL of refluxing ether for 1 h. After the mixture was acidified carefully with diluted HCl, the ether layer was separated, dried over MgSO_4 , and evaporated to give the *trans*-1,2-cyclohexanedimethanol which was directly treated with 7 mL of concentrated H_2SO_4 and 11 mL of 48% HBr at 90 °C for 6 h. The reaction mixture was poured into ice-water, extracted twice with ether. The ether extract was washed with water, dried over MgSO_4 , and evaporated to give 3.0 g of *trans*-1,2-bis(bromomethyl)cyclohexane: ^1H NMR(CDCl_3) δ 3.48 (br s, 4H), 1.8-1.2 (m, 10H).

The *trans*-1,2-bis(bromomethyl)cyclohexane (3.0 g) was heated with thiourea (3.5 g) in 10 mL of refluxing EtOH for 3 h. A solution of 6 g of KOH in 20 mL of H_2O was added and reflux was continued for another hour. The reaction mixture was acidified with HCl and extracted twice with ether. The ether extract was washed with water, dried over MgSO_4 and evaporated to give 1.8 g (92%) of *trans*-1,2-bis(mercaptomethyl)cyclohexane as a yellowish oil: ^1H NMR(CDCl_3) δ 2.6 (m, 4H), 2.0-1.0 (m, 10H), 1.21 (t, 2H, $J = 8$ Hz).

The *trans*-1,2-bis(mercaptomethyl)cyclohexane (1.8 g) was treated with 4.8 g of $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$ in 10 mL H_2O to obtain the corresponding lead dithiolate as a yellow solid. The lead dithiolate was dried over vacuum and stirred with 0.3 g of powdered sulfur in 20 mL benzene for 1 h. The lead sulfide was filtered and benzene was removed by vacuum to

give a residue which was chromatographed on silica gel with hexane as eluent to give 0.85 g (48%) of **119**: $^1\text{H NMR}(\text{CDCl}_3)$ δ 2.5 (m, 4H), 2.0-1.0 (m, 10H).

3-Methyl-1,2-dithiane (120)

The procedure used was that of Isenberg and Herbrandson.³⁵ 1,4-Dibromopentane (6 g) was added to a boiling solution of potassium thiocyanate (5.2 g) in 25 mL of MeOH. The reaction mixture was heated to reflux for 3 h after which KBr was removed by filtration. To this solution was added 20 g of KOH in 30 mL of MeOH. The mixture was allowed to stand overnight, and was then poured onto ice-water and extracted with ether. The ether extract was washed with water, dried over MgSO_4 , and evaporated to give a residue which was purified by chromatography to yield 1.97 g (56%) of **120** as a yellowish liquid: $^1\text{H NMR}(\text{CDCl}_3)$ δ 3.8-3.0 (m, 3H), 2.7-1.8 (m, 4H), 1.7 (m, 3H).

2,3-Dithiatetralin (121)

α,α' -Dibromo-*o*-xylene (10 g) was treated with thiourea (11.5 g) in refluxing EtOH (40 mL) for 20 minutes. A solution of 20 g KOH in 50 mL of water was then added and the reflux continued for another hour. The reaction mixture was acidified with diluted HCl and extracted with ether. The ether extract was washed with water, dried and evaporated to give 5.6 g (87%) of *o*-bis(mercaptomethyl)benzene.

The *o*-bis(mercaptomethyl)benzene (2.6 g) was treated with 6.5 g $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$ in 15 mL H_2O to give the corresponding lead dithiolate which was filtered, dried, and stirred with 0.43 g of powdered sulfur in 15 mL of benzene for 1 h. The lead sulfide was removed by filtration and the solvent was evaporated to give a residue which was purified by recrystallization from hexane/ CH_2Cl_2 to give 1.78 g of **121** as a white solid; mp 78-79 °C [lit.³⁶ 80 °C].

