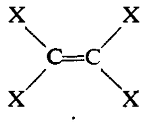
Tetrathioethylenes[1]

D. L. Coffen,*[2a] J. Q. Chambers,[2b] D. R. Williams,[2a] P. E. Garrett,[2a] and N. D. Canfield[2b]

Contribution from the Department of Chemistry, University of Colorado, Boulder, Colorado 80302, and The University of Tennessee, Knoxville, Tennessee 37916. *Received April 29, 1970*

Abstract: A survey of methods for synthesizing tetrathioethylenes and a detailed discussion of a highly efficient new method, orthothiooxalate pyrolysis, are given. Syntheses of tetrathiafulvalene and a dihydrotetrathiafulvalene are described. The electrochemistry of representative tetrathioethylenes has been investigated and found to be characterized by two "clean" one-electron oxidations. E^0 values and the electronic absorption and esr spectra of the radical cations are discussed in relation to electronic and molecular structure. The ultraviolet spectra of tetrathioethylenes and their electrochemical properties can be rationalized by extended Hückel calculations provided the 3d orbitals of sulfur are included in the basis sets. A search for conventional "electron-rich olefin" chemistry has given negative results. This lack of reactivity in contrast to oxygen and nitrogen analogs can also be rationalized by including d orbitals in the π-bonding model.

Ethylenes of the general formula i have introduced a wealth of fascinating and often useful chemistry.



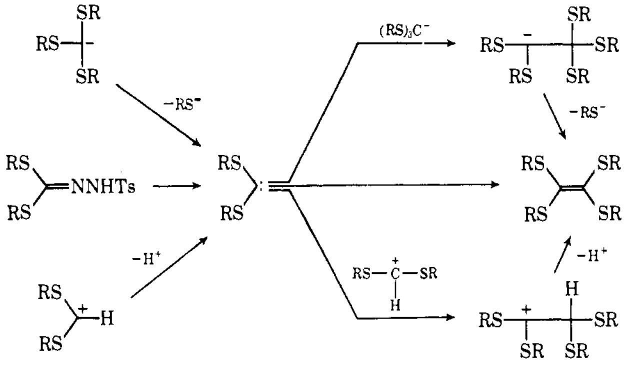
i

Among those which are well known and thoroughly studied are the parent in which X = H and such derivatives as X = CN, X = F, and X = other halogens. More recently attention has been directed to ethylenes in which X is a π-electron-donating group, the so-called "electron rich olefins."[3] The olefins of this type in which X = R_2N and X = RO have been carefully studied from the viewpoints of synthesis, chemical properties, and physical properties and reviews of this chemistry have appeared recently.[3,4] Although tetrathioethylenes, formula i with X = RS, have been known for almost 100 years,[5] relatively little is known about their properties compared to the other olefins of this type and the study whose results are described in this paper was initiated with a view to filling partly this gap. Much of the existing literature on tetrathioethylenes is reviewed and presented with the discussion of new results.

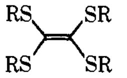
Synthesis of Tetrathioethylenes

Many of the syntheses of tetrathioethylenes described in the literature and the new syntheses described here fall into one of two categories. A few miscellaneous methods will be discussed separately.

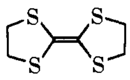
Scheme I



(a) The Carbene Route. Three methods have been utilized for the generation of dithiocarbenes which, either by dimerization or reaction with their precursors, produce tetrathioethylenes. These methods are summarized in Scheme I. Tetrathioethylenes **1** and **2** have been prepared by decomposition of tosylhydrazones of dithiocarbonates.[6,7] The sulfur-stabilized carbanions produced by metalation of orthothioformates, either with sodium[8] or potassium[9] amides or with organolithium reagents,[10,11] lose mercaptide ions giving carbenes. The tetrathioethylenes **1**,[8,9] **2**,[9] **3**,[3,7] **4**,[8,10] and **6**[10,11] have been produced in this manner. The intermediacy of a carbene in this method has been carefully established in but one instance,[12] the prepara-



1, R = Me
2, R = Et
3, R = *i*-Pr
4, R = C_6H_5



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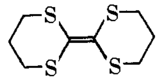

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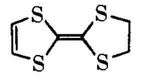

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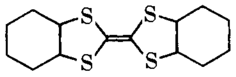

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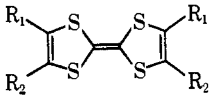
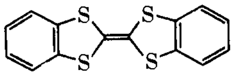


9, $R_1 = R_2 = H$
10, $R_1 = H$; $R_2 = Me$
11, $R_1 = H$; $R_2 = C_6H_5$
12, $R_1 = R_2 = C_6H_5$



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[1] The support of the National Science Foundation (Grant No. GP-10950) is gratefully acknowledged.

[2] (a) University of Colorado; (b) University of Tennessee.

[3] R. W. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 7, 754 (1968).

[4] N. Wiberg, *ibid.*, 7, 766 (1968).

[5] P. Claesson, *J. Prakt. Chem.*, 15, 193 (1877).

[6] U. Schöllkopf and E. Wiskott, *Angew. Chem., Int. Ed. Engl.*, 2, 485 (1963).

[7] D. M. Lemal and E. H. Banitt, *Tetrahedron Lett.*, 245 (1964).

[8] A. Fröling and J. F. Arens, *Recl. Trav. Chim. Pays-Bas*, 81, 1009 (1962).

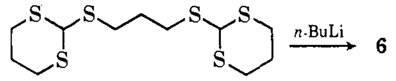
[9] J. Hine, R. P. Bayer, and G. G. Hammer, *J. Amer. Chem. Soc.*, 84, 1751 (1962).

[10] D. Seebach, *Angew. Chem., Int. Ed. Engl.*, 6, 442 (1967).

[11] R. M. Carlson and P. M. Helquist, *Tetrahedron Lett.*, 173 (1969).

[12] D. Seebach, *Angew. Chem., Int. Ed. Engl.*, 6, 443 (1967); D.

tion of compound **4** from triphenyl orthothioformate. This intermediate has been inferred in other syntheses although attempts to trap it were unsuccessful.[8] We have found additional evidence for the carbene intermediate in comparing the behavior of compounds **14** and **15** when exposed to *n*-butyllithium. Compound **14** gives the tetrathioethylene **6** in good yield[10,11] but no trace of **5** is produced from **15** under the same conditions. The carbene **16** is known to fragment to ethylene and carbon disulfide[7] and, in accord with this fact, the isolated products of the reaction of compound **15** with *n*-butyllithium are ethylene (converted to the dibromide for isolation) and ethylene trithiocarbonate (**20**). The latter is probably formed in a secondary reaction between carbon disulfide and the lithium salt of ethanedithiol. These products do not unequivocally prove a carbene intermediate as a fragmentation pathway analogous to that described for the reaction of 4,4,5,5-tetraphenyl-1,3-dithiolane with phenyllithium[13] could be involved.



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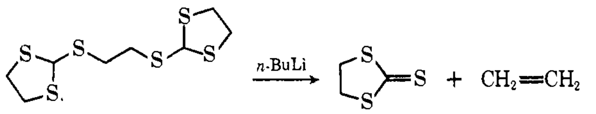

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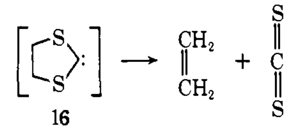

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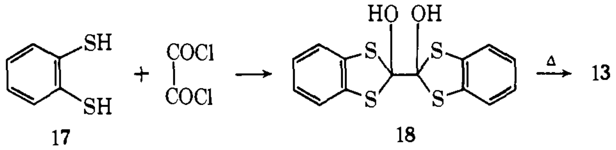
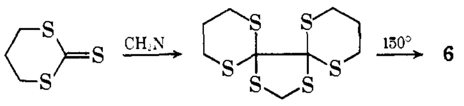
Deprotonation of dithiocarbonium ions offers a third method of generating the dithiocarbene intermediates. Compound **1** has also been obtained by this method[14] although it has been applied more extensively to the preparation of tetrathiafulvalenes from 1,3-dithiolium salts.[15] The tetrathiafulvalene derivatives **10**,[16] **11**,[17] and **12**[18] have been synthesized by this method and we have successfully applied it to the preparation of the parent compound **9** from 1,3-dithiolium bisulfate.[19] The yield of tetrathiafulvalene is high but its sensitivity to air oxidation causes considerable loss during purification.[19a]

(b) From Orthothiooxalates. Hurtley and Smiles reported in 1926 that *o*-benzenedithiol (**17**) condensed with oxalyl chloride to give an unstable condensation product, formulated as compound **18**, which produced the tetrathioethylene **13** on heating.[20] Based on more recent findings, the compound formulated as **18** was probably an orthothiooxalate.



17 **18**

We have investigated the synthesis and solution pyrolysis of orthothiooxalates in some detail and find this to be an excellent method for the synthesis of tetrathioethylenes, restricted mainly by the availability of orthothiooxalates. During the course of this study, Seebach[10] and Oae[21] reported that pyrolysis of hexaphenyl orthothiooxalate, either neat,[10] or in chlorobenzene solution,[21] gave quantitative yields of tetrathioethylene **4** and diphenyl disulfide. Both authors indicate that the pathway followed in this instance involves C–C bond cleavage giving trisphenylthiomethyl radicals which fragment to the corresponding dithiocarbene. The available evidence indicates that only C–S bond cleavages are involved in the pyrolysis of hexaalkyl orthothiooxalates.



