

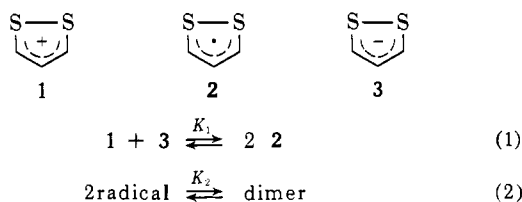
Electrochemistry of Organic Sulfur Compounds. V.^{1a} Radicals, Dimers, and 1,3-Dithioketones Derived from Cathodic Reduction of 3,5-Disubstituted 1,2-Dithiolylium Ions

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Abstract: Cathodic reduction of 3,5-diaryl-1,2-dithiolylium ions in acetonitrile or dichloromethane results in the formation of the corresponding 1,2-dithioly radicals which exist in equilibrium with their dimers. The equilibria involved have been investigated using variable-temperature voltammetry, coulometry, visible absorption spectrometry, and electron spin resonance spectrometry. The radical-dimer equilibria were found to be somewhat sensitive to electronic factors but more profoundly affected by the bulk of the 3,5 substituents. Regardless of the substitution, the equilibria lie far to the side of the dimer at -70° . One-electron reduction of the 1,2-dithioly radicals is accompanied by rapid ring opening and the formation of the corresponding 1,3-dithioketone anions which are stable in either dichloromethane or acetonitrile. Further reversible one-electron reduction of the 1,3-dithioketone anion producing the unstable dianion radical is observed at more cathodic potentials.

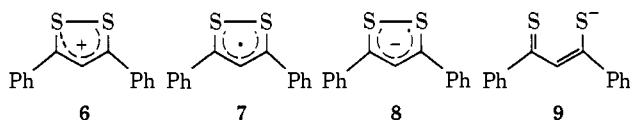
A recent theoretical study² predicted the stability of radicals (2) derived from the reduction of 1,2-dithiolylium ions (1). It was pointed out that in order to observe the radical, the equilibrium (eq 1) must be



favorable; *i.e.*, K_1 must be large. Other requirements for the observation of 2 are that it must be inert to the medium and equilibrium 2 must be such that measurable concentrations of 2 exist. Although the stability of the 1,2-dithioly radicals (2) was predicted,² their experimental observation had not been achieved. The observation of a number of 1,2-dithioly radicals in acetonitrile and their dimerization at low temperature were reported in a preliminary account of this work.¹ We now report the results of a detailed investigation of the cathodic reduction of 3,5-disubstituted 1,2-dithiolylium salts and the corresponding 1,2-dithioly radicals.

Results

Radical, Anion, Dianion, and Dimer from 3,5-Diphenyl-1,2-dithiolylium Ion. The solution equilibria set up as a consequence of the reduction of 6 are illustrated by the steady state cyclic voltammogram of Figure 1. In acetonitrile containing tetra-*n*-butylammonium tetrafluoroborate (0.2 M), 6 undergoes quasi-

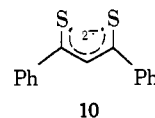


(1) (a) Part IV: C. Th. Pedersen, K. Bechgaard, and V. D. Parker, *J. Chem. Soc., Chem. Commun.*, 430 (1972); (b) University of Copenhagen; (c) Odense University.

(2) R. Zahradnik, P. Čárský, S. Hunig, G. Kresslich, and D. Scheut-zow, *Int. J. Sulfur Chem., Part C*, 109 (1971).

reversible one-electron reduction. The ratio of peak currents, i_{p_a}/i_{p_c} , is close to 1.0, and the peak separation, $E_{p_c} - E_{p_a}$, is equal to 60 mV. Thus the couple; R_1-O_1 , approaches electrochemical reversibility at a platinum electrode. Extension of the voltage scan to more negative values results in the observation of a second, irreversible peak, R_2 , and on the anodic going scan a new oxidation peak (O_2) is observed very close to the couple R_1-O_1 . Still another reversible redox couple, R_3-O_3 , is uncovered by scanning more negative. The stability and nature of the intermediates were demonstrated by exhaustive coulometric reduction followed by voltammetric and spectral analysis. The product formed at R_1 is the corresponding radical which was obtained quantitatively by reduction at a platinum electrode accompanied by the consumption of precisely 1.0 faraday/mol. The radical 7 is deep green in solution with visible maxima at 400 and 650 nm. The esr spectrum of 7 is discussed below. The steady-state cyclic voltammogram of 7 in acetonitrile was identical with that of 6, showing R_1 , O_1 , R_2 , O_2 , R_3 , and O_3 , which indicates that no irreversible chemical reactions take place during reduction.

