Radical Ions, 78 [1, 2]

The Oxidative Desulfuration of Organic Cyclic Polysulfides to Disulfide Radical Cations in AlCl₃/H₂CCl₂ Solution

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Organodisulfide radical cations $R_2S_2^{.\oplus}$ and $R_2C_2S_2^{.\oplus}$ can be generated from aliphatic as well as aromatic cyclic polysulfides in AlCl₃/H₂CCl₂ solutions and characterized by their ESR spectra. Examples presented are the oxidations of 1,2,3-trithiolanes to 1,2-dithiolane radical cations, in which energetically favored planarized 3 electron/2 center bonds $-S\overset{\oplus}{\because}S-$ are formed.

Stimulated by the probable participation of the benzodithiete radical cation in the industrial, sulfur-catalyzed Friedl/Crafts-type 1,4-dichlorination of benzene [3], we have investigated other potential routes for its generation [2−4]:

$$\tag{1}$$
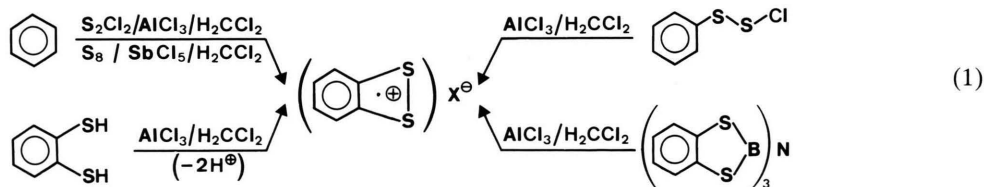
The AlCl₃/H₂CCl₂ reaction solution frequently used is a powerful, oxygen-free and selective one-electron transfer reagent exhibiting an oxidation potential of ~ +1.6 V [5], which provides convenient access to many air- and water-sensitive radical cations of main group element compounds [6] including those of sulfur [7]. Because of its applicability to generate disulfide radical cations from a variety of precursors [8−12]:

$$\tag{2}$$

The following polysulfides have also been subjected to AlCl₃/H₂CCl₂ treatment:

$$\tag{3}$$
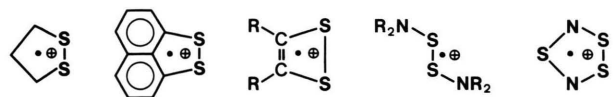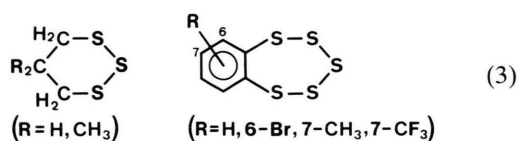
Here we report on the paramagnetic oxidation products identified by their ESR spectra in the resulting reaction solutions.

Oxidation of 1,2,3-Trithianes to 1,2-Dithiolane Radical Cations

The photoelectron spectra of 1,2,3-trithiane [13] and of its 5,5-dimethyl derivative [13] exhibit first vertical ionisation energies of 8.36 eV and 8.15 eV, respectively, to radical cation ground states $\bar{X}(A'')$
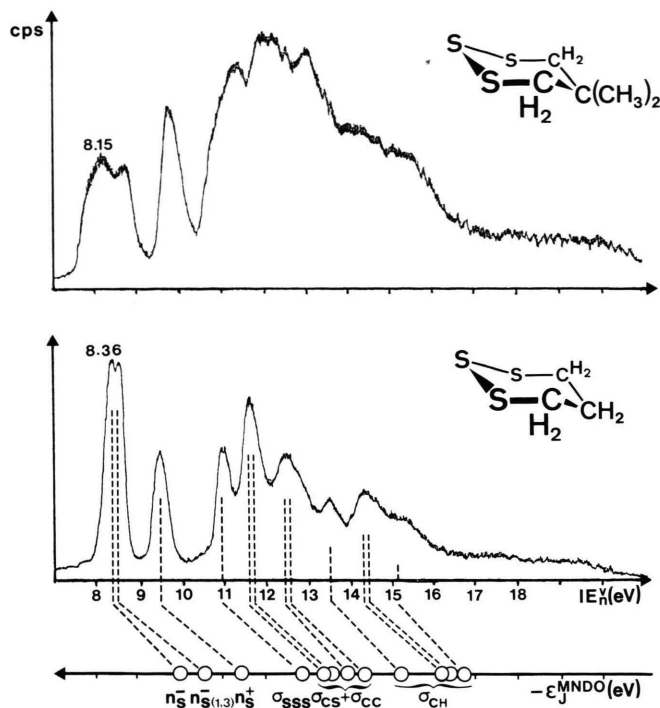
Fig. 1. He(I) photoelectron spectra of 5,5-dimethyl-1,2,3-trithiane and the unsubstituted parent compound assigned *via* Koopmans correlation, $IE_n^v = -\varepsilon_J^{MNDO}$, with MNDO eigenvalues.