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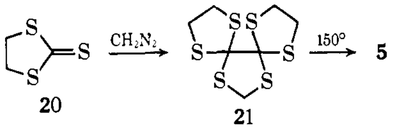


20 **21**

An ethereal solution of trimethylene trithiocarbonate reacted smoothly with diazomethane to give the orthothiooxalate **19**. The structure of this adduct is consistent with its spectroscopic properties, analysis, and the precedents for this reaction.[22] Heating the adduct in refluxing bromobenzene for several hours effected pyrolysis, and the tetrathioethylene **6** was readily isolated in 82% yield. Similarly ethylene trithiocarbonate **20** reacted with diazomethane to give the orthothiooxalate **21**. Pyrolysis of this material in boiling bromobenzene produced the tetrathioethylene **5** in 70% yield. Compounds **5** and **6** most probably arise from a fragmentation in which two carbon–sulfur bonds are cleaved and the fragment CH_2S_2 is expelled, although attempts to isolate this fragment or its secondary products were unsuccessful. The possibility of applying this method to the synthesis of other tetrathioethylenes was examined. However, because of unexpected sensitivity to ring size in the reaction of diazomethane with cyclic trithiocarbonates, the required orthothiooxalates cannot always be prepared by this reaction. Methylene trithiocarbonate (**22**) shows no appreciable reactivity with diazomethane.

Seebach and A. K. Beck, *J. Amer. Chem. Soc.*, **91**, 1540 (1969); see also G. A. Wildschut, H. J. T. Bos, L. Brandsma, and J. F. Arens, *Monatsh. Chem.*, **98**, 1043 (1967).

(13) A. Schönberg, D. Cernik, and W. Urban, *Chem. Ber.*, **64**, 2577 (1931).

(14) R. A. Olofson, S. W., Walinsky, J. P. Marino, and J. L. Jernow, *J. Amer. Chem. Soc.*, **90**, 6554 (1968).

(15) Discussed by H. Prinzbach and E. Futterer in "Advances in Heterocyclic Chemistry," Vol. 7, A. R. Katritsky and A. J. Boulton, Ed., Academic Press, New York, N. Y., 1966, p 121.

(16) H. Prinzbach, H. Berger, and A. Lüttringhaus, *Angew. Chem., Int. Ed. Engl.*, **4**, 435 (1965).

(17) A. Takamizawa and K. Hirai, *Chem. Pharm. Bull.* **17**, 1931 (1969).

(18) K. M. Pazdro, *Rocz. Chem.*, **43**, 1089 (1969).

(19) E. Klingsberg, *J. Amer. Chem. Soc.*, **86**, 5290 (1964).

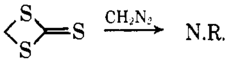
(19a) NOTE ADDED IN PROOF. Professor S. Hünig (Würzburg) has also synthesized this and related tetrathioethylenes and investigated their electrochemical and spectral properties (private communication). See also F. Wudl, G. M. Smith, and E. J. Hufnagel, *Chem. Commun.*, 1453 (1970).

(20) W. R. H. Hurtley and S. S. Smiles, *J. Chem. Soc.*, 2263 (1926).

(21) K. Uneyama, T. Sadakage, and S. Oae, *Tetrahedron Lett.*, 5193 (1969). See also D. Seebach and A. K. Beck, *ibid.*, 1933 (1970).

(22) A. Schönberg, S. Nickel, and D. Cernik, *Chem. Ber.*, **65**, 289 (1932); E. Taeger, Z. El-Heweri, and F. Runge, *J. Prakt. Chem.*, **18**, 269 (1962).

Diphenyl trithiocarbonate reacts with diazomethane to give the orthothiooxalate **23**.[22] Pyrolysis of this substance in boiling xylene yields a complex mixture of products from which only diphenyl disulfide can be readily isolated. The mixture is felt to arise from C–S homolysis competing with C–S homolysis.



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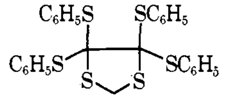

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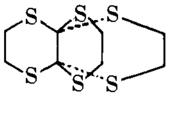
An alternative preparation of orthothiooxalates was suggested by the fact that in some instances[23] orthothio esters can be formed directly from acid chlorides and mercaptans. This method was quite successful and an orthothiooxalate was obtained directly from the reaction of oxalyl chloride with 1,2-ethanedithiol. Both the propellane structure **24** and the dispirotricyclic structure **25** are possible for this condensation product. A distinction between the two should be possible by nmr spectroscopy since all the hydrogen atoms of **24** have the same environment whereas those of **25** do not.



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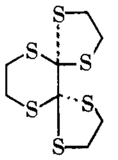

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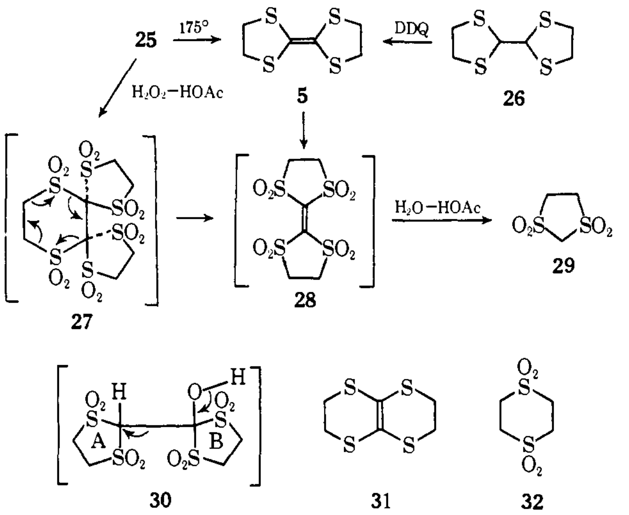
The observed spectrum consists of a single line at 3.46 ppm with a band width at half-height of 1.5 cps. Structure **24** was therefore assigned until the chemistry of the condensation product (Scheme II) was found to be interpretable only in terms of structure **25**.

Scheme II



Compound **25** was pyrolyzed in a refluxing decalin solution. The product, which crystallized from the cooled solution, was found to be identical with the tetrathioethylene obtained by DDQ oxidation of 2,2′-bi(1,3-dithiolanyl) (**26**).[24] Since this tetrathioethylene presumably has structure **5**, it follows that the oxalyl chloride condensation product must have structure **25** since the propellane compound **24** should give rise to a tetrathioethylene with structure **31**. The possibility that **24** is correct and that a thermal rearrangement to **25** precedes fragmentation is a remote one, but it cannot be excluded. Independent evidence for structure **25** would be available if the protons of the corresponding dodecaoxide **27** no longer showed magnetic equivalence and oxidation of the condensation product to the hexasulfone was therefore attempted. Ortho thioesters can be oxidized to trisulfones in the usual manner, heating with aqueous hydrogen peroxide in glacial acetic acid.[25] Under these conditions the oxidation of compound **25** produced a vigorous exothermic reaction with copious gas evolution. The crystalline product of this reaction was found, initially by its spectroscopic properties, and finally by comparison with an authentic sample, to be 1,3-dithiolane 1,1,3,3-tetraoxide (**29**).

The available evidence from the reaction leading to **29** supports the possibility that the dodecaoxide (**27**) of compound **25** spontaneously fragments evolving sulfur dioxide and ethylene and producing the tetrasulfonylethylene **28**. Further degradation of **28** could then lead to **29** by addition of water to the double bond and further fragmentation of intermediate **30** in the indicated manner (Scheme II) to produce compound **29** from ring A and a readily hydrolyzed carbonyl species from ring B. In support of this scheme it was observed that oxidation of the tetrathioethylene **5** under identical conditions also produced **29**, presumably again through the intermediacy of compound **28**. No significant gas evolution was observed during this oxidation. The gas evolved during the oxidation of compound **25** was shown by vpc analysis[26] to consist mainly of ethylene. The sulfur dioxide produced in the fragmentation of **27** was evidently oxidized to sulfuric acid by excess hydrogen peroxide. The presence of sulfuric acid in the reaction mixture was indicated by the low pH (~1) and by precipitation of barium sulfate on addition of aqueous barium chloride solution.

The proposed fragmentation of the dodecaoxide **27** bears an element of novelty. It is probably encouraged by repulsive interactions among the accumulated sulfone groups as the simple analog, 1,4-dithiane 1,1,4,4-tetraoxide (**32**),[27] is thermally stable in the solid state up to 300°. It is unlikely on orbital symmetry grounds that this fragmentation is a concerted process. A pathway involving sulfonyl radical intermediates is considered more probable, particularly in view of the precedents for reactions involving such intermediates.[28]

Clearly the overall scheme is consistent only with structure **25** for the ethanedithiol–oxalyl chloride condensation product and the magnetic equivalence of all 12 hydrogen atoms must be coincidental. This struc-

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[23] For example, H. J. Backer and F. L. Wiggerink, *Recl. Trav. Chim. Pays-Bas*, 60, 453 (1941).

[24] L. B. Brahde, *Acta Chem. Scand.*, **8**, 1145 (1954); D. L. Coffen, K. C. Bank, and P. E. Garrett, *J. Org. Chem.*, **34**, 605 (1969).