Coulometric reduction of 7 gave a deep red colored solution (λ_{max} 483 nm) and required 1.0 faraday/mol. The steady-state cyclic voltammogram showed all the features of that of 6 and 7. Coulometric oxidation of the resulting solution yielded successively 7 (after 1.0 electron (e)) and 6 (after 2.0 e) which provides definitive evidence for both the stability of the reduction product of 7 and the complete chemical reversibility of the couples R_1-O_1 and R_2-O_2 . The structure of the reduction product is discussed later. Further one-electron reduction resulted in destruction of the system, indicating that the reduction product, presumably the dianion radical 10, although stable during the time scale of cyclic voltammetry, is short lived. The voltam-



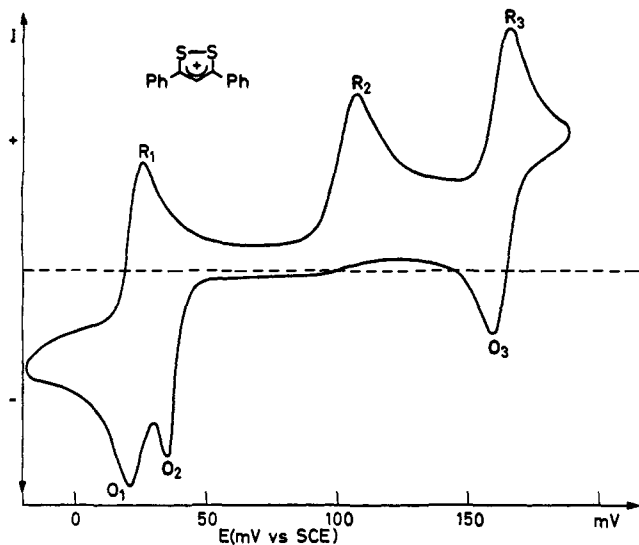


Figure 1. Steady-state cyclic voltammogram of **6** in CH_3CN containing Bu_4NBF_4 (0.2 M), sweep rate = 300 mV/sec. The initial scan shows all the peaks present in the steady-state voltammogram.

metry of **6** in dichloromethane is essentially the same as in acetonitrile with the exception that $\text{R}_3\text{-O}_3$, being beyond the cathodic limit of the solvent, is not observed. One-electron coulometry was observed during reduction of **6** to **7**.

On cooling a dichloromethane solution of **7** to -80° , the esr spectrum completely disappeared and on warming reappeared showing the same temperature dependence as on the cooling cycle, a phenomenon consistent with a reversible monomer-dimer equilibrium. Further support for the rapid formation of the dimer at low temperature was found on examining the cyclic voltammetry of the reduction of **6** in dichloromethane at -70° . Under these conditions, the reduction was completely irreversible with no oxidation peak for the radical being observed.

The equilibrium constant for dissociation of the dimer was determined quantitatively from the uv-visible spectra in dichloromethane, and values as a function of temperature are given in Table I.³ From a plot of log

Table I. Temperature Dependence of the Equilibrium Constant, $K^{a,b}$

Temp, °C	dimer \xrightleftharpoons{K} 2monomer						
	21	7					
	+25	+20	+15	+10	+5	0	-5
$K(M) \times 10^6$	57	37	25	16	9.7	5.7	3.2

^a Total concentration, $2(\mathbf{21}) + (\mathbf{7})$ was 1.0×10^{-3} M. ^b Measured in dichloromethane containing $n\text{-Bu}_4\text{NBF}_4$ (0.2 M).

K vs. $1/T$, an enthalpy of cleavage of 16.0 kcal/mol was estimated and the entropy at 0° was calculated to be equal to 38.9 cal/(deg mol).

At 25° in either acetonitrile or dichloromethane, the ratio of peak currents (i_{pa}/i_{pc}) observed during cyclic voltammetry for reduction of **6** and reoxidation of **7** was found to be very close to 1.0. Yet, at this temperature only about 40% of the reduced species is in form of the

(3) The radical, **7**, exhibits an absorption maximum at 650 nm ($\epsilon = 2.7 \times 10^4$) in dichloromethane.

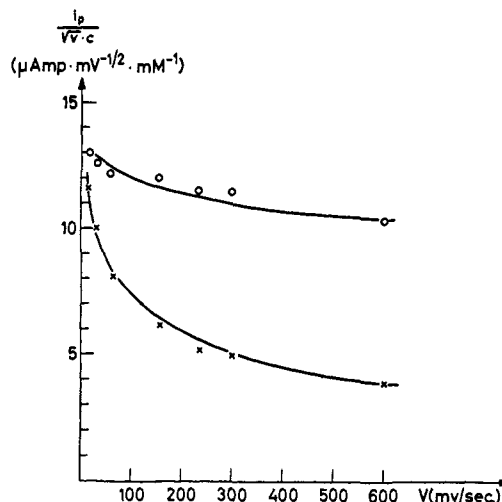
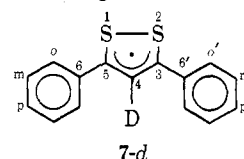