with predominant sulfur lone pair contribution [14] at centers 1 and 3 (Fig. 1).

Although both vertical first ionisation potentials seem to be rather low, they are still well above the oxidation limit of $IE_1^v < 8$ eV usually required for radical cation generation in $AlCl_3/H_2CCl_2$ solution [5–7, 9–11]. On the other hand, the five-membered ring disulfide, 1,2-dithiolane, with $IE_1^v = 8.22$ eV, has been successfully oxidized under these conditions [8, 15], due to the additional adiabatic stabilization provided by flattening the dihedral CSSC angle (~30°) in the neutral disulfide: the temperature-dependent ESR spectra recorded [8] show already at 220 K a time-averaged quintet for the 4 now equivalent hydrogens of the adjacent H_2C-groups:
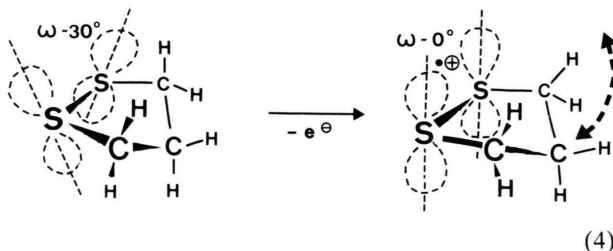
The activation barrier for the oscillatory movement in the 1,2-dithiolane radical cation (4) has been determined experimentally from an Arrhenius plot based on ESR line widths to amount to only ~8 kJ/mole. It is, therefore, comparable to the ~10 kJ/mole needed to activate pseudorotation in neutral 1,2-dithiolane as approximated by a semiempirical hypersurface calculation [8]. For cyclic vicinal trisulfides $(H_2C)_nS_3$ much higher barriers have been measured by temperature-dependent NMR, *e.g.* 1,2,3-trithiane ($n = 3$) requires a free activation enthalpy of 55 kJ/mole [13].

On treatment of 1,2,3-trithiane as well as its 5,5-dimethyl derivative with $AlCl_3/H_2CCl_2$ or $SbCl_5/H_2CCl_2$ solution, much to our surprise the known ESR spectra (*cf.* Fig. 2) of the corresponding 1,2-dithiolane radical cations are recorded [2, 14]:

(4)

(5)
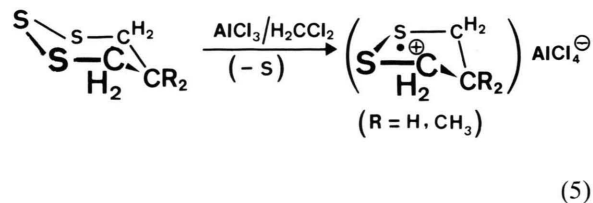
The oxidative desulfuration of 1,2,3-trithianes (5: R = H, CH_3) to the obviously favorable five-membered ring disulfide radical cations, which are also detectable by ESR in $AlCl_3/H_2CCl_2$ solutions of propane-1,3-dithiol [2, 14], can be rationalized from the ESR data [2, 8]: Both the rather high g-values (2.0183) and ^{33}S coupling constants (1.33 mT) measured in natural abundance (0.76%) on hundred-fold amplification indicate considerable spin density ϱ_S at the sulfur centers. Assuming planarity and, therefore, applicability of the empirical relationship, $\Sigma \varrho_S = -202.98 + 101.34\ g$ [9], a value $\varrho_S \sim 0.3$ results. Introducing the ^{33}S coupling constant into a simplified Karplus/Fraenkel relation, $\varrho_S \sim a_{33_S}/|Q_S| = 1.33\ mT/3.3\ mT \sim 0.4$, a slightly higher sulfur spin density is estimated. These ESR results suggest − in agreement with the PE-spectroscopic assignment of the radical cation ground state $\tilde{X}(A'')$ of 1,2-dithiolane to a predominant sulfur lone pair contribution [8] (*cf.* Fig. 1) − that a considerable amount of the positive charge accumulates at the electron-rich sulfur centers and thus energetically stabilizes the adiabatically relaxed 1,2-dithiolane radical cation in solution. As concerns the desulfuration mechanism (5), however, no information can be obtained from the ESR spectra, which in general allow to detect paramagnetic species in rather low concentration, and which for the 1,2,3-trithianes investigated do not show any additional signal at any temperature (Fig. 2) indicating formation of radical intermediates *e.g.* between the $AlCl_3$ Lewis acid and a paramagnetic sulfur-containing Lewis base fragment.