1.1-Dideutero-2,3-dithiatetralin (d_2 -121)

Phthalide (1.8 g) was treated with lithium aluminum deuteride (0.6 g) in 35 mL of refluxing ether for 3 h. The mixture was acidified carefully by aqueous HCl. The ether layer was separated, dried over MgSO₄, and evaporated to give the dideutero-1,2-benzenedimethanol which was treated with 4.36 g of phosphorous tribromide in 30 mL of benzene at room temperature overnight. The benzene layer was washed with water, dried over Na₂SO₄ and evaporated to give a residue which was chromatographed on silica gel with hexane/EtOAc (95 : 5) as eluent to give 2.96 g (83%) α,α -dideutero- α,α' -dibromo-*o*-xylene as a white solid: ¹H NMR(CDCl₃) δ 7.3 (m, 4H), 4.7 (s, 2H).

The α,α -dideutero- α,α' -dibromo-*o*-xylene (2.95 g) was treated with thiourea (3.38 g) following the procedure for the synthesis of *o*-bis(mercaptomethyl)benzene to give 1.18 g (62%) of 1-dideuteromercaptomethyl-2-mercaptomethylbenzene as a white solid: ¹H NMR(CDCl₃) δ 7.2 (br s, 4H), 3.84 (d, 2H), 1.80 (t (1:6:1), 2H).

The 1-dideuteromercaptomethyl-2-mercaptomethylbenzene (1.18 g) was treated with Pb(OAc)₂·3H₂O (2.86 g) following the same procedure used for the synthesis of 121 to give 620 mg (53 %) of d_2 -121 as a white solid: ¹H NMR(CDCl₃) δ 7.1 (m, 4H), 4.05 (s, 2H).

cis-1,4-Cyclohexanedithiol (123)

The procedure of Haviv and Belleau⁴⁰ was used. *cis*-1,4-Cyclohexadiene bisepoxide (6 g) was added at 0 °C to a stirred suspension of thiourea (11 g) in 2 N H₂SO₄ (15 mL) under N₂. The ice bath was removed and stirring continued for 1 h during which time the product dissolved gradually and was replaced by a white precipitate of the bisisothiuronium salt. Aqueous Na₂CO₃ was added to bring the pH to 8.5 and the mixture immediately extracted with benzene. The benzene extract was dried and evaporated to give

cis-1,4-cyclohexadiene bisepisulfide (3.8 g, 49%): $^1\text{H NMR}(\text{CDCl}_3)$ δ 3.10 (s, 4H), 3.16-2.28 (m, 4H).

A solution of *cis*-1,4-cyclohexadiene bisepisulfide (3.8 g) in dry THF (20 mL) was added dropwise to a refluxing suspension of lithium aluminum hydride (2.0 g) in ether (20 mL) under N_2 and the heating continued for 2 h after which time a mixture of aqueous HCl-THF was carefully added while cooling in ice. The organic layer was separated, dried and evaporated to give **123** (3.3 g) as a colorless oil.

***trans,trans*-2,5-Dideutero-*cis*-1,4-cyclohexanedithiol(*d*₂-**123**)**

Reaction of *cis*-1,4-cyclohexadiene bisepisulfide (1.28 g) with lithium aluminum deuteride (0.45 g) following the same procedure for the synthesis of **123** gave 0.85 g *d*₂-**123** as a colorless oil. GCMS showed that this compound had a molecular weight of 150 ($\text{C}_6\text{H}_{10}\text{D}_2\text{S}_2$).

Temperature Dependence of Rate Constants *k* for the Ring Inversion

Processes of Some Sulfur-Centered Radical Cations

Table 8. Temperature dependence of rate constant *k* for the ring inversion process of radical cation **21**^{†83}

T(K)	1000/T(K ⁻¹)	<i>k</i> (sec ⁻¹) ^a	ln (<i>k</i> /T)	Δ Width ⁸⁴ (G)
203	4.93	1.0×10^7	10.82	0.165
193	5.18	4.84×10^6	10.13	0.345
188	5.32	3.01×10^6	9.68	0.555
183	5.46	1.70×10^6	9.14	0.980
178	5.62	1.19×10^6	8.81	1.405

^aBased upon the assumption that a^{H} (axial) = $2a^{\text{H}}$ (equatorial).²⁷

Table 9. Temperature dependence of rate constant k for the ring inversion process of radical cation 26^+

T(K)	1000/T(K ⁻¹)	k (sec ⁻¹) ^a	ln (k/T)	Δ Width(G)
208	4.81	1.35×10^7	11.08	0.03
203	4.93	8.08×10^6	10.59	0.05
198	5.05	5.05×10^6	10.15	0.08
193	5.18	3.37×10^6	9.77	0.12
188	5.32	2.69×10^6	9.57	0.15
183	5.46	1.76×10^6	9.17	0.23
178	5.62	1.30×10^6	8.90	0.31

^aBased upon the assumption that a^H (axial) = $8a^H$ (equatorial).