[25] W. von E. Doering and L. K. Levy, *J. Amer. Chem. Soc.*, 77, 509 (1955).

[26] We wish to thank Mr. W. H. Schroeder for this determination.

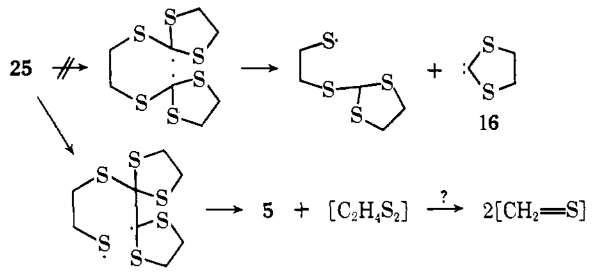
[27] K. D. Gundermann and C. Burba, *Chem. Ber.*, **94**, 2157 (1961). The sample examined in this study was prepared by direct oxidation of 1,4-dithiane with 30% hydrogen peroxide in hot acetic acid.

[28] See, for example, S. J. Cristol and D. I. Davies, *J. Org. Chem.*, **29**, 1282 (1964).

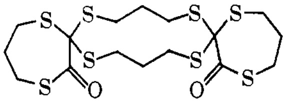
tural assignment was eventually confirmed by the natural abundance ^{13}C nmr spectrum of the substance. In benzene solution the spectrum consists of *three* signals which appear at 35.4, 41.1, and 88.0 ppm from TMS.

C–C bond homolysis can definitely be excluded as a pathway for the thermal transformation of orthothiooxalate **25** (and **21**) into tetrathioethylene **5** as this pathway subsequently involves (Scheme III) the carbene **16** which is known to fragment to carbon disulfide and ethylene faster than it dimerizes.[7] The pathway involving C–S bond homolysis and loss of the $C_2H_4S_2$ fragment is more likely. Attempts to isolate this fragment or its secondary products have been unsuccessful. It possibly splits into thioformaldehyde which subsequently polymerizes. The stench of thioformaldehyde is evolved during the pyrolysis.

Scheme III



The condensation of 1,3-propanedithiol with oxalyl chloride was also carried out. Under the same conditions which gave a clean condensation reaction with ethanedithiol, the propanedithiol gave a mixture of several products. The tetrathioethylene **6** could be isolated from this mixture but its precursor, the expected tricyclic orthothiooxalate, was not obtained. A second crystalline product isolated from the mixture exhibited spectral properties and gave analytical data which can be best accommodated by structure **33**.



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(c) Miscellaneous Methods. Other routes to tetrathioethylenes are also available. Displacement of chlorine from tetrachloroethylene by mercaptide ion has been used to prepare compounds **2**[5] and **13**[20] although the yields are poor. Reduction of carbon disulfide with sodium amalgam followed by treatment with methyl chloride is reported to give tetrathioethylene **1** in addition to several other products.[29] The reaction of 1,3-dithiolan-2-thiones with phosphites normally yields olefins *via* 1,2-elimination.[30] However, in a system where the olefin would be *trans*-cyclohexene, the tetrathioethylene **8** was formed.[30] This reaction may be another example of the carbene route in which fragmentation of the intermediate carbene is blocked by the unfavorable geometry of the incipient olefin.

We recently reported[31] that certain thioacetals are oxidized at carbon by DDQ. The bisthioacetal of glyoxal (**26**)[24] is oxidized by this reagent in boiling toluene giving tetrathioethylene **5** as the major product. This compound suffers further oxidation under the conditions of the reaction giving tetrathioethylene **7** as a minor product. We were thus fortunate to have the series of compounds **26**, **5**, **7**, and **9** available in which the effects of systematically extending the π-electron system could be studied.

Electrochemistry

The properties of the simple ethylene molecule can be drastically changed by substituting other groups for the hydrogen atoms. Thus tetracyanoethylene is a well-known electron acceptor and is easily reduced, while tetraaminoethylenes are electron donors and are easily oxidized. The chemistry of the latter compounds is dominated by the relative ease of oxidation *via* successive simple electron-transfer steps. This behavior is typified by the oxidation of tetraaminoethylene analogs of Wurster's blue by bromine,[32] silver(I),[33] and anodic oxidation.[34]

While the electrochemistry of the tetraaminoethylenes has been extensively studied and reviewed,[4] little has been reported on the tetrathioethylene analogs. Polarographic oxidation potentials at a rotating platinum electrode for two tetrathioethylenes (**6** and **13**) have been reported by Hünig.[3,35,36] In a recent article, Geske and Merritt[37] reported the electrochemical oxidation of three tetraalkyltetrathioethylenes (**1**, **2**, and **3**) and tetraphenyltetrathioethylene (**4**) and described the esr spectra of the corresponding radical cations in terms of a temperature dependent intramolecular process. A radical cation of tetrathioethylene **5** has been identified as an intermediate in the anodic oxidation of compound **25** and its esr spectrum reported.[38]

In general the electrochemical study of the tetrathioethylenes proved to be far more fruitful than a search for conventional reactivity. Five of these compounds (**4**, **5**, **6**, **7**, and **9**) have been carefully studied and the results, together with the previously published work,[36,37] make electrochemical data available for nine compounds of this class. Electrochemical and spectroscopic data for the five tetrathioethylenes studied are given in Table I. Typical cyclic voltammograms are shown in Figures 1 and 2. All five compounds exhibit the expected electrochemical behavior and are oxidized in two successive one-electron steps. At slow sweep rates (<0.2 V sec^{-1}) both steps are electrochemically reversible for compounds **7**, **9**, and **6** while the second steps are irreversible for **4** and **5**. At faster sweep rates (*ca.* 1 V sec^{-1}) the second wave in the cyclic voltammogram of **5** becomes reversible. Evidently the dications of **4** and **5** are unstable and react with solvent

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(29) B. Fetkenheuer, H. Fetkenheuer, and H. Lecus, *Chem. Ber.*, 60, 2528 (1927).

(30) E. J. Corey, F. A. Carey, and R. A. E. Winter, *J. Amer. Chem. Soc.*, 87, 934 (1965).

(31) D. L. Coffen and P. E. Garrett, *Tetrahedron Lett.*, 2043 (1969).

(32) N. Wiberg and J. W. Buchler, *Angew. Chem., Int. Ed. Engl.*, 1, 406 (1962).

(33) D. M. Lemal and K. I. Kuwano, *J. Amer. Chem. Soc.*, 84, 1761 (1962).

(34) K. Kuwata and D. H. Geske, *ibid.*, 86, 2101 (1964).

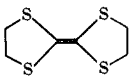
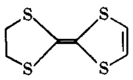
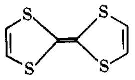
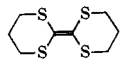
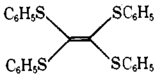
(35) S. Hünig, *Pure Appl. Chem.*, 15, 109 (1967).

(36) S. Hünig, H. Schlaf, H. Kiesslich, and D. Schentzow, *Tetrahedron Lett.*, 2271 (1969).

(37) D. H. Geske and M. V. Merritt, *J. Amer. Chem. Soc.*, 91, 6921 (1969).

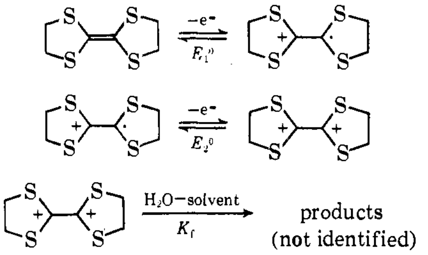
(38) N. D. Canfield, J. Q. Chambers, and D. L. Coffen, *J. Electronal. Chem. Interfac. Electrochem.*, 24, A7 (1970).

Table I. Electrochemical and Spectroscopic Parameters

	 **5**	 **7**	 **9**	 **6**	 **4**
$E_1^{0\prime a}$	0.68	0.405	0.33	0.695	1.2
$E_2^{0\prime}$	1.12	0.89	0.70	0.84	1.4[b]
$E_2^{0\prime} - E_1^{0\prime}$	0.44	0.485	0.37	0.145	0.2
$D^{1/2} \times 10^{3\,c}$	4.4	4.1	4.8	4.2	3.8[i]
$\lambda_{max}{}^d$	568	470	435, 580	391	488, 611
ϵ^e	5050		22,500, 5,910	7600	Unstable
$a_H{}^f$	2.41	1.7	*g*		*h*

[a] Formal reduction potentials in CH_3CN, 0.1 *M* TEAP (units, volts *vs.* sce). [b] This value was estimated from the second peak potential [c] Chronoamperometric diffusion coefficient in CH_3CN, 0.1 *M* TEAP (units, cm sec$^{-1/2}$). [d] λ_{max} of the radical cations in nm. [e] Molar extinction coefficients in cm^{-1} M^{-1}. [f] Hydrogen coupling constants, see text for details. [g] A broad signal *ca.* 3 G wide was observed. [h] Geske and Merritt[37] report an unresolved spectrum *ca.* 2 G wide. [i] Not corrected for background.

or residual water in the solvent on the time scale of the electrochemical experiment. The scheme is illustrated for **5** in eq 1–3. As the π-electron system increases in