The temperature dependence of the ESR spectrum of 4,4′-dimethyl-1,2-dithiolane radical cation (Fig. 2) can be rationalized by a switch of the R_2C group, due to which the signals connected by dashed lines change their quantum number

Fig. 2. ESR spectra of 4,4-dimethyl-1,2-dithiolane radical cation, generated by $AlCl_3/H_2CCl_2$ treatment of 5,5′-dimethyl-1,2,3-trithiane or of independently synthesized $(H_3C)_2C(CH_2)_2S_2$ at different temperatures 233 K, 253 K and 313 K. The 293 K spectrum has been recorded in H_2SO_4 [2].

$$(6)$$

and, therefore, can no longer be distinguished once the coalescence point has been reached. Due to completely "frozen" molecular dynamics, below 220 K an intensity-correct triplet of triplets (6) is recorded. On slow warming some signals (6: ----) start to broaden (Fig. 2: 233 K and 253 K) and vanish at 260 K in $AlCl_3/H_2CCl_2$ solution (*cf.* Fig. 2: 293 K in H_2SO_4). Above the coalescence temperature, broad signals denoted by quantum numbers $+1$, -1 start to appear (Fig. 2: 313 K), and above 320 K a hydrogen quintet with intensities $1:4:6:4:1$ is observed. Transferring line-widths changes (*cf.* Exp. Part) into an Arrhenius correlation yields an activation barrier of ~ 18 kJ/mole for the oscillatory movement of the R_2C group in the 4,4-dimethyl-1,2-dithiolane radical cation, *i.e.* more than twice the value for the unsubstituted parent species $(H_2C)_3S_2^{\cdot\oplus}$ (4). Increasing barriers for molecular dynamic processes on $H \rightarrow CH_3$ substitution have been reported for various other five-membered ring radicals [16] and radical cations [17].

Summarizing, $AlCl_3/H_2CCl_2$ oxidation of 1,2,3-trithiane derivatives proceeds *via* desulfuration to 1,2-dithiolane radical cations which are obviously energetically favorable due to charge accumulation at the electron-rich sulfur centers as well as the adiabatic planarization accompanied by formation of a 2 center/3 electron $\pi(S \overset{\oplus}{\cdots} S)$-bond and to the low barrier for ring deforming oscillation.

Oxidation of Benzopentathiepines to Benzodithiete Radical Cations

In analogy to the oxidative desulfuration of 1,2,3-trithianes yielding stabilized 1,2-dithiolane radical cations (5), also benzopentathiepines [18] in $AlCl_3/H_2CCl_2$ solution above 250 K eliminate sulfur and form 1,2-benzodithiete radical cations [2−4]:

$$(7)$$

The rather simple ESR spectra (Fig. 3) show 3 (R = H, Br) or 5 signals (R = CH_3, CF_3), respectively, due to ^1H or ^{19}F coupling. On 100-fold amplification, also ^{33}S satellites (I = 3/2, nat. abundance 0.76%) can be detected on the low-field side both for the parent radical cation and its methyl derivative (Table I) [2−4].

Table I. ESR data for 1,2-benzodithiete radical cations with substituents R = H, 3-Br, 4-CH_3 and 4-CF_3 (in brackets number of coupling nuclei).