Figure 2. Current functions of **6** and **7** in CH_3CN at -31° , **6** (O), **7** (X).

radical (Table I), the remainder being the dimer. The latter can only be due to rapid dissociation of the dimer as the radical is being consumed by oxidation at the electrode. The dissociation must be very rapid since we were unable to appreciably diminish the oxidation current for the radical by going to very rapid sweep rates (30 V/sec) during cyclic voltammetry at room temperature. However, at -31° the dissociation is sufficiently slow to allow differences in the ratio of anodic to cathodic currents to be observed as a function of voltage sweep rate at moderate sweep rates.⁴ The current function,⁵ for reduction of **6** and oxidation of **7**, is plotted vs. the voltage sweep rate in Figure 2.

Esr Spectra Data. The low-field halves of the esr spectra of **7** and **7-d**, together with the corresponding



simulated spectra are shown in Figure 3. Spin density calculations using the McLachlan perturbation procedure⁶ were performed in order to assign the proton hyperfine coupling constants, which were tested by computer simulation of the spectra. The results are summarized in Table II.

The following parameters were used in HMO and McLachlan calculations of spin densities. $\alpha_s = \alpha_s + 1.2\beta_{CC}$ and $\beta_{CS} = 0.65\beta_{CC}$. These parameters have been shown to give good results in various sulfur-containing compounds.⁷ The resonance integral β_{SS} was assigned the "reasonable" value $0.7\beta_{CC}$ which reproduced the experimentally determined spin densities very nicely. Q in the McConnell relation was taken as -27 G which appears to give valid results for neutral radicals.⁸ The

(4) A detailed study of the kinetics of dissociation and dimerization using the changes occurring in the voltammetric peaks, shapes, and potentials, as a function of temperature and voltage sweep rate, is under way.

(5) R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).

(6) A. D. McLachlan, *Mol. Phys.*, **3**, 233 (1960).

(7) (a) P. D. Sullivan, *J. Amer. Chem. Soc.*, **90**, 3618 (1968); (b) I. Degani, L. Lunazzi, A. Manginini, G. Pedulli, and C. Vincenzi, *Mol. Phys.*, **18**, 613 (1970).

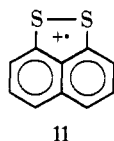
(8) F. Gerson and J. H. Hammons in "Nonbenzenoid Aromatics," Vol. II, J. P. Snyder, Ed., Academic Press, New York, N. Y., 1971, p 81.

Table II. Parameters of the ESR Spectra of 7 and 7-d

Center μ	HMO c_{μ}^2	McLachlan (λ 1.1)	a_{H} , G ^{a,b}	$ a_{\text{H}} $ exptl, G
1,2	0.128	0.124		
3,5	0.190	0.242		
4	0.000	-0.073	1.97, $a_{\text{D}} = 0.30$	1.92, $a_{\text{D}} = 0.296$
6,6'	0.011	-0.012		
<i>o,o,o',o'</i>	0.054	0.075	-2.02	1.92-1.96
<i>m,m,m',m'</i>	0.001	0.024	-0.65	0.68
<i>p,p'</i>	0.059	0.081	-2.18	2.10

^a $Q = -27$ G. ^b $a_{\text{D}} = a_{\text{H}}(78/508)$.

parameters were further tested by calculation of McLachlan spin densities of another radical (11) containing



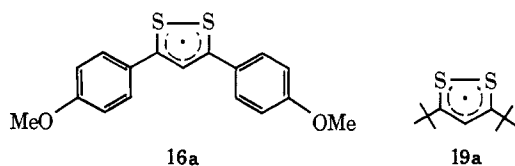
the disulfide linkage, the cation radical spectrum of which has been reported⁹ and excellent agreement was found.

The isotropic g values of 7 and 7-d were found to be equal to 2.003, very close to the spin only value of 2.0023. One might expect to find larger deviations in sulfur containing radicals due to spin-orbit coupling^{10,11} but the relatively small spin density on sulfur (0.124×2) found in the calculations support the experimental findings. The small differences between the simulated and experimental spectra may be due to line-width variations found in the experimental spectra which are not reflected in the computer simulation.

The esr spectrum of the *tert*-butyl substituted radical (19a) showed a proton hyperfine splitting equal to 1.9 G. The spin density in the 3 and 5 positions was calculated to be equal to 0.46 (as compared with 0.24 for 7).