(1)

(2)

(3)

the series **5**, **7**, and **9**, the dication becomes less reactive. This scheme (eq 1–3) is in accord with the report by Shine and Murata that decay of the thianthrene radical cation proceeds *via* the dication.[39] The cyclic voltammograms of **4** (Figure 2) also correspond to this scheme and clarify the broad wave obtained at a rotating platinum electrode by previous workers.[37]

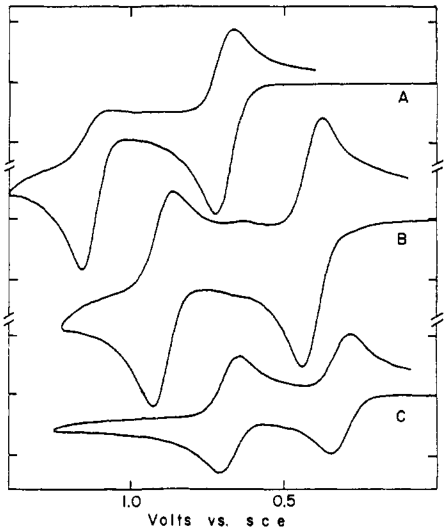


Figure 1. Cyclic voltammograms of (A) 1.0 × 10⁻³ *M* **5**, 0.1 *M* TEAP, (B) 6.05 × 10⁻³ *M* **7**, 0.1 *M* KPF_6, (C) 1.0 × 10⁻³ *M* **9**, 0.1 *M* TEAP in CH_3CN. Sweep rates: (A) 0.024 V/sec; (B) 0.12 V/sec; (C) 0.12 V/sec. Current range: (A and B) 0.02 mA/div; (C) 0.05 mA/div.

Remarkable correlations among polarographic half-wave potentials, spectroscopic data, and molecular orbital calculations have been pointed out by many workers in the last 20 years.[40] Several good correlations for polarographic half-wave data have been reported for nitrogen and sulfur heterocycles.[41–44] In many cases, where polarographic oxidation potentials have been correlated for a series of heterocycles, the potential data have contained unknown kinetic terms because of the complexity of the electrode processes. Although the number of compounds studied in this work is too limited to justify any general conclusions, the E^0 data are well defined and some of the trends in the data are interesting. Several aspects of the results will be briefly discussed in the following paragraphs.

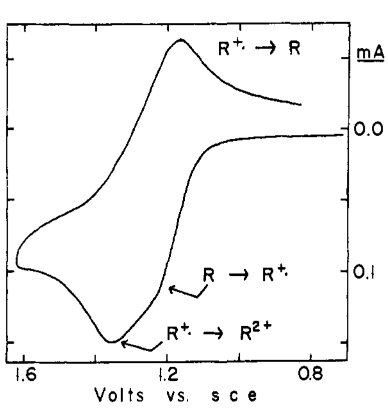


Figure 2. Cyclic voltammogram of 1 × 10⁻³ *M* **4**, 0.1 *M* TEAP, CH_3CN. Sweep rate: 0.3 V/sec; current range: 0.05 mA/div.

E^0 Values. The difference between the formal reduction potentials, $E_2^{0\prime} - E_1^{0\prime}$, represents the $E^{0\prime}$ for the coproportionation reaction between the parent tetrathioethylene and the dication. For the tetrathio-

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(39) H. J. Shine and Y. Murata, *J. Amer. Chem. Soc.*, 91, 1872, 7556 (1969).

(40) For a recent review, see M. E. Peover, "Electroanalytical Chemistry," Vol. III, A. J. Bard, Ed., Marcel Dekker, New York, N. Y., 1968.

(41) A. Zweig, W. G. Hodgsow, and W. H. Jura, *J. Amer. Chem. Soc.*, 86, 4124 (1964); A. Zweig, J. E. Lancaster, M. T. Neglia, and W. H. Jura, *ibid.*, 86, 4130 (1964); A. Zweig and J. E. Lehnsen, *ibid.*, 87, 2647 (1967); A. Zweig, A. H. Maurer, and B. G. Roberts, *J. Org. Chem.*, 32, 1322 (1967).

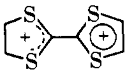
(42) F. P. Billingsley and J. E. Bloor, *Theoret. Chim. Acta*, 11, 325 (1968).

(43) J. Fabian, A. Mehlhorn, and R. Zahradnik, *J. Phys. Chem.*, 72, 3975 (1968).

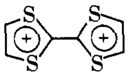
(44) M. E. Peover, *Electrochim. Acta*, 13, 1086 (1968).

ethylenes with five-membered rings, this difference is on the order of 0.4–0.5 V, while it is on the order of 0.1 V for the six-membered ring compound. A similar value is observed for the tetraphenyltetrathioethylene and the tetralkyl derivatives reported by Geske and Merritt.[37] Apparently, the SCS angle has a critical influence on the magnitude of this value. A possible explanation of this difference is that the positive charges on the dication species can be stabilized by the 3p electrons on the sulfur atoms more easily if the sulfur atoms are permitted to move so as to minimize coulombic interaction. However, care must be taken in any interpretation in variations of $E_2^{0\prime} - E_1^{0\prime}$ because this difference will include the solvation energy of the dication species. These values will be large (6–8 eV[44]) and could vary appreciably between compounds as similar as **5**, **7**, and **9**.

The $E_1^{0\prime}$ values for compounds **5**, **7**, and **9** decrease as the π network available for delocalization of the positive charge on the radical cations increases. In these compounds there are ten, twelve, and fourteen p electrons distributed over six, eight, and ten atoms, respectively. Compound **6**, which has the same π configuration as **5**, has the same E_1^0. Both the dication formed from **7**, which has ten π-electrons, and the dication, $\mathbf{9}^{2+}$, which electronically resembles biphenyl, are exceptionally stable organic dications.



$\mathbf{7}^{2+}$



$\mathbf{9}^{2+}$

Radical Cation Spectra. The radical cations generated from **5**, **7**, **9**, **6**, and **4** in acetonitrile and nitromethane solutions are all highly colored, stable species. The esr spectra (Table I) are in accord with the above description but unfortunately the spectra are not well enough resolved to show all possible couplings. No ^{33}S or ^{13}C splittings were observed. The radical cation of $\mathbf{5}\cdot^+$ gives a nine-line spectrum, seven lines of which can be readily detected, due to coupling with eight equivalent protons. The esr spectrum of $\mathbf{7}\cdot^+$ is not as well resolved (Figure 3), but a splitting due to at least four equivalent protons is clearly evident. Because there are only two protons on the aromatic half of the molecule, this coupling must arise from interaction with the $-CH_2CH_2-$ group. Thus this radical can be described as an aromatic dithiolium cation substituted by a 2-(1,3-dithiolanyl) radical.

Because the esr spectrum of this radical is poorly resolved it is difficult to set an upper limit on the coupling constant of the two protons on the aromatic half of this molecule. It is possible that, by coincidence, all six protons have approximately equal coupling constants. This interpretation would be consistent with the MO calculations on **7** discussed below. Unfortunately, the esr spectra of $\mathbf{9}\cdot^+$ and $\mathbf{4}\cdot^+$ exhibit no hyperfine splittings; only an intense structureless absorption is observed.

Most workers have interpreted coupling through a thioether linkage to an alkyl group in terms of a hyperconjugation effect. A McConnell relation of the type $a_H = Q\rho_S$ has been used to relate the magnitude of the coupling constant to the spin density on the sulfur atom. Values of the constant Q of 21[45] and 18.5 G[46] have been determined. However, in cases in which the alkyl groups are constrained in some manner such that maximum overlap with the sulfur $3p_z$ orbital is not possible, coupling constants less than predicted by the simple equation will be observed. For example, Geske and Merritt[37] found that tetraethyltetrathioethylene has three different kinds of α hydrogens at $-90°$. These workers proposed a $\cos^2$ law to account for the results. The angle θ is the angle between the HCS plane and the $3p_z$ orbital on the sulfur atom. A $\cos^2\theta$

$$a_H = Q\rho_s\langle\cos^2\theta\rangle \tag{4}$$

dependence of this type is a well known consequence of hyperconjugation in radical species.[47]

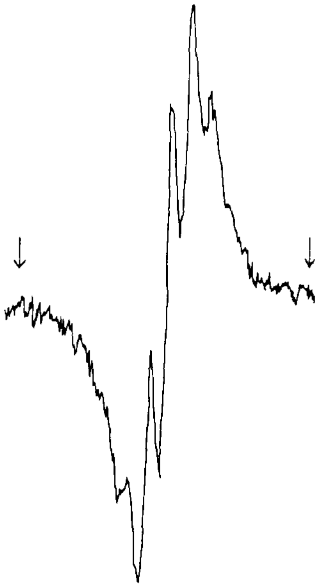


Figure 3. Esr spectrum of the radical cation of **7** in CH_3NO_2. Conditions: 0.2×10^{-3} *M* **7**, 0.05 *M* TEAP, CH_3NO_2; platinum electrode, 0.45 V *vs.* sce. The distance between the arrows is 25.0 G.

