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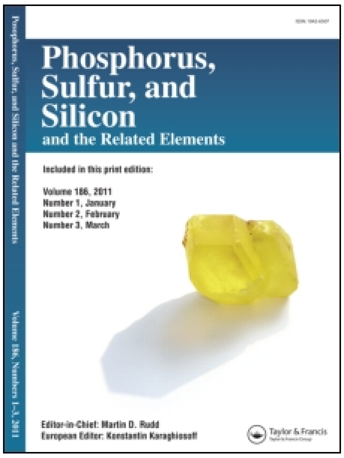

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RADICAL IONS 56[1,2] ONE-ELECTRON OXIDATION OF 1,2-DITHIETE DERIVATIVES

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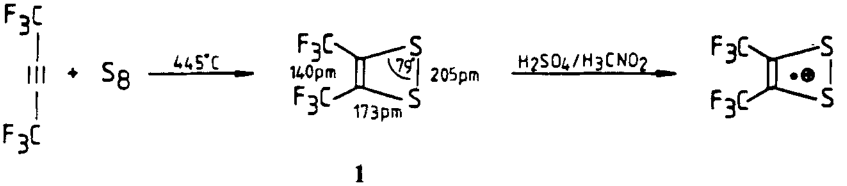
Novel 1,2-dithiete derivatives $R_2C_2S_2$ with R = —$C(CH_3)_3$ and —$C(CH_3)_2$—CH_2—CH_2—CH_2—$C(CH_3)_2$— are readily oxidized by the one-electron transfer system $AlCl_3/H_2CCl_2$ to their radical cations. The single line ESR spectra, on high amplification, exhibit ^{33}S satellites in natural abundance. Both the ESR data, i.e. rather large *g* values and ^{33}S hyperfine coupling constants as well as MNDO closed and open shell calculations for the parent molecule $H_2C_2S_2$ illustrate that spin and positive charge are predominantly located in the SS bridge of the four-membered ring.

Neuartige 1,2-Dithiet-Derivate $R_2C_2S_2$ mit R = —$C(CH_3)_3$ und —$C(CH_3)_2$—CH_2—CH_2—CH_2—$C(CH_3)_2$— werden durch das Einelektronentransfer-System $AlCl_3/H_2CCl_2$ rasch oxidiert. Die Einlinien-ESR-Spektren zeigen bei Randlinien-Verstärkung ^{33}S-Satelliten in natürlicher Häufigkeit. Sowohl die ESR-Daten, d.h. die relativ großen g-Faktoren und ^{33}S-Hyperfeinkopplungskonstanten als auch MNDO closed und open shell-Berechnungen für den Grundkörper $H_2C_2S_2$ belegen, daß Spin und positive Ladung überwiegend in der SS-Brücke des Vierrings lokalisiert sind.

An ESR study of the sulfur-catalyzed Friedel/Crafts dichlorination of benzene revealed benzo-1,2-dithiete radical cation as a possible intermediate.[3] In order to gain more insight into this complex electron transfer system, other isolable 1,2-dithiete derivatives and other disulfides[4,5] were investigated.

The first stable molecule containing an unsaturated four-membered ring, 3,4-bis(trifluoromethyl)-1,2-dithiete, has been synthesized 1960 by reacting hexafluorobutyne-2 with boiling sulfur:[6]



1

(1)

Its structure, as determined by electron diffraction in the gasphase,[7] unexpectedly shows[8] a normal SS bond length. The first vertical ionization energy, $IE_1^v = 10.2$ eV,[2,9] is quite high for a disulfide and allows one to rationalize, why a powerful oxidizing agent like H_2SO_4 in H_3CNO_2 has been used to generate the radical cation.[10]