$R-C_6H_3S_2^{\cdot\oplus}$	g	a_{1H}, a_{19F} (mT)	a_{33S} (mT)
H	2.0153	0.112(2)	0.81 [19]
3-Br	2.0156	0.110(2)	
4-CH_3	2.0153	0.142(4)	0.82 [19]
4-CF_3	2.0157	0.110(4)	

The ESR data (Table I) are rationalized as follows: Both the rather high g values and ^{33}S coupling constants again indicate predominant spin population at the sulfur centers. As concerns the hyperfine splitting pattern, the ^1H triplet of the parent radical cation originates from the hydrogens at centers 4 and 5 − as proven by ESR-comparison of numerous substituted derivatives [2]. The 3-bromo-1,2-benzodithiete radical cation also shows only a ^1H triplet due to the (nearly) equivalent 4- and 5-hydrogens,
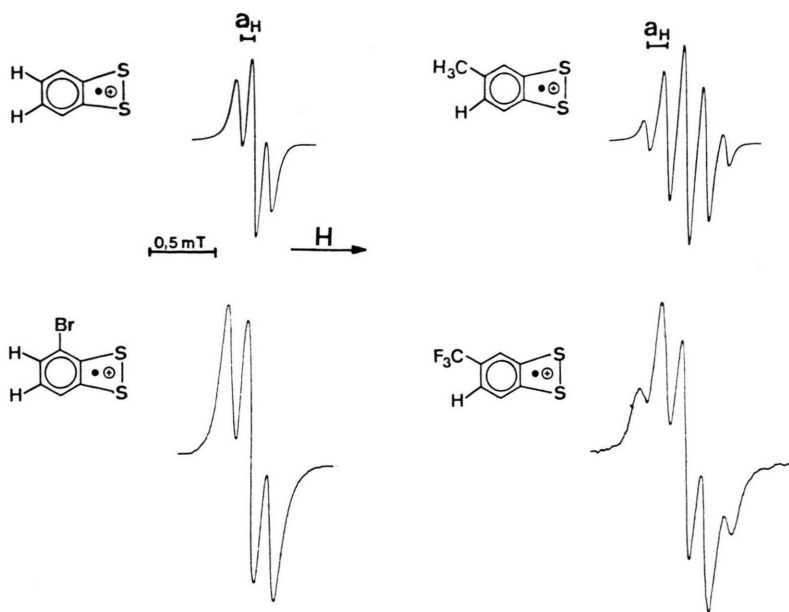
Fig. 3. ESR spectra of the radical cations of 1,2-benzodithiete as well as of its 3-bromo, 4-methyl and 4-trifluoromethyl derivatives, each generated by $AlCl_3/H_2CCl_2$ oxidation of the corresponding benzopentathiepines at 270 K.

thereby confirming the existence of a spin nodal plane close to the ring carbon centers 3 and 6 as well as an almost negligible perturbation by the bromine substituent. As concerns the quintets observed for both the 4-CH$_3$ and 4-CF$_3$ substituted radical cations, near degeneracy for the $a_H^{CH_3}$ or $a_F^{CF_3}$ and the $a_{H.5}^{Ring}$ coupling constants has to be assumed.

The basic question, which of the valence tautomers, 1,2-benzodithiete or *ortho*-dithiobenzoquinone radical cation, is present in the $AlCl_3/H_2CCl_2$ solutions investigated here, has to be settled relying on additional calculations [2, 10, 20], which unequivocally favor the 4-membered ring disulfide radical cation structure [2, 20]. To support the calculations, in return, some of their predictions can be checked by correlation with experimental data: for instance, the difference in MNDO heats of formation between M and $M^{\cdot\oplus}$ as independently calculated in closed and open shell runs, $\Delta Hf^{MNDO}(M^{\cdot\oplus}-M) = 852$ kJ/mole = 8.8 eV, nicely reproduces the first vertical ionization energy, $IE_1^v = 8.46$ eV, measured by photoelectron spectroscopy [20].