In compounds **5** and **7**, the C–H bonds are fixed in space relative to the π network of the tetrathioethylene bridge and the dihedral angle θ is 30° ($\cos^2\theta = 0.75$). Assuming 0.19 for ρ_s in $\mathbf{5}\cdot^+$, a value of 17 G is calculated for Q in eq 4. This is significantly lower than Q values calculated from the data of Forbes and Sullivan[46] or Geske and Merritt[37] for radical cations of thioethers with freely rotating methyl groups ($\langle\cos^2\theta\rangle = 0.5$). It appears that the simple equation (4) does not satisfactorily account for the coupling constants of thioalkyl radical cations. Details of our interpretation of the spectra will appear elsewhere.[48]

The data in Table I show that the energies of the transitions in the absorption spectra of the radical cations exhibit a fair correlation with the $E^{0\prime}$ values for **5**, **7**, and **9** (Figure 4). However, interpretation of this result is tenuous because of the limited number of data and the complexity of the theoretical treatment. Furthermore, the correlation breaks down for the radical cation of **6**.

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(45) A. Zweig and W. G. Hodgsow, *Proc. Chem. Soc. London*, 417 (1964).

(46) P. D. Sullivan and W. F. Forbes, *Can. J. Chem.*, **46**, 317 (1968).

(47) A. Carrington and A. D. McLachlan, "Introduction to Magnetic Resonance," Harper and Row, New York, N. Y., 1967, p 84.

(48) J. Q. Chambers, N. D. Canfield, D. R. Williams, and D. L. Coffen, *Mol. Phys.*, **19**, 581 (1970).

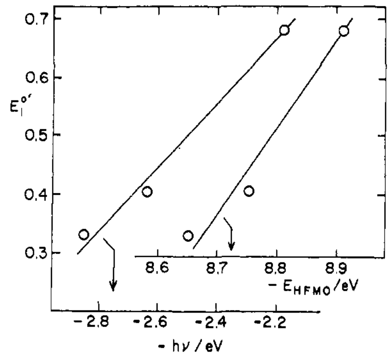


Figure 4. Plot of the formal reduction potential for the couple, $R\cdot^+/R$, *vs.* the energy of the highest filled molecular orbital (d orbitals included) and *vs.* the energy of the absorption band of the radical cation in the visible region.

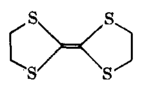
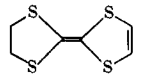
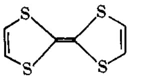
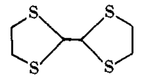
In Figure 4 the $E_1^{0\prime}$ values are also plotted *vs.* the energy of the highest filled MO. While the predicted variation is in the right direction, the slope deviates considerably from the theoretical value of unity.

Electronic Spectra

This section deals with the electronic spectra of compounds **5**, **7**, **9**, and **26**, *i.e.*, tetrathioethylenes containing five-membered rings. The discussion of their spectra may not then be taken to be representative of all tetrathioethylenes; however, it will be indicative of the factors that control the electronic spectra of this class of compounds. A number of authors have examined the ultraviolet spectra of organic sulfides[42,49–53] and although opinion is by no means unanimous, it is becoming more clear that d orbitals must be included in the basis set if satisfactory results are to be obtained. Semiempirical self-consistent-field calculations of the CNDO type on smaller cyclic organic sulfides indicate that transition energies are a factor of 2 too high if d orbitals are not included on sulfur atoms.[54] The compounds that we will discuss are too large for any reasonable self-consistent calculation. We have therefore chosen to examine the spectra in terms of extended Hückel theory.[55] This theory yields results for small cyclic organic sulfides that are reasonably compatible with those of the more sophisticated CNDO method.[54] In addition, the calculations are successfully used in this paper to interpret the esr spectra of tetrathioethylenes. Once again, it is imperative that d orbitals are included in the basis set. A calculation not including d orbitals for compound **5** predicts the first possible transition to be a factor of 3 too high in energy.

The electronic spectra of compounds **5**, **7**, **9**, and **26** in the visible and ultraviolet regions were taken using a Cary Model 14 spectrophotometer. The peak maxima positions, corresponding extinction coefficients, and solvents used are given in Table II.

Table II. Electronic Absorption Spectra of Tetrathioethylenes

Compd	Solvent	λ_{max}, mμ	ΔE, eV	ε
 **5**	95% ethanol	358	3.46	470
		286	4.34	8,900
		268	4.63	12,000
		(262)[a]	4.73	11,600
		222	5.59	9,600
 **7**	95% ethanol	420	2.95	400
		305	4.07	8,700
		292	4.25	9,000
 **9**	Cyclohexane	450	2.76	270
		368	3.37	1,900
		317	3.91	12,500
		303	4.09	13,000
 **26**	Ethanol	242	5.12	660

[a] Indicates shoulder.

Compounds **5**, **7**, and **9** each have a low intensity band at low energy with a variety of strong intensity bands at higher energies. Compound **26** has a single band which appears with low intensity at high energy. The spectrum of compound **26** is identical with the spectrum of 1,3-dithiolane[50] with the exception that the extinction coefficient for **26** is approximately double that observed for 1,3-dithiolane.

Although the band positions of **5**, **7**, and **9** differ appreciably, the overall character of their spectra is similar. Our initial assumptions gave compound **5** a nonplanar ring structure with **7** having only one ring planar, and **9** being completely planar. Calculations based on structures of this type gave results which could not account for the observed spectra even in the most approximate manner. We then assumed planar ring geometries for all three compounds.

These geometries were based on C–C, C=C, and CH bond lengths of 1.52, 1.34, and 1.09 Å respectively. C–S bonds involving an sp^3 hybridized carbon were taken as 1.81 Å, those involving an sp^2 carbon as 1.75 Å. In addition the angle between C–H bonds for a saturated carbon was assumed to be 109°; the C–H bond for an unsaturated carbon was assumed to bisect the CCS angle. It then becomes possible to make distinctions between molecular orbitals constructed from in-plane atomic orbitals (σ) and molecular orbitals made up of out-of-plane atomic orbitals (π). Because of the large atomic orbital basis set (68 for **5**), it is not feasible to reproduce the coefficients of the molecular orbitals. We have, instead, given appropriate MO energies and an approximate description for each appropriate MO.

The data for the lowest vacant and the highest filled MO's of **5** are given in Table III. There is a series of π–σ transitions between the three highest filled and two lowest vacant MO's. The highest and lowest energy transitions of this group are allowed with out-of-plane polarization and will occur with weak intensity. The low-energy π–σ excitation matches with the observation of a low intensity band at 358 mμ (ϵ = 470). The higher energy π–σ band is almost certainly hidden under the high-intensity transitions at lower wavelength. Three π–π transitions emanating from the levels at

(49) E. A. Fehnel and M. Carmack, *J. Amer. Chem. Soc.*, 71, 84 (1949).

(50) S. Oae, W. Tagaki, and A. Ohno, *Tetrahedron*, 20, 437 (1964).

(51) G. Jeminet and A. Kergomard, *Bull. Soc. Chim. Fr.*, 3233 (1967).

(52) D. R. Williams, D. L. Coffen, P. E. Garrett, and R. N. Schwartz, *J. Chem. Soc. B*, 1132 (1968).

(53) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," Wiley, New York, N. Y., 1962.

(54) D. R. Williams and L. T. Kontnik, *J. Chem. Soc. B*, 312 (1971).

(55) R. Hoffmann, *J. Chem. Phys.*, 39, 1397 (1963); 40, 2047, 2474 (1964); *Tetrahedron*, 22, 521 (1966).

Table III. Energies and Approximate Descriptions of the Molecular Orbitals of Compound **5**[a]

Energy, eV	Symbol	Description	D_{2h} symmetry label
−3.81	σ	Largely in-plane d orbitals on sulfur	b_{1g}
−4.23	σ	Largely in-plane d orbitals on sulfur	a_g
−4.51	σ	Largely in-plane d orbitals on sulfur	b_{3u}
−4.60	σ	Largely in-plane d orbitals on sulfur	b_{2u}
−7.08	π	Delocalized over bridging carbons and sulfurs	b_{3g}
−7.44	σ	Largely in-plane d orbitals on sulfur	b_{3u}
−8.24	σ	Largely in-plane d orbitals on sulfur	a_g
−8.91	π	Delocalized over bridging carbons and sulfur atoms	b_{1u}
−9.60	π	Large coefficients on sulfurs, node at bridging carbons	a_u
−10.85	π	Large coefficients on sulfurs, node at bridging carbons	b_{2g}
−12.92	σ	Bonding orbital for bridging carbons and sulfurs	b_{1g}
−13.85	π	Delocalized over bridging carbons and sulfurs	b_{3g}
−14.17	σ	Bonding orbital for sulfurs and nonbridging carbons	b_{2u}

[a] MO's below the line are filled in the ground state and those above the line are vacant.

−8.91, −9.60, and −10.85 eV and going to the −7.08 eV are possible. The lowest two of these are allowed with in-plane polarization (short and long axis). We do, in fact, observe three transitions that lie fairly close together at 286, 268, and 262 mμ. The 262-mμ transition presumably corresponds to the forbidden π–π excitation, the large extinction coefficient being present because of its proximity to the allowed bands. The only other allowed transitions that will appear in the ultraviolet region come from the π and σ levels −10.85 and −12.92 eV to a common σ MO at −7.44 eV. The π–σ transition is out-of-plane polarized and will be weak; the σ–σ transition is short axis polarized and correlates with the observed band at 222 mμ (ϵ = 9600).