Voltammetry of 3,5-Disubstituted 1,2-Dithiolium Ions. Voltammetric studies were carried out on a variety of 1,2-dithiolium salts in both dichloromethane (Table III) and in acetonitrile (Table IV). Peak potentials and potential differences (ΔE) between successive reduction steps are tabulated.

Equilibrium Data for the Dissociation of the Dimers of 16a and 19a. The equilibrium constant for dissociation



of the dimer of 16a was calculated from changes in the visible absorption spectrum as a function of the total concentration, $2[\text{radical}] + [\text{dimer}]$, and ΔH was determined from the temperature dependence of K . For 19a, the corresponding parameters were obtained in similar fashion from the intensity of the esr signal. The equilibrium constants at 25° along with other

(9) (a) A. Zweig and A. K. Hoffman, *J. Org. Chem.*, **30**, 3997 (1965); (b) B. I. Stephanow, W. Ya. Radinow, A. Ya. Zheltov, and V. V. Orlov, *Tetrahedron Lett.*, 1071 (1971).

(10) H. M. McConnell and R. E. Robertson, *J. Phys. Chem.*, **61**, 1018 (1957).

(11) A. J. Stone, *Mol. Phys.*, **6**, 609 (1963); **7**, 311 (1964).

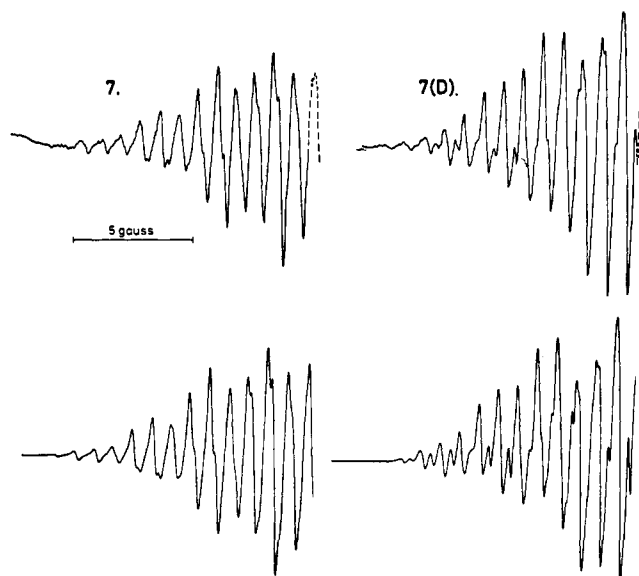


Figure 3. Experimental (upper) and simulated esr spectra of 7 and 7-d.

Table III. Voltammetry of 1,2-Dithiolium Salts in Dichloromethane^{a,b}

Structure	R ₁	R ₂	$E_{\text{P}1\text{c}}$	$E_{\text{P}1\text{a}}$	$E_{\text{P}2\text{c}}$	ΔE
6	Ph	Ph	-0.17	-0.10	-1.14	0.97
12	Ph	<i>p</i> -An ^c	-0.24	-0.17	-0.96	0.72
13	Ph	<i>p</i> -Tol ^c	-0.20	-0.13	-1.25	1.05
14	Ph	<i>p</i> -BrPh ^c	-0.13	-0.07	-1.10	0.97
15	Ph	Me	-0.26			
16	<i>p</i> -An	<i>p</i> -An	-0.30	-0.23	-1.01	0.71
17	<i>p</i> -An	<i>p</i> -DMAPh ^c	-0.46	-0.38	-1.04	0.58
18	<i>p</i> -Tol	<i>p</i> -Tol	-0.23	-0.17	-1.28	1.05
19	<i>t</i> -Bu	<i>t</i> -Bu	-0.64	-0.51		
20	Me	Me	-0.53			

^a Supporting electrolyte *n*-Bu₄NBF₄ (0.2 M), voltage scan rate 150 mV/sec. ^b Volts vs. sce. ^c *p*-An = *p*-anisyl, *p*-Tol = *p*-tolyl, *p*-BrPh = *p*-bromophenyl, *p*-DMAPh = *p*-dimethylaminophenyl.

Table IV. Voltammetry of 1,2-Dithiolium Salts in Acetonitrile^{a,b}

Structure	$E_{\text{P}1\text{c}}$	$E_{\text{P}1\text{a}}$	$E_{\text{P}2\text{c}}$	$E_{\text{P}2\text{a}}$	$E_{\text{P}3\text{c}}$	$E_{\text{P}3\text{a}}$	ΔE_{2-1}	ΔE_{3-2}
6	-0.27	-0.20	-1.07	-0.35	-1.75	-1.65	0.80	0.68
12	-0.32	-0.26	-1.15	-0.42	-1.72	-1.64	0.83	0.57
13	-0.30	-0.22	-1.19	-0.40	-1.73	-1.63	0.89	0.54
14	-0.19	-0.13	-0.94	-0.30	-1.55	-1.47	0.75	0.61
16	-0.38	-0.32	-1.27	-0.45	-1.73	-1.65	0.89	0.46
19	-0.64	-0.58						

^a Supporting electrolyte, *n*-Bu₄NBF₄ (0.1 M); voltage scan rate, 150 mV/sec. ^b Volts vs. sce.

thermodynamic parameters for 16a, 19a, and for comparison 7, are tabulated in Table V.