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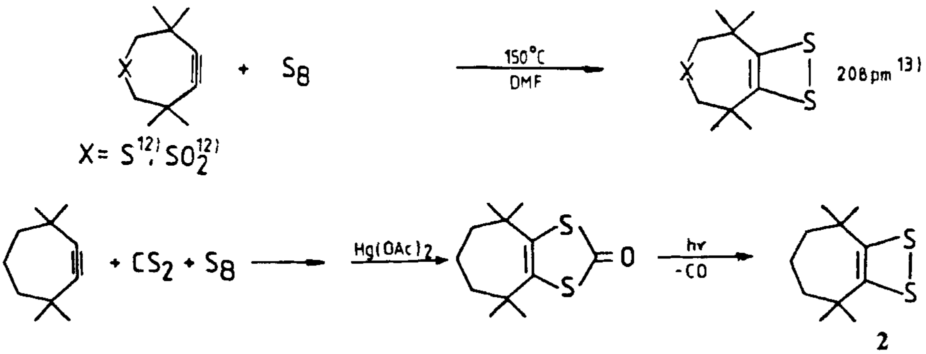
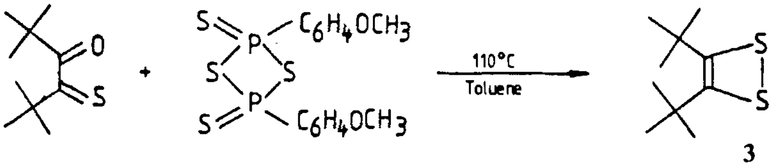
A second stable dithiete derivative, 3β-acetoxy-6,7-epidithio-19-norlanosta-5,7,9,11-tetraene, has been synthesized in 1976 by photochemical extrusion of ethylene from an 1,4-dithiane ring;[11] its X-ray structure discloses an elongated SS bond length of 212 pm.[11]

Since then, new synthetic routes using strained acetylenes[12,13] or Lawesson's reagent[14] have made possible the preparation of alkyl-substituted 1,2-dithiete derivatives:

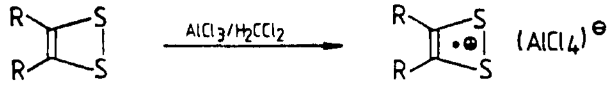


(2)



(3)

2 and 3 exhibit both a rather low first vertical ionization potential, $IE_1^{\mathrm{v}} = \sim 7.95$ eV,[9] and, therefore, are expected to form radical cations by one-electron transfer to the selective, oxygen-free oxidizing system $AlCl_3/H_2CCl_2$:[15]



(4)

The ESR spectra (cf. Experimental Part) of 3′,3′,7′,7′-tetramethylcyclohepteno [1′,2′-c]-1,2-dithiete radical cation **2**$^{\cdot\oplus}$ (Figure 1) and of 3,4-di-tert.butyl-1,2-dithiete radical cation **3**$^{\cdot\oplus}$ (Figure 2) expectedly exhibit only a single signal for the spin-flip of the odd electron. All hyperfine splittings due to the nearest hydrogens, which are in γ positions to the four-membered ring, therefore, must be smaller than the respective ESR signal half-widths subdivided by the multiplet caused by the equivalent ^{1}H nuclei, i.e. for the tetramethylcyclo-hepteno-1.2-dithiete radical cation smaller than 0.1 mT : 13 = 0.007 mT (Figure 1) or for the di(tert.butyl) substituted one smaller than 0.1 mT : 19 = 0.005 mT (Figure 2). On hundred-fold amplification, ^{33}S satellites in natural abundance of only 0.76% begin to appear. Due to the nuclear magnetic moment of the ^{33}S isotope, $I = 3/2$, a quartet is expected. For both dialkyl-1,2-dithiete radical cations, 2 signals are recorded on the low-field side due to the rather narrow ESR central line (Figure 2), the high-field half being obscured by

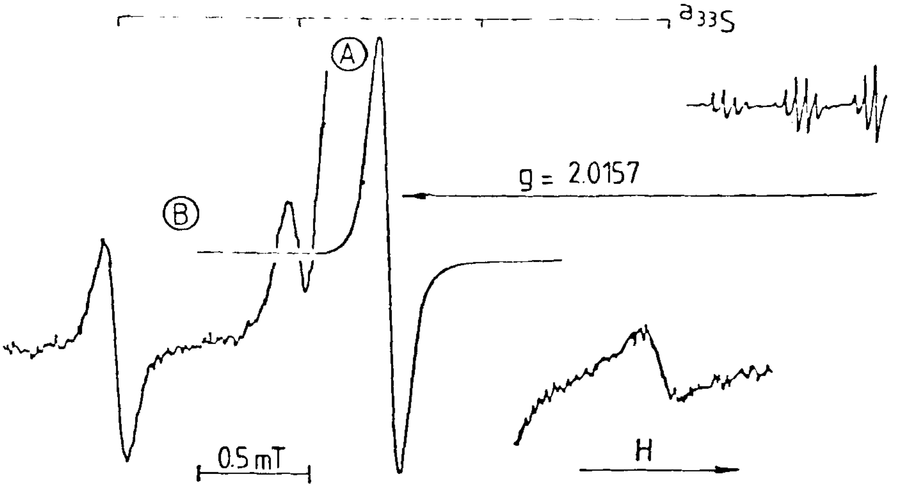


FIGURE 1 ESR spectrum of 3′,3′,7′,7′-tetramethylcyclohepteno[1′,2′-c]-1,2-dithiete radical cation Ⓐ together with the ^{33}S satellites recorded on 100-fold amplification Ⓑ.