Table IV contains the MO descriptions for compound **7**. The lowest set of transitions are π–σ in character ($b_1 \rightarrow a_1$, $b_1 \rightarrow b_2$). They occur with out-of-plane polarization, and these are assumed to account for the low-intensity band at 4200 mμ (ϵ = 400). The next set of transitions are π–π in character. All six possible transitions are symmetry allowed. Table IV indicates that some of the π MO's are predominantly confined either to the saturated or to the unsaturated ring. A large transition moment and therefore intensity will result if the excitation is localized in one or the other rings. Thus transitions from −10.33 to −7.07 eV and −12.74 to −6.56 eV will give rise to strong bands at 3.26 and 5.90 eV. Other π–π transitions, although symmetry allowed, will have small transition moments and are presumably hidden by the overlapping of the allowed bands. A pair of allowed σ–σ transitions are calculated to occur at 4.42 and 5.32 eV. The observed spectrum shows two high intensity peaks at 305 and 292 mμ. These probably correspond to the lowest of the strong π–π and σ–σ transitions just discussed. The envelope of the spectrum is very broad in this region and could well hide further allowed transitions. Alternatively, the higher π–π and σ–σ transitions are hidden in the end absorption of the ultraviolet region.

Table IV. Energies and Approximate Descriptions of the Molecular Orbitals of Compound **7**[a]

Energy, eV	Symbol	Description	C_{2v} symmetry label
−4.22	σ	Largely in-plane d orbitals on sulfur	a_1
−4.33	σ	Largely in-plane d orbitals on sulfur	b_2
−4.60	σ	Largely in-plane d orbitals on sulfur	a_1
−6.56	π	Large coefficients on sulfurs and carbons of unsaturated ring, node at bridging carbons	a_2
−7.07	π	Delocalized over bridging carbons and sulfur atoms	b_1
−7.45	σ	Largely in-plane d orbitals on sulfur	b_2
−8.30	σ	Largely in-plane d orbitals on sulfur	a_1
−8.75	π	Delocalized over bridging carbons and sulfur atoms	b_1
−10.33	π	Delocalized over saturated ring only	a_2
−12.74	π	Delocalized over unsaturated ring only	a_2
−12.98	σ	Bonding orbital for C–S bonds	b_2
−13.08	π	Delocalized over both rings	b_1
−14.18	σ	Bonding orbitals for C–S bonds	a_1

[a] MO's below the line are filled in the ground state and those above the line are vacant.

Table V. Energies and Approximate Descriptions of the Molecular Orbitals of Compound **9**[a]

Energy, eV	Symbol	Description	D_{2h} symmetry label
−4.21	σ	Largely in-plane d orbitals on sulfur	a_g
−4.62	σ	Largely in-plane d orbitals on sulfur	b_{2u}
−5.52	π	Node at bridging carbons	a_u
−7.06	π	Delocalized over whole molecule	b_{3g}
−7.47	σ	Largely d orbitals on sulfur	b_{3u}
−7.67	π	Node at bridging carbons	b_{2g}
−8.36	σ	Largely in-plane d orbitals on sulfur	a_g
−8.65	π	Delocalized over whole molecule	b_{1u}
−12.35	π	Delocalized over whole molecule	b_{3g}
−12.60	π	Node at bridging carbons	a_u
−12.86	π	Node at bridging carbons	b_{2g}
−13.06	σ	Bonding orbitals for C–S bonds	b_{1g}
−14.19	σ	Bonding orbitals for C–S bonds	b_{2u}

[a] MO's below the line are filled in the ground state and those above the line are vacant.

Table V contains the pertinent information for the MO's of compound **9**. The lowest allowed transition occurs between the highest filled and lowest vacant MO's of the ground state (π–σ). This matches with the band at 450 mμ (ϵ = 270). The calculations indicate that next in order of increasing energy there is both an allowed π–π and a π–σ transition coming from the −8.65 level. The spectrum shows that the weak π–σ transition (368 mμ) lies on the tail of the band due to the π–π transition (317 mμ). The MO's of Table V show the σ and π levels to which the electron is excited as 0.2 eV apart. It may well be that our calculations have inverted the order of these orbitals. The next allowed π–π transition is between levels at −8.65 and −7.06 eV which is presumed to be responsible for the maximum at 303 mμ. Further allowed π–π transitions are calculated to be over 3 eV higher and will not be seen in the spectrum. Any further allowed π–σ excitations are swamped by the high intensity π–π bands.

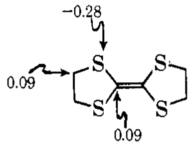
The transitions that give rise to the highly colored nature of the radical cations of **5**, **7**, and **9** are probably due to the same type of transitions that are present for the neutral molecules. The calculations show that removal of an electron corresponds to placing approximately 0.25 positive charge on each sulfur atom in **5**, **7**, and **9**. We would expect orbitals that contain large coefficients on sulfur to be lowered in energy by a relatively large amount. The vacant MO with the highest sulfur atom coefficients is the σ-orbital occurring at -8.24 and -8.30 eV for compounds **5** and **7**, respectively. We might then expect to see a low energy transition for the cation which corresponds to the π–σ excitation of the neutral species. The intensity of this type of transition is largely dependent upon the coefficient of s and p_π orbitals on the same atom. Placing a partial positive charge on the sulfur will tend to increase these coefficients and thus increase the intensity. The visible spectra of the radical cations of **5**, **7**, and **9** are given in Table I. Unfortunately we do not have the extinction coefficient for $\mathbf{7}\cdot^{+}$. We do see only a moderate intensity transition in the visible for $\mathbf{5}\cdot^{+}$ The interpretation of the visible spectrum of $\mathbf{7}\cdot^{+}$ is more open to doubt because of the large shift in the $\lambda_{\max}$ (568 mμ in $\mathbf{5}\cdot^{+}$, 470 mμ in $\mathbf{7}\cdot^{+}$). It may well be that this band is due to excitation between π orbitals that are fully occupied in the neutral molecule. If this is the case the band at 470 mμ should have large intensity.

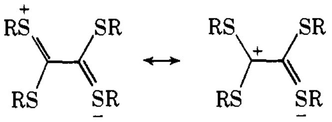
The visible spectrum of $\mathbf{9}\cdot^{+}$ contains two bands of differing intensity in contrast to the single band of $\mathbf{5}\cdot^{+}$ and $\mathbf{7}\cdot^{+}$. The extended Hückel MO's of **9** are able to account for this in a qualitative manner. The 580-mμ band has the right sort of intensity and peak position to correspond to a π–σ transition as in $\mathbf{5}\cdot^{+}$. This is in agreement with the relative ordering of the MO's. The π orbital of b_{2g} symmetry (-7.65 eV) has larger coefficients on sulfur than the σ orbital (-8.36 eV). It also lies close in energy to the σ orbital. This is not the case in **5** and **7**. We then propose that this π orbital is lowered sufficiently that the symmetry allowed excitation from the π level (-8.65 eV) to the b_{2g} π orbital accounts for the very intense band at 435 mμ (ϵ 22,500). Our analysis has not taken into account the effect of the positive charge on the MO's in a numerical manner; in view of possible changes in molecular geometry as well as large solvation effects on oxidation, we feel that this approach is justified.

Chemical Reactivity and Electronic Structure

In his review of the extensive chemistry of tetraamino- and tetraalkoxyethylenes, Hoffmann observed that little was known about the corresponding tetrathioethylenes.[3] We were thus prompted to investigate the chemical properties of the tetrathioethylenes provided by the orthothiooxalate pyrolyses. The most striking feature of their chemistry is the lack of reactivity, particularly toward electrophilic reagents. In contrast to tetramethoxyethylene which is decomposed by such weak acids as methanol and water,[3] the tetrathioethylenes **5** and **6** can be dissolved in concentrated sulfuric acid and recovered quantitatively by dilution with water. Various other electrophilic reagents known to either oxidize or cycloadd to nitrogen and oxygen analogs failed to react with tetrathioethylene **5**, even after prolonged heating. The reagents with which reactions were attempted include dimethyl acetylenedicarboxylate, phenyl isocyanate, tosyl isocyanate, phenyl azide, diethyl azodicarboxylate, and tetracyanoethylene. The last reagent, which oxidizes tetraaminoethylenes[56] and cycloadds to tetramethoxyethylene,[3] reacts with **5** to the extent of forming a (green) charge-transfer complex, but the complex is decomposed into its components by dilution.

The lack of significant reactivity and the remarkable stability in concentrated acid are readily understood in terms of the charge density distribution calculated by the extended Hückel method (*vide supra*). The charge density distribution calculated for compound **5** is shown below. This charge density distribution may also be viewed as a consequence of significant contribution from the 12 dipolar resonance structures of types A and B.[57] Electrophilic species, in particular protons, will therefore be directed to one of the sulfur atoms rather than one of the central carbon atoms and the central double bond survives exposure to such reagents.