Discussion

The results of the voltammetric, coulometric, and spectral studies of the reduction of 3,5-disubstituted 1,2-dithiolium salts in acetonitrile and dichloromethane clearly show that the substrates undergo one-electron reduction to produce the corresponding radicals. The radicals are highly reactive and very sensitive

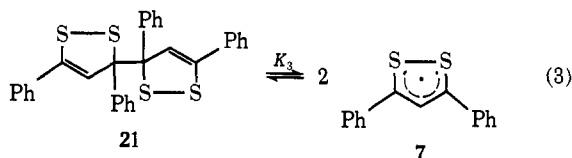
Table V. Thermodynamic Parameters for Dissociation of Dimers in Dichloromethane

Structure	K , mol/l.	ΔH , kcal/mol	ΔS , eu
16a	5.5×10^{-6} ^a	10.4	20
19a	8.2×10^{-2} ^{a,b}	13.4	40
7	5.7×10^{-4} ^{a,c}	16.0	39.8

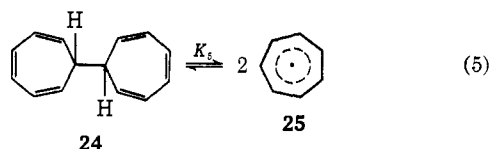
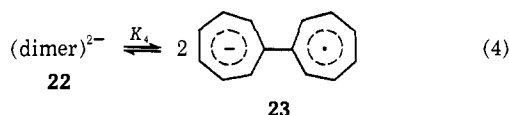
^a Value at 25°. ^b Extrapolated from values obtained at lower temperature. ^c Solvent contained *n*-Bu₄NBF₄.

to oxygen and solvent impurities but are stable in carefully purified solvents when protected from the atmosphere.

The monomer-dimer equilibria are apparently very rapidly established and for the 3,5-diphenyl compound (6) the monomer is favored at room temperature. It is of interest to compare the equilibrium constant for cleavage of the dimer (21) with that of related cases;



the cleavage of bi-2,4,6-cycloheptatrien-1-yl to form cycloheptatrienyl radical and the dissociation of the heptafulvalene anion radical dimer.¹² The equilibrium constant for dissociation of the heptafulvalene anion radical dimer (22) is equal to about 10^{-7} at 66°¹⁵ while that for bi-2,4,6-cycloheptatrien-1-yl (24)¹⁶ extrapolated from 133 to 66° is of the order of 10^{-16} . The equilibrium constant for reaction 3 is 5.7×10^{-4} at 25° with an enthalpy of cleavage of 16 kcal/mol (Table I) and entropy of 38.9 cal/(deg mol) which gives an equilibrium constant of 1.5×10^{-2} at 66°. Thus, K for the cleavage of 21 is about 5 and 14 orders of magnitude greater than that for 22 and 24, respectively. While the



repulsion of like charges in 22 could account for the great difference between the ease of cleavage of it and 24, other factors must be responsible for the much more facile dissociation of 21. Clearly, a deciding factor must be the steric interaction between the phenyl groups attached at the positions of ring juncture. This is strongly supported by the fact that the 3,3',4,4'-phenyl substituted dimer (26), formed by cathodic reduction of the

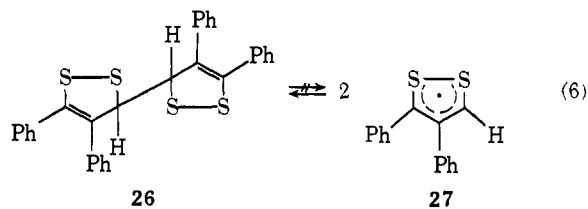
(12) It is probably not appropriate to describe the latter as a cleavage reaction since the nature of the bonding in ion radical dimers is not known with certainty, although the occurrence of charge transfer type association rather than covalent bonding has been implicated. Related cases are the tetracyanoquinodimethane anion radical¹³ and the cation radicals of perylene and tetracene.¹⁴

(13) R. H. Boyd and W. D. Phillips, *J. Chem. Phys.*, **43**, 2927 (1965).

(14) K. Kimura, T. Yamazaki, and S. Katsumata, *J. Phys. Chem.*, **75**, 1768 (1971).

(15) M. D. Sevilla, S. H. Flajser, G. Vincow, and H. J. Dauben, Jr., *J. Amer. Chem. Soc.*, **91**, 4139 (1969).