The ESR-spectroscopically determined considerable spin population at the sulfur centers of 1,2-benzodithiete radical cations (Table I) is, however, smaller than the one in 1,2-dithiolane radical cations already discussed (g values 2.0153 *vs.* 2.0183 and ^{33}S

coupling constants 0.81 mT *vs.* 1.33 mT, respectively). The concurring assumption that the positive charge might also be delocalized over the adjacent benzene system is in accord with MNDO calculated charge distributions [2]


$$(8)$$
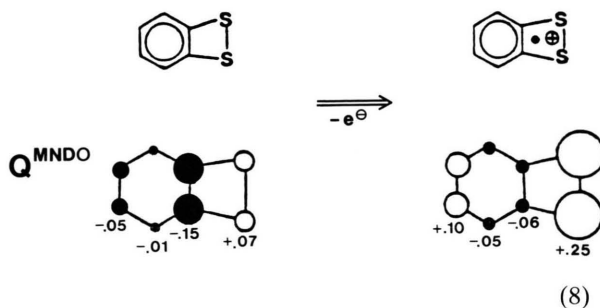
and suggests additional stabilization of the 1,2-benzodithiete radical cations generated due to delocalization of the positive charge [21].

Concluding Remarks

The oxidative desulfuration of both cyclic tri- and pentasulfides $\text{S}_{n=3.5}$ to corresponding disulfide radical cations $\text{S}_2^{\cdot\oplus}$ as detected by ESR in $AlCl_3/H_2CCl_2$ solution has several implications:

The ESR data of cyclic disulfide radical cations with presumably planarized $-C-S \overset{\cdot\oplus}{\cdots} S-C-$ bridges

| g	2.0183[8]	2.0153[2,4]	2.0112[9]	2.0086[9]
a_{33S}(mT)	1.33	0.81	1.09	0.73
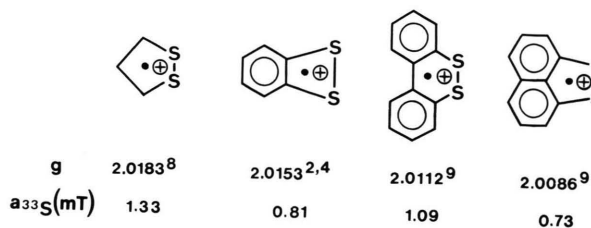
$$(9)$$

illustrate the predominant localization of spin and, concurrently, of the positive charge at the sulfur centers of the saturated 1,2-dithiolane derivative as well as its increasing delocalization in larger systems. Thus, the g values (9) correlate (linearly [9]) with the nuclear spin/orbit coupling constants of the radical center elements. The ^{33}S coupling constants confirm the general trend (9), although they depend to some extent on the different second order sulfur perturbation of the individual parent systems.

Altogether the ESR data (9) provide evidence that planar disulfur bridges are well-suited "electron buffers" for positive charges, an experimental result corroborated by the rather low first vertical ionisation energies of disulfides [14], which furthermore strongly depend on their dihedral angles CSSC [8].

The energetically favorable formation of 3 electron/2 center π bonds $-S \overset{\oplus}{\cdots} S-$ in planar disulfide radical cations bears some resemblance to the unexpected $>S \overset{\oplus}{\cdots} S<$ dimers detected ESR spectroscopically in solutions of oxidized open-chain [22] and cyclic [22, 23] dialkylsulfides:

$$(10)$$
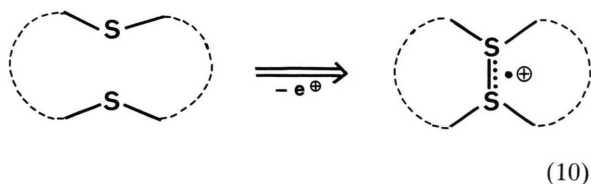
Although a σ-type bond results on electron removal, the driving force for dimerisation is again the delocalization of the positive charge generated at one $>S^{\cdot\oplus}$ center to another electron-rich dialkyl substituted sulfur. The reduced repulsion between adjacent lone pairs due to a positive charge and the ac-

companying structural changes on one-electron oxidation become especially evident for hydrazine and its derivatives [6a, 24, 25]:

$d_{NN} \sim 150$pm $d_{NN} = 128$pm(calc.)[24]
                                                      127pm(X–Ray)[25]
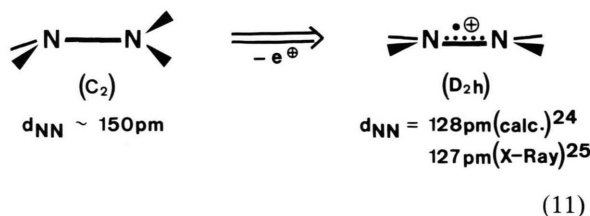
$$(11)$$

In addition to planarization, a tremendous NN bond contraction occurs on removal of a single electron.