A

B

The chemical stability of the tetrathioethylenes in contrast to oxygen and nitrogen analogs is thus accounted for by implicating d orbitals in the π-electron distribution. Comparison of the electronic spectra of the tetrathioethylenes with the spectra of oxygen and nitrogen analogs corroborates this interpretation. Tetrakisdimethylaminoethylene has two absorption bands at 221 (13,000) and 270 mμ (11,000)[58] and tetramethoxyethylene shows only end absorption at 212 mμ (3900).[59] The tetrathioethylenes exhibit the much more elaborate absorption spectra given in Table II. Inclusion of d orbitals in the description of the electronic structure gives rise to several low-lying energy states (Table III) and these complex spectra are then to be expected.

Conclusions

Tetrathioethylenes can be synthesized by a variety of methods of which the most convenient for large-scale preparations are metalation of orthothioformates and pyrolysis of orthothiooxalates. The chemical, electrochemical, and spectral properties of these compounds are understood in terms of a molecular orbital description which includes the 3d orbitals of the sulfur atoms. Their chemical behavior is not consistent with the description "electron rich olefins" and they should not be included in that class of compounds .

Experimental Section

Computational Method. The method of extended Hückel theory has been described elsewhere.[55] Slater orbitals were used on all atoms, and $H_{ij} = -kS_{ij}$ was used to determine off-diagonal Hamiltonian matrix elements. In all calculations reported, the value 35 eV was chosen for k. Changing this constant over a fairly wide range did not result in any marked improvement of the

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[59] D. M. Lemal, E. P. Gosselink, and S. D. McGregor, *J. Amer. Chem. Soc.*, **88**, 582 (1966).

results. Valence orbital ionization potentials were taken from the work of Basch, Viste, and Gray.[60] The valence state data for the sulfur 3d orbitals were taken from Cusachs and Linn.[61]

Electrochemical Methods. The procedures and instrumentation were standard and have been described in part elsewhere.[62] In most experiments a 0.228-cm^2 Beckmann platinum inlay electrode was used which was polished with 0.5-μ lapping compound before recording individual current potential curves. The counterelectrode was a large platinum gauze which was immersed directly in the electrolysis solution. An aqueous sce was separated from the test solution by a fine-porosity glass frit and a salt bridge filled with the solution under study. All potentials are reported *vs.* an aqueous sce.

Visible and uv spectra were recorded on a Cary 14 spectrophotometer and esr spectra on a Varian Model V4502 X-band spectrometer using conventional *in situ* techniques.[63] Esr spectra were obtained in both acetonitrile and nitromethane solvents. In general better resolution was obtained in nitromethane at a concentration of parent compounds of 0.2×10^{-3} *M*. A low concentration was used in an effort to minimize electron exchange between the radical cations and the neutral compounds. The supporting electrolyte was 0.05 *M* tetraethylammonium perchlorate (TEAP) in the esr experiments and either 0.1 *M* TEAP or 0.1 *M* KPF_6 in the cyclic voltammetry experiments.

The acetonitrile was purified following Mann's procedure[64] and the nitromethane was distilled under reduced pressure prior to use. In agreement with Osa and Kuwana,[65] we found that chromatography over alumina introduces an oxidizable impurity ($E_p \simeq 1.5$ V) into nitromethane.

Synthetic Procedures.[66] **1,2-Bis-2-(1,3-dithiolanyl)thioethane (15).** Ethyl orthoformate (8.6 g, 0.055 mol) in glacial acetic acid (50 ml) was treated with boron trifluoride ethereate (0.6 ml). 1,2-Ethanedithiol (8.0 g, 0.085 mol) was added dropwise with stirring during 0.5 hr. After stirring at room temperature for 12 hr, the precipitate was filtered off to yield 6.64 g (74%) of white powder. Recrystallization from ethanol gave fine white needles: mp 103–104° (lit.[20] mp 104–105°); ir ν_{max} 1270, 1235, 1190, 1160, 1130, 1115, 970, and 750 cm^{-1}; nmr 3.01 (4 H, s), 3.4 (8 H, m), and 5.73 ppm (2 H, s); and mass spectrum *m/e* 302 (M$^+$), 197, 147, 142, 109, 105, 95, and 77.

Anal. Calcd for $C_8H_{14}S_6$: C, 31.76; H, 4.66; S, 63.79. Found: C 31.90; H, 4.40; S, 61.15.

Reaction of 1,2-Bis-2-(1,3-dithiolanyl)thioethane (15) with *n*-Butyllithium. Compound **15** (2.0 g, 6.62 mmol) was dissolved in 60 ml of tetrahydrofuran freshly distilled from $LiAlH_4$. The flask was swept with nitrogen which was led *via* a gas diffusion tube into a solution of excess bromine in carbon tetrachloride. The stirred solution was immersed in a Dry Ice–acetone bath and *n*-butyllithium (5.84 ml of 2.3 *M* solution) was added in one portion. The mixture turned bright yellow and some gas evolution was observed. During an additional 18 hr stirring under the nitrogen flow, the flask was gradually warmed to room temperature. The solution was diluted with water and extracted with methylene chloride. The extracts were combined, dried, and evaporated leaving 37 mg of yellow oil. This was identified by tlc and infrared and mass spectral analysis as crude ethylene trithiocarbonate. The bromine–carbon tetrachloride solution was concentrated to a small volume. Gas chromatographic and mass spectral analysis established that the residue was mainly ethylene bromide.

Tetrathiafulvalene (9). A sample of 1,3-dithiolium hydrogen sulfate was prepared by oxidation of 1,3-dithiole-2-thione using the method described by Klingsberg[19] except that *m*-chloroperbenzoic acid was used as the oxidizing agent. The crude salt (0.9 g) was slurried in acetonitrile (15 ml) and treated with triethylamine (1 ml). The salt dissolved leaving a black solution. This was poured into water and extracted with methylene chloride. The extract was dried with sodium sulfate and evaporated giving 430 mg (93%) of a yellow-brown crystalline solid. The crude product was fairly pure (tlc). Further purification was accomplished by eluting through an alumina column with chloroform. The yellow eluate was evaporated with minimal exposure to air leaving a yellow solid: mp 98–102°; ir ν_{max} 1600, 1525, 1490, 1245, 791, 777, and 729 cm^{-1}; nmr (CCl_4) 6.27 ppm (sharp singlet); mol wt, 204 (mass spectrum). The sensitivity to air oxidation of this compound precluded preparation of an analytically pure sample.

1,3-Dithiolane-4,4-dione Bis(trimethylene thioketal) (19). Solid 1,3-dithiane-2-thione[67] (432 mg) was added to ethereal diazomethane (20 ml). Evolution of nitrogen commenced at once. Additional diazomethane was added in portions during several hours until the starting material was consumed (tlc). Ether was evaporated and the residue extracted with hot 95% ethanol. The insoluble material was recrystallized from methanol giving 177 mg (40%) of product in two crops of pale yellow crystals: mp 151–153°; nmr 2.1 (4 H, multiplet), 3.2 (8 H, multiplet), and 3.98 ppm (2 H, singlet); mol wt, 314 (mass spectrum).

Anal. Calcd for $C_9H_{14}S_6$: C, 34.34; H, 4.49; S, 61.17. Found: C, 34.52; H, 4.46; S, 61.23.

2,2′-Bi(1,3-dithianylidene) (6). A solution of compound **19** (505 mg) in bromobenzene (30 ml) was heated to reflux for 24 hr. The solvent was evaporated under high vacuum and the residue extracted with hot ethanol. The extracts were concentrated and cooled giving 312 mg (82%) of brownish white crystals. An analytical sample recrystallized from ethanol was obtained as pale yellow crystals: mp 140–142° (lit.[10] mp 141–142°); nmr 3.0 (8 H, multiplet) and 2.2 ppm (4 H, multiplet); mol wt, 236 (mass spectrum).

1,3-Dithiolane-4,5-dione Bis(ethylene thioketal) (21). Ethylene trithiocarbonate (**20**, 1.50 g, 11.0 mmol) was slurried in 10 ml of ether and treated with 30 ml of freshly prepared ethereal diazomethane solution (*ca.* 0.1 *M*). The resulting solution was stirred for 18 hr during which some gas evolution was observed. A second 30-ml portion of ethereal diazomethane solution was added and stirring continued for a further 24 hr. The solvent was allowed to evaporate and the residue was extracted several times with hot dichloromethane. The extracts were combined, concentrated, and refrigerated giving 0.697 g (44%) of amorphous yellow solid. Recrystallization from methanol gave colorless plates (0.465 g) with mp 166–168°; ir ν_{max} 1275, 1235, 1005, 975, 950, 870, 840, and 740 cm^{-1}; nmr 3.55 (8 H, s) and 4.00 ppm (2 H, s); mass spectrum *m/e* 286 (M$^+$), 208, 150 (100%), 122, 104, 88, and 76.

Anal. Calcd for $C_7H_{10}S_6$: C, 29.34; H, 3.52; S, 67.03. Found: C, 29.21; H, 3.52; S, 67.10.