(16) W. V. Volland, Ph.D. Thesis, University of Washington, 1965.



corresponding 1,2-dithiolium salt,¹⁷ shows no tendency to dissociate upon heating. That the dimer of 3-phenyl-5-methyl-1,2-dithiolium ion (15) behaves nearly identical with 26 shows that methyl is not sufficiently bulky to provide driving force for the dissociation reaction.

A qualitative assessment of the effect of steric *vs.* electronic factors in determining the position of the monomer-dimer equilibria can be gained from the voltammetric data. The peak current for the reduction of the 1,2-dithiolium ion is a measure of the total concentration of species produced (radical + dimer) while the reduction peak for the radical should reflect only the concentration of free radical.¹⁸ Thus equilibrium constants based on the reduction currents R_1 and R_2 (Figure 1) obtained in dichloromethane at room temperature were calculated and the relative values referred to eq 3 as the standard reaction are summarized in Table VI.

Table VI. Estimate of Relative Equilibrium Constants for Dimer Dissociation in Dichloromethane at Room Temperature

Compd	(Monomer) ^a $\times 10^{-3}$ M	(Dimer) ^a $\times 10^{-3}$ M	K_x/K_3^b
16 (<i>p</i> -An, <i>p</i> -An)	0.38	0.43	0.06
12 (<i>p</i> -An, Ph)	0.51	0.37	0.13
17 (<i>p</i> -An, <i>p</i> -DMAPh)	0.65	0.30	0.26
18 (<i>p</i> -Tol, <i>p</i> -Tol)	0.80	0.22	0.54
13 (<i>p</i> -Tol, Ph)	0.81	0.22	0.55
6 (Ph, Ph)	0.93	0.16	1.0
14 (<i>p</i> -BrPh, Ph)	0.94	0.15	1.1

^a Estimated from peak currents during sweep voltammetry at 150 mV/sec. Substrate concentration = 1.25×10^{-3} M. ^b Equilibrium constant for the compound divided by K for reaction 3.

The validity of the qualitative data (Table VI) as a measure of the equilibrium constants for dissociation is supported by the more quantitative data (Table V) for radicals 16a and 7. The voltammetric data predict that K for 7 should exceed that for 16a by a factor of about 17 while the actual K ratio was found to be 10, which is not in serious disagreement.

The thermodynamic data in Table V deserves further comment. The equilibrium constant for dissociation of the dimer of 19a is about 10^2 as great as the corresponding value for 7, and in keeping with the latter, the ΔH value was found to be about 2.6 kcal/mol less for 19a while ΔS was 40 eu for both reactions. Considering only ΔH (10.4 kcal/mol) for the dissociation of the dimer of 16a, one might predict K for this case to be of

(17) C. Th. Pedersen and V. D. Parker, *Tetrahedron Lett.*, 767 (1972).

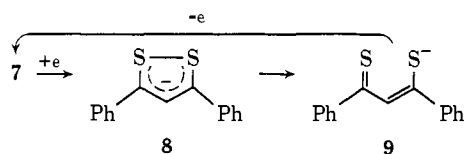
(18) It was expected that quantitative data could be obtained for the equilibria from analysis of these two quantities but apparently, kinetic factors (rapid dissociation of the dimer) bring about increased current at R_2 thus giving too large an estimate of the radical concentration. Nevertheless, the analysis is useful in that it gives a rough estimate of the relative concentrations of monomer and dimer. The kinetic character of the voltammetric peaks for 6 is clearly shown by the current functions (Figure 2).

the order of 10^4 times as great as that of the reaction involving **7**. Yet, K for dissociation of the dimer of **16a** was found to be 10^{-1} times that for **7**. Thus, the low value of the entropy change (20 eu) gives rise to a greatly decreased value for the equilibrium constant.

With regards to the relative importance of steric and electronic factors in controlling the position of the dimer–monomer equilibrium, we can be somewhat less speculative. Since ΔS for the dimers of **7** and **19a** is the same, the difference in position of equilibrium is directly proportional to the strength of the bond holding the monomeric units together. Thus, the much lower value for **19a** indicates that steric repulsion of the *tert*-butyl groups overwhelms any gain in stabilization by the phenyl groups on the radicals thus showing that steric factors are of primary importance. This is further indicated by the fact that **15**, with one phenyl and one methyl group, gives a very short-lived radical which cannot be detected by cyclic voltammetry during reduction of **15**. The same can be said for the dimethyl compound (**20**).