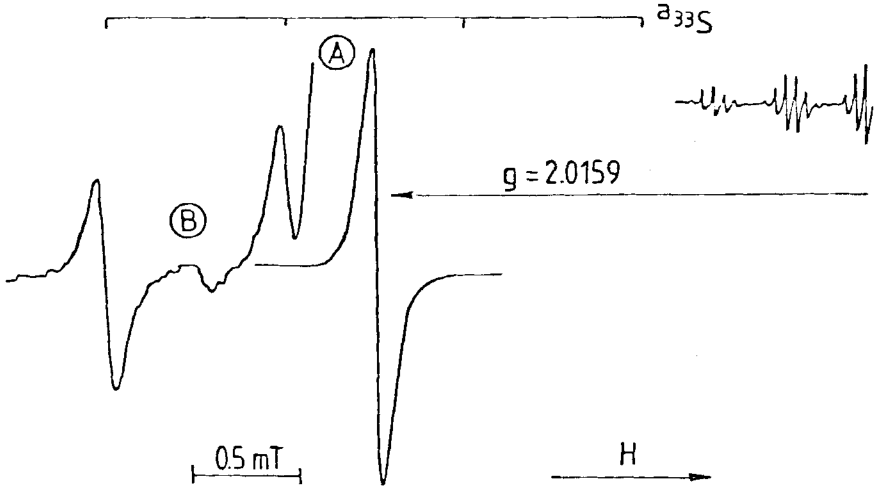
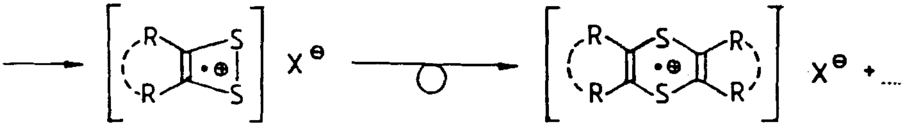


FIGURE 2 ESR spectrum of 3,4-di(tert.butyl)-1,2-dithiete radical cation Ⓐ together with the ^{33}S satellites recorded on 100-fold amplification Ⓑ.

signals of some other, presumably subsequently formed paramagnetic species like the corresponding 1,4-dithiine radical cations repeatedly detected by ESR in solutions of oxidized sulfur compounds:[2-5,10,16]



(5)

In case of the tetramethylcyclohepteno-1,2-dithiete radical cation $\mathbf{2}^{\cdot\oplus}$, the outer ^{33}S

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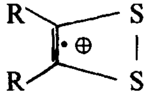
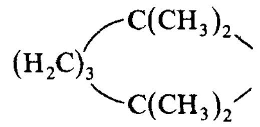
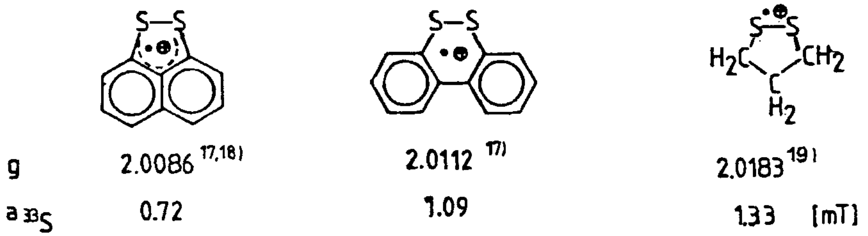
signal is also observed on the high-field side of the central line (Figure 1). The inner ^{33}S satellite line, however, due to an analogous line broadening is submerged under the high-field wing of the central line.