2,2′-Bi(1,3-dithiolanylidene) (5). Pyrolysis of Compound 21. Compound **21** (51 mg) was dissolved in bromobenzene (5 ml) and heated to reflux for 24 hr. The solvent was removed under high vacuum leaving 49 mg of light brown solid. Recrystallization from ethanol afforded 26 mg (70%) of compound **5**, identified by comparison of infrared and nmr spectra and of tlc behavior with an authentic sample.[31]

Pyrolysis of 4,4,5,5-Tetrakisphenylthio-1,3-dithiolane (23). Compound **23** was prepared from diphenyl trithiocarbonate and diazomethane as described by Schönberg and coworkers,[22] colorless crystals from ether with mp 121–129° dec and nmr 7.5 (20 H, m) and 3.41 ppm (2 H, s). Pyrolysis in boiling xylene for 4.5 hr converted this orthothiooxalate to a dark red oil. A 2.94-g sample of this oil was chromatographed on a 4-ft alumina column and 33 fractions were collected. The first few fractions afforded 0.89 g of diphenyl disulfide and all subsequent fractions were colored, oily mixtures. Kugelrohr distillation of another sample of the pyrolyzed orthothiooxalate also gave diphenyl disulfide as the only pure and identifiable product.

1,3-Dithietane-2-thione (22). Hydrogen sulfide gas was bubbled into a cooled suspension of potassium *tert*-butoxide (7.43 g, 66 mmol) in dimethoxyethane (100 ml) for 15 min resulting in the formation of a grayish white precipitate. Carbon disulfide (5 g, 66 mmol) was added causing the color to change to orange. After stirring for 2 hr, the flask was immersed in a hot water bath to expel excess hydrogen sulfide. Methylene iodide (17.4 g, 66 mmol) was added dropwise during 30 min. The mixture was stirred at room temperature for 20 hr, then poured into cold water and extracted with methylene chloride. The combined extracts were dried and solvents evaporated. Fractional distillation of the residual yellow oil gave 9.65 g of recovered methylene iodide and 2.11 g (65% on

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(66) Melting points are uncorrected. Infrared spectra were recorded with Nujol mulls on a Perkin-Elmer 137 instrument, nmr spectra were recorded on a Varian A-60A instrument using deuteriochloroform as solvent and tetramethylsilane as internal standard, and mass spectra were recorded on an Atlas CH-5 instrument. The analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

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CH_2I_2 consumed) of compound **22**, bp 59° (0.05 mm). The product crystallized to give yellow plates: mp 47–48°; nmr 4.13 ppm (s); ir ν_{max} 1140, 1100, 850, and 830 cm^{-1}; mol wt, 122 (mass spectrum).

Anal. Calcd for $C_2H_2S_3$: C, 19.62; H, 1.63; S, 78.71. Found: C, 19.66; H, 1.54; S, 78.81.

1,4-Dithiane-2,3-dione Bis(ethylene thioketal) (25). 1,2-Ethanedithiol (35 g, 0.37 mol) was added to a solution of oxalyl chloride (15.8 g, 0.124 mol) in benzene (500 ml). The solution turned yellow and evolved hydrogen chloride. It was heated to reflux for 16 hr, then 100 mg of *p*-toluenesulfonic acid was added and reflux continued for 3 days while collecting water in a trap. The solution was kept at room temperature for 2 weeks and the crystals which formed were filtered and washed with cold benzene. Three additional crops of crystals were obtained by concentrating this filtrate; total yield 30.0 g (81%). Recrystallization from benzene afforded a sample with mp 210–213°; ir ν_{max} 1270, 1235, 1140, 870, 747, and 730 cm^{-1}; nmr 3.46 ppm (s);[68] mass spectrum *m/e* 300 (M^+), 272, 208, 149, and 137.

Anal. Calcd for $C_8H_{12}S_6$: C, 31.98; H, 4.02; S, 64.02. Found: C, 31.76; H, 4.02; S, 64.23.

2,2′-Bi(1,3-dithiolanylidene) (5). A mixture of compound **25** (20 g) in decalin (200 ml) was heated to reflux with stirring. After 60 hr, the brown solution was allowed to cool. The crystalline product (13.07 g, 96%) was filtered out and purified by recrystallization from methylene chloride giving pale yellow leaflets: mp 202–204° (lit.[31] mp 200–202°); ir ν_{max} 1400, 1260, 1225, 863, 836, and 756 cm^{-1}; nmr 3.49 ppm (s); mass spectrum *m/e* 208 (M^+), 148, 105, 104, and 76.

Oxidation of 1,4-Dithiane-2,3-dione Bis(ethylene thioketal). A mixture of compound **25** (500 mg) in glacial acetic acid (20 ml) and 30% aqueous hydrogen peroxide (5 ml) was heated on the steam bath until an exothermic reaction and gas evolution began. The temperature was kept slightly below the boiling point by intermittent cooling. The gas evolved was collected in a liquid nitrogen cooled trap and shown by vpc analysis[26] to be mainly ethylene. The solution was heated for 30 min on the steam bath and then concentrated to a syrup under reduced pressure. This syrup was taken up in ethanol and chilled giving 98 mg (35%) of compound **29**. Recrystallization from ethanol gave colorless needles: mp 204–206° (lit.[69] mp 204° and 210–211°); mol wt, 170 (mass spectrum). The infrared and nmr spectra (singlets at 4.00 and 4.95 ppm, ratio 2:1) were identical with those of an authentic sample prepared by oxidation of 1,3-dithiolane.

Oxidation of 2,2′-Bi(1,3-dithiolanylidene). A solution of compound **5** (100 mg) in glacial acetic acid (4 ml) was treated with 30% aqueous hydrogen peroxide (1 ml) and heated on the steam bath for 30 min. Evaporation under reduced pressure left a solid residue. This was triturated with ethanol, chilled, and filtered giving 26 mg (32%) of compound **29** as colorless needles, mp 204–207°. The infrared spectrum was identical with that of an authentic sample.

The preparation of compound **28** by oxidation of **5** with *m*-chloroperbenzoic acid in methylene chloride was attempted but was unsuccessful.

Condensation of 1,3-Propanedithiol with Oxalyl Chloride. Oxalyl chloride (25 g, 0.2 mol) in dry benzene (1900 ml) was treated with 1,3-propanedithiol (65 g, 0.6 mol). The solution turned pale yellow, became warm, and evolved HCl. It was heated under reflux for 2 weeks, then cooled, washed with aqueous sodium bicarbonate, dried, and concentrated to 150 ml. Crystals separated on standing in the cold. These were collected and washed with cold benzene giving 3.45 g (3.5%) of compound **33**. The filtrate contained (tlc) at least five products. The crystals were recrystallized from methylene chloride giving large colorless crystals with mp 242–244°; ir ν_{max} 1667, 1445, 1425, 1415, 1395, 1288, 1275, 1270, 1245, 1235, 1050, 1040, 995, 734, and 720 cm^{-1}, and an nmr spectrum with two broad multiplets centered at 2 and 3 ppm (areas 1:2).

Anal. Calcd for $C_{16}H_{24}O_2S_8$: C, 38.06; H, 4.79; S, 50.81; mol wt, 504. Found: C, 37.91; H, 4.73; S, 51.08; mol wt, 506.

The filtrate was concentrated to an oil, taken up in xylene (350 ml), treated with *p*-toluenesulfonic acid (0.5 g), and heated under reflux for 15 hr during which the solution turned black. Cooling this mixture gave a dark solid which was filtered out, and evaporation of the filtrate left a dark, viscous oil. These fractions were extracted separately with hot ethanol. The extracts gave a total of 1.20 g of tetrathioethylene **6**, identified by tlc comparison and its nmr spectrum. If the anticipated orthothiooxalate was formed, it may have decomposed to compound **6** under the condensation conditions. Compound **33** is fairly stable in boiling xylene containing *p*-toluenesulfonic acid.

DDQ Oxidation of 2,2′-Bi(1,3-dithiolanyl). Dihydrotetrathiafulvalene 7. A solution of 2,2′-bi(1,3-dithiolanyl)[70] (210 mg, 1 mnol) and DDQ (227 mg, 1 mmol) in dry toluene (10 ml) was heated to reflux for 1 hr. The solution was cooled and filtered through Celite, and the solid washed thoroughly with benzene. The filtrate and washings were washed with aqueous sodium carbonate solution, dried, and evaporated leaving 189 mg of solid residue. The crude product was shown by tlc to be a mixture of compounds **5**, **7**, and **26**. Recrystallization from methylene chloride–ethanol followed by vacuum sublimation afforded 140 mg (67%) of fairly pure **5** as pale yellow crystals. Alternatively the product mixture was chromatographed on a silica gel column eluting with benzene to give a pure sample of **5** with melting point and ir, nmr, and mass spectra all identical with those of a sample obtained by pyrolysis of orthothiooxalate **25**. The material eluted in the yellow bands of several such column chromatographs were combined and further purified by preparative tlc (silica gel–benzene) to give 29 mg of pure compound **7** as yellow crystals: mp 115°; nmr 3.47 (4 H, s), and 6.22 ppm (2 H, s); and mass spectrum *m/e* 206 (M^+) 178, 146, 102 (100%), and 76.

Oxidation of pure compound **5** with DDQ in boiling toluene produced a mixture of compounds **5** and **7**.

Acknowledgment. We are greatly indebted to Professor J. B. Stothers, University of Western Ontario, for the ^{13}C nmr spectrum of compound **25**.

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(68) The band width at half-height is 1.5 cps. This increased to 5.5 cps when the spectrum was recorded at −90° and to 7 cps when recorded in benzene solution.

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