The preparative usefulness of the AlCl$_3$/H$_2$CCl$_2$ desulfuration of cyclic polysulfides remains to be demonstrated. On the other hand, this ESR investigation suggests that despite of AlCl$_3$ present as a Lewis acid, the first reaction step might be well be an electron transfer followed by radical cation stabilization. Therefore, electrophilic degradation of polysulfur compounds with Lewis acids [26] like SO$_3$ or SbF$_5$ could possibly also proceed *via* an initial single electron transfer as has been proven for several nucleophilic attacks and a variety of other reaction in nonaqueous solvents [27].

Experimental Part

The cyclic polysulfides have been synthesized according to published procedures: 1,2,3-trithiane from disodium trimethylene di(thiosulphate) [28], its dimethyl derivate from 2,2-dimethyl-1,3-dibromopropene and Na$_2$S$_3$ [29] and benzopentathiepin as well as its derivatives by thermal decomposition of the corresponding 1,2,3-benzothiadiazoles in the presence of elemental sulfur [18]. The purity of the volatile cyclic trisulfides has been established by photoelectron spectroscopy (*cf.* Fig. 1); the benzopentathiepines have been characterized by elemental analysis, NMR, IR as well as UV spectra and, partly by X-ray structure determination [18, 30].

The photoelectron spectra have been recorded on a Perkin-Elmer PS 16 spectrometer equipped with a heated inlet system and calibrated using the Xe(^{2}P$_{3/2}$) = 12.13 eV and Ar(^{2}P$_{3/2}$) = 15.76 eV peaks.

Radical cation generation was performed in 2 mm i. d. glass capillary tubes under N$_2$ by the following procedure: 1 mg of the compound was dissolved in 0.5 ml of oxygen-free dichloromethane, which had been kept dry over AlCl$_3$, and 5 mg of AlCl$_3$ was added to this solution.

The electron spin resonance spectra were recorded using a Varian E 9 spectrometer, equipped with a variable temperature unit E 257, at 9.5 GHz-frequency and 330 mT-magnetic field, and a field modulation of 100 kHz. The proton coupling constants a_H (*cf.* Table II) are assumed to be correct within $\pm 1\%$; calibration was performed with Fremy's salt $(2 a_N = 2.618 \text{ mT})$. g-Values were determined by the double cavity technique using perylene radical anion in DME for calibration.

For the Arrhenius plot, the following relations between ESR line widths LW and rate constant K have been used [31]: below coalescence temperature, $k = LW$, and above, $k = (a_{H,1} - a_{H,2})^2/8 \, \Delta LW$. Correlating ln k and 1/T values (Table II) *via* the Arrhenius equation yields an activation energy $E_A \sim 18 \text{ kJ/mole}$ for the $(H_3C)_2C$ switch oscillation.

The MNDO calculation has been performed by Dipl.-Chem. G. Rohn at our VAX 11/750 computer using a modified version of the original procedure [32], kindly provided by Prof. M. J. S. Dewar, Au-stin, Texas. The C_3S_2 skeleton has been fully geometry-optimized ($\Delta Hf^{MNDO} = 57.8 \text{ kJ/mole}$).

Table II. Temperature-dependent ESR line widths LW (Hz) and rate constants k (Hz) calculated (*cf.* text) for the R_2C switch oszillation in 4,4-dimethyl-1,2-dithiolane radical cation (*cf.* Fig. 2).

LW (Hz)	k (Hz)	ln k	T (k)	1/T (k−1)
$1.1 \cdot 10^7$	$2.0 \cdot 10^{8*}$	19.11	313	$3.19 \cdot 10^{-3}$
$6.1 \cdot 10^6$	$6.1 \cdot 10^6$	17.93	253	$3.95 \cdot 10^{-3}$
$4.6 \cdot 10^6$	$4.6 \cdot 10^6$	17.64	233	$4.29 \cdot 10^{-3}$

* For conversions $\Delta LW \rightarrow k$ above coalescence temperature, relation $k = (a_1 - a_2)/8 \, LW$ holds [31].