The values of the first reduction potentials (E_{p1c}) for the dithioliyl salts in either dichloromethane or acetonitrile (Tables III and IV) fall in the expected order. The alkyl derivatives, **19** and **20**, are the most difficult to reduce. In the diaryl series, the salt with the strongest electron-donating substituents, **17**, is the most difficultly reduced, while **14** with electron-withdrawing *p*-Br is slightly easier to reduce than **6**. No trend is found in the potentials for the second reduction step which is not surprising since the occurrence of the rapid followup reaction gives rise to a potential reflecting both kinetic and thermodynamic factor.

In contrast to the quasi-reversible redox couple, 1,2-dithioliyl ion–1,2-dithioly radical, addition of an electron to the 1,2-dithioly radicals to give the anions is totally irreversible. The peak separation, $E_{p2c} - E_{p2a}$, ranges from 640 to 820 mV (Table IV) which is indicative either of a slow charge transfer¹⁹ or that the initial reduction product (for example, **8**) undergoes a



chemical reaction. The latter turns out to be the case. One-electron reduction of **7** in acetonitrile was accompanied by the formation of a deep red colored solution showing a visible absorption maximum at 483 nm (ϵ 25,000). The reduction product was assigned structure **9** on the basis of comparing the spectrum (Figure 4) to the known spectra of the nickel²⁰ and the zinc²¹ chelates of dithiodibenzoylmethane which show the characteristic dithioketonate band at 480 nm (ϵ 23,000). The origin of this band is tentatively assigned to a π - π transition. Although transition metal salts of 1,3-dithioketones have been reported to be stable in several cases,^{20,22} previous attempts to prepare uncomplexed 1,3-dithioketonate ions have not been success-

(19) R. S. Nicholson, *Anal. Chem.*, **37**, 1351 (1965).

(20) A. Ouchi, M. Nakatani, and Y. Takahashi, *Bull. Chem. Soc. Jap.*, **41**, 2044 (1968).

(21) K. Bechgaard and V. D. Parker, unpublished work.

(22) R. L. Martin and I. M. Stewart, *Nature (London)*, **210**, 522 (1966).

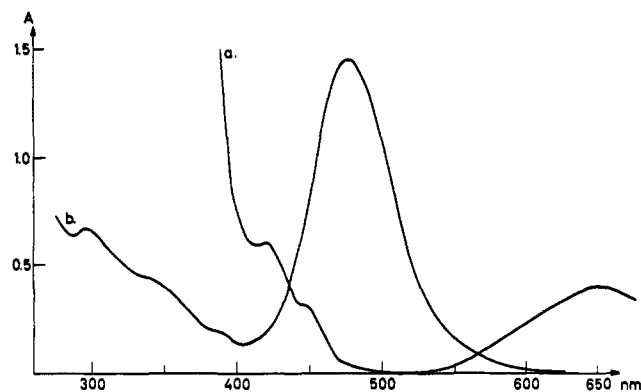
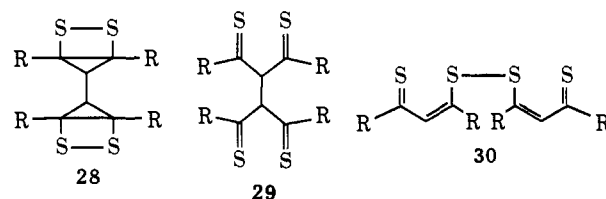


Figure 4. (a) Visible spectrum of **7** + dimer (total concentration 3.3×10^{-4} M) in CH_3CN containing Bu_4NBF_4 (0.1 M). (b) Uv and visible spectrum of **9** (total concentration 5.6×10^{-5} M) in CH_3CN containing Bu_4NBF_4 (0.1 M).

ful. This is generally attributed to the extreme sensitivity of the ions toward oxygen and moisture. Thus, our observation of stable solutions of **9** is to our knowledge the first case of an uncomplexed 1,3-dithioketonate anion. The 1,3-dithioketonate anion (**9**) is oxidized stepwise first to the radical (**7**) and then to the 1,2-dithioliyl ion (**6**). The anion (**8**) must be very short lived since we failed to observe any reversibility during cyclic voltammetry of **7** at very rapid scan rates.

Voltammetry of solutions of **9** or of the 1,2-dithioliyl salts in acetonitrile (Table IV) show that the 1,3-dithioketonate anions are reversibly reduced (couple $\text{R}_3\text{-O}_3$, Figure 1) to the corresponding dianion radicals (**10** for the diphenyl case). Coulometric reduction of **9** showed that 1.0 faraday/mol was consumed; however, the product was not stable under the conditions employed. A similar example is known in the analogous oxygen series. The sodium salt of dibenzoylmethane has been reduced to the dianion radical by both electrochemical and chemical means.²³

In addition to **21**, three other symmetrical structures were considered for the dimers. If bonding were to occur through the 4 positions, a dimer containing two cyclopropane rings would result (**28**), which could conceivably undergo ring opening to **29**. Alternatively, ring opening could occur before bond formation accompanied by the formation of **29** or the disulfide linked dimer, **30**. There are also nine possible unsymmetrical structures involving the units of **21**, **28**, **29**, and **30**. Structures containing the thioketone linkage (**29**, **30**, and unsymmetrical combinations) were ruled out since solutions of the dimers are colorless while known aromatic thioketones are highly colored.²⁴ Structures containing the cyclopropane rings (*i.e.*, **28**) cannot be ruled



out but are unfavorable compared to **21**. It should be

(23) N. L. Bauld and M. S. Brown, *J. Amer. Chem. Soc.*, **89**, 5413 (1967).