The ESR data including those for the F_3C-substituted radical cation:[2,10]

	g	$a_{^{33}S}$ (mT)	a_X (mT)	
	2.0157	0.78	< 0.007 (12H)	(6)
$(H_3C)_3C$—	2.0159	0.81	< 0.005 (18H)	
F_3C—	2.0160	0.86	0.135 (6F)	

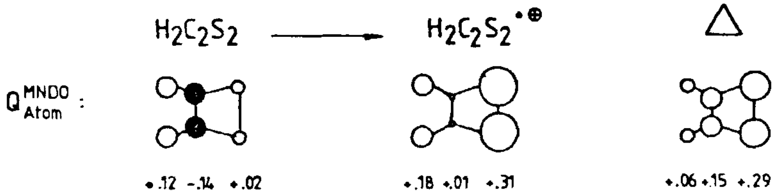
can be discussed as follows: both the g values and the ^{33}S hyperfine coupling constants $a_{^{33}S}$ are hardly substituent dependent. Based on qualitative perturbation arguments, substitution of the electron-withdrawing CF_3 group of **1** by the electron-donating alkyl groups in $\mathbf{2}^{\cdot\oplus}$ and $\mathbf{3}^{\cdot\oplus}$ does not change the spin population in 1,2-dithiete radical cations significantly. The g values of $\mathbf{1}^{\cdot\oplus}$ to $\mathbf{3}^{\cdot\oplus}$, predominantly determined by the spin/orbit coupling of the sulfur ring centers,[17] are in accord with those of 3,4-benzo-, and 3-phenyldithiete radical cations[3] are rather high as compared with cyclic disulfide radical cations of similar structure, and are lower than that of the saturated 1,2-dithiolane radical cation:[8]



(7)

Also the large ^{33}S hyperfine coupling constants of 0.8 mT (cf. (6)) illustrate that the spin population in dithiete radical cations $R_2C_2S_2^{\cdot\oplus}$ is preferentially located in the SS bridge.

To obtain some information on the distribution of the positive charge in the radical cations $\mathbf{1}^{\cdot\oplus}$, $\mathbf{2}^{\cdot\oplus}$ and $\mathbf{3}^{\cdot\oplus}$ (6), net atomic charges have been calculated by MNDO closed shell for the neutral parent molecule and by MNDO open shell for its radical cation:



(8)

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The MNDO results (8) suggest that neutral 1,2-dithiete should be polarized according to the effective nuclear charges towards the C=C bridge. For its radical cation, an accumulation of almost 2/3 of the positive charge at the "electron-rich" sulfur centers is predicted. The net atomic charge differences Δ show that on oxidation of the parent molecule, the electron is essentially removed from the four-membered ring, which contains 6π electrons i.e. two more than an isoconjugate cyclobutadiene π system.[20]

Two additional results should be mentioned: the MNDO eigenvalue for the lowest unoccupied orbital amounts to only $\varepsilon_J^{\mathrm{MNDO}} = -0.79$ eV[2], in agreement with the observation that 3,4-di(tert.butyl)-1,2-dithiete is also capable of forming a radical anion.[14] MNDO calculations for 3,4-bis(trifluoromethyl)-1,2-dithiete and its radical cation[2] yield results similar to those for the parent system (8) and thus provide a rationale for the ESR data presented in table (6): The missing substituent perturbation can be traced back to the special features of the unsaturated electron-rich four-membered ring, which after one-electron transfer accommodates most of the spin population and the positive charge in its disulfide bridge.

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EXPERIMENTAL SECTION

Compounds used for study. The synthesis of the alkylated 1,2-dithiete derivatives has been reported elsewhere;[12–14] both, 3′,3′,7′,7′-tetramethylhepteno[1′,2′-c]-1,2-dithiete and 3.4-di(tert.butyl)-1,2-dithiete are not air-sensitive. Nevertheless, all operations were carried out under nitrogen. 3,4-Bis(trifluoromethyl)-1,2-dithiete has been prepared according to the known literature procedure.[6] A small impurity of CS_2 can be detected on fractional distillation into a PE spectrometer by its characteristic ionization needles at 10.06 eV and 14.47 eV.

Generation of radical cations. The samples for study were all prepared by first evacuating an ESR tube and, under a stream of dry N_2, adding the compound of interest. The tube, continually under N_2, was then placed in a −196 °C bath and water-free $AlCl_3$ was added. H_2CCl_2 that was dried and kept over $AlCl_3$ was condensed in and the tube sealed off under vacuum. The solid solvent (H_2CCl_2) was not allowed to melt into the sample until immediately before the tube was placed into a pre-cooled (−60 °C) ESR cavity. The ESR signals develop above −20 °C.

Electron spin resonance spectra. The ESR spectra were recorded on a Varian E 9 instrument and calibrated by the perylene radical anion ($g = 2.002656$[21]). For measurement of the ^{33}S satellites concentrated solutions were used and the gain increased by a factor 100 at optimized modulation amplitude.

MNDO calculations. The MNDO calculations were performed at the Hochschul-Rechenzentrum Frankfurt using the program kindly given to us by M.J.S. Dewar and W. Thiel.[22]

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