Table 10. Temperature dependence of rate constant k for the ring inversion process of radical cation 34^+

T(K)	1000/T(K ⁻¹)	k (sec ⁻¹)	ln (k/T)	$[(a_A^H - a_B^H)^2 - \langle a_a^H - a_e^H \rangle^2]^{1/2}$ (G)
263	3.80	2.17×10^6	9.24	0.436
273	3.66	3.78×10^6	9.54	0.608
283	3.53	4.21×10^6	9.61	0.678
293	3.41	4.98×10^6	9.74	0.800
303	3.30	5.93×10^6	9.88	0.95
313	3.19	7.01×10^6	10.01	1.13

Table 11. Temperature dependence of rate constant k for the ring inversion process of radical cation 43^{\ddagger}

T(K)	1000/T(K ⁻¹)	k (sec ⁻¹)	ln (k/T)	$[(a_A^H - a_B^H)^2 - \langle a_a^H - a_e^H \rangle^2]^{1/2}$ (G)
283	3.53	1.52×10^6	8.59	0.245
288	3.47	1.92×10^6	8.80	0.308
293	3.41	2.52×10^6	9.06	0.405
298	3.36	3.09×10^6	9.22	0.484
308	3.25	3.78×10^6	9.42	0.608
313	3.19	4.74×10^6	9.62	0.762

Table 12. Temperature dependence of rate constant k for the ring inversion process of radical cation 62^{\ddagger}

T(K)	1000/T(K ⁻¹)	k (sec ⁻¹)	ln (k/T)	Δ Width(G)
248	4.03	3.16×10^8	14.06	0.07
243	4.12	2.46×10^8	13.83	0.09
238	4.20	2.00×10^8	13.64	0.11
233	4.29	1.47×10^8	13.36	0.15
228	4.39	1.10×10^8	13.09	0.20
218	4.59	5.74×10^7	12.48	0.385

Table 13. Temperature dependence of rate constant k for the ring inversion process of radical cation **63**⁺

T(K)	1000/T(K ⁻¹)	k (sec ⁻¹) ^a	ln (k/T)	Δ Width(G)
183	5.46	2.07×10^7	11.64	0.85
193	5.18	4.00×10^7	12.24	0.44
203	4.93	5.42×10^7	12.49	0.325
213	4.69	7.04×10^7	12.70	0.25
223	4.48	9.78×10^7	12.98	0.18
233	4.29	1.35×10^8	13.27	0.13
243	4.12	2.20×10^8	13.71	0.08

^aBased upon the assumption that a^H (axial) = $2a^H$ (equatorial).²⁷

Table 14. Temperature dependence of rate constant k for the ring inversion process of radical cation **14**⁺

T(K)	1000/T(K ⁻¹)	k (sec ⁻¹)	ln (k/T)	Δ Width(G)
278	3.60	3.37×10^7	11.71	0.46
273	3.66	2.77×10^7	11.53	0.56
268	3.73	2.31×10^7	11.37	0.67
263	3.80	2.12×10^7	11.30	0.73
258	3.88	1.91×10^7	11.21	0.81
253	3.95	1.68×10^7	11.11	0.92

Table 15. Temperature dependence of rate constant k for the ring inversion process of radical cation **12⁺**

T(K)	1000/T(K ⁻¹)	k (sec ⁻¹)	ln (k/T)	Δ Width(G)
228	4.39	2.79×10^7	11.71	2.21
233	4.29	3.48×10^7	11.91	1.77
238	4.20	4.74×10^7	12.20	1.30
243	4.12	5.70×10^7	12.37	1.08
248	4.03	6.48×10^7	12.47	0.95

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