(24) E. Campaigne in "Chemistry of the Carbonyl Group," S. Patai, Ed., Interscience, New York, N. Y., 1966, p 936.

Table VII. Analytical and Nmr Data for New 1,2-Dithiolylium Salts

R ¹	R ²	R ³	Found, %			Formulas	Calcd, %			Mp, °C	¹ H nmr ^a
			C	H	S		C	H	S		
C ₆ H ₅	D	C ₆ H ₅	50.71	3.21	17.98	C ₁₅ H ₁₀ DClO ₄ S	50.69	3.12	18.03	242	7.45–8.2 m
C ₆ H ₅	H	4-Br-C ₆ H ₄	41.55	2.31	14.74	C ₁₅ H ₁₀ BrClO ₄ S	41.53	2.32	14.78		7.53–8.16 m (9 H) R ¹ + R ³ ; 8.94 s (1 H), H-4
C ₆ H ₅	H	4-CH ₃ -C ₆ H ₄	52.00	3.57	17.22	C ₁₅ H ₁₁ ClO ₄ S	52.10	3.55	17.38	176	2.42 s (3 H, CH ₃), 7.41 and 7.9 q (4 H, J = 9 cps, R ¹), 7.55–8.2 m (5 H, R ³), 8.83 s (1 H, H-4)
4-CH ₃ -C ₆ H ₄	H	4-CH ₃ -C ₆ H ₄	53.40	3.94	16.62	C ₁₇ H ₁₁ ClO ₄ S ₂	53.35	3.95	16.73	230	2.42 s (6 H, CH ₃), 7.41 and 7.91 q (J = 9 cps, 18 H, R ¹ + R ³), 8.73 s (1 H, H-4)
<i>t</i> -C ₄ H ₉	H	<i>t</i> -C ₄ H ₉	42.07	6.19	19.83	C ₁₁ H ₁₅ ClO ₄ S ₂	41.96	6.08	20.38	<i>b</i>	1.62 s (18 H), 8.35 s (1 H)

^a ¹H nmr spectra were obtained from ca. 5% solutions in acetonitrile-*d*₃. ^b Decomposes over a wide temperature range.

pointed out that the spin densities of the radicals are highest in the 3,5 positions and lowest in the 4 positions (Table II) which is a strong argument against bond formation in that position. Thus, the most reasonable structures for the dimers are those bonded through the 3 and 5 positions as in 21.

Experimental Section

Reagent grade acetonitrile and dichloromethane were purified by passing through neutral alumina (Woelm W-200) immediately before use. Equipment and techniques used for voltammetry and coulometry have been described.^{25,26} The reference electrode was a saturated aqueous calomel electrode separated from the electrolysis solution by a salt bridge containing acetonitrile and Bu₄

NBF₄ (0.2 M). The working electrode for voltammetry was a Beckman platinum button and for coulometry a platinum gauze was used.

3,5-Diaryl-substituted 1,2-dithiolylium salts were prepared by a modification of the method of Duguay and Quiniou.²⁷ Instead of the hazardous extraction of the reaction mixtures from β-diketones and phosphorus pentasulfide with perchloric acid in acetic acid, the chlorides were first prepared by extracting with boiling 4 N hydrochloric acid. The chlorides were then transformed to the perchlorates in the cold.

3-Monoalkyl- and 3,5-dialkyl-substituted 1,2-dithiolylium salts were prepared according to the method of Hartman, *et al.*²⁸ All compounds gave satisfactory elemental analyses. Analytical and ¹H nmr data for new 1,2-dithiolylium salts are summarized in Table VII.

(25) O. Hammerich and V. D. Parker, *J. Chem. Soc., Perkin Trans. 1*, 1718 (1972).

(26) V. D. Parker, *Acta Chem. Scand.*, **24**, 2768 (1970).

(27) G. Duguay and H. Quiniou, *Bull. Soc. Chim. Fr.*, 1918 (1970).

(28) H. Hartman, K. Fabian, B. Bartho, and J. Faust, *J. Prakt. Chem.*, **312**, 1197 (1970).