[1] Part 77: H. Bock, M. Bankmann, P. Hänel, and U. Lechner-Knoblauch, Abstr. X. Int. Conf. Phosphorus Chem., Bonn (1986).

[2] Part of Ph. D. Thesis P. Rittmeyer, University Frankfurt am Main (1986); *cf.* also Ph. D. Thesis U. Stein, University Frankfurt am Main (1980).

[3] H. Bock, U. Stein, and P. Rittmeyer, Angew. Chem. **94**, 540 (1982); Angew. Chem. Int. Ed. Engl. **21**, 533 (1982) as well as l. c.

[4] J. Giordan and H. Bock, Chem. Ber. **115**, 2548 (1982); *cf.* also H. Bock and B. Roth, Phosphorus Sulfur **14**, 211 (1983).

[5] H. Bock and U. Lechner-Knoblauch, J. Organomet. Chem. **294**, 295 (1985) and literature quoted.

[6] The one-electron oxidation of various main group element compounds by $AlCl_3/H_2CCl_2$ solutions can be illustrated by the following examples:
a) organosilicon radical cations (*cf.* H. Bock and W. Kaim, Acc. Chem. Res. **15**, 1 (1982));
b) B/N radical cations (*cf.* H. Nöth, W. Winterstein, W. Kaim, and H. Bock, Chem. Ber. **112**, 2494 (1979));
c) oxidation of tetrakis(*tert*-butyl)tetrahedrane (*cf.* H. Bock, B. Roth, and G. Maier, Chem. Ber. **117**, 172 (1984)) or
d) the radical cation of tetrakis(dimethylamino)-*p*-benzochinon (*cf.* H. Bock, P. Hänel, W. Kaim, and U. Lechner-Knoblauch, Tetrahedron Lett. **26**, 5115 (1985)).

[7] *Cf. e. g.* thiomethyl-substituted naphthalenes (H. Bock and G. Brähler, Chem. Ber. **112**, 3081 (1979)), tetraphenylthieno[3,4-c]thiophene (R. Gleiter, R. Bartetzko, G. Brähler, and H. Bock, J. Org. Chem. **43**, 3893 (1978)), tetrakis(thioalkyl)ethenes (H. Bock, G. Brähler, U. Henkel, R. Schlecker, and D. Seebach, Chem. Ber. **113**, 289 (1980)), 1,4,5,8-tetrathiatetralin (H. Bock, B. Roth, M. V. Lakshmikantham, and M. P. Cava, Phosphorus Sulfur **21**, 67 (1984)) or tetrathiafulvalenes (H. Bock, B. Roth, and R. Schumaker, Phosphorus Sulfur **21**, 79 (1984)).

[8] H. Bock, U. Stein, and A. Semkow, Chem. Ber. **113**, 3208 (1980) and l. c.

[9] H. Bock, G. Brähler, D. Dauplaise, and J. Meinwald, Chem. Ber. **114**, 2622 (1981).

[10] a) H. Bock, P. Rittmeyer, A. Krebs, K. Schütz, J. Voss, and B. Köpke, Phosphorus Sulfur **19**, 131 (1984) and l. c.;
b) H. Bock, P. Rittmeyer, and U. Stein, Chem. Ber. **119**, 3766 (1986).

[11] H. Bock, W. Schulz, and U. Stein, Chem. Ber. **114**, 2632 (1981).

[12] J. Giordan, H. Bock, M. Eiser, and H. W. Roesky, Phosphorus Sulfur **13**, 19 (1982).

[13] Preparation: B. Milligan and J. M. Swan, J. Chem. Soc. London **1965**, 2901 (R = H) or H. J. Backer and A. F. Tasma, Rec. Trav. Chim. Pays-Bas **57**, 1183 (1938); molecular dynamics: S. Kabuss, A. Lüttringhaus, H. Friebolin, and R. Mecke, Z. Naturforsch. **21b**, 320 (1966).

[14] For a summary of sulfur lone pair ionisations *cf.* R. Gleiter and J. Spanget-Larsen, Topics Curr. Chem. **86**, 139 (1979), or [8].

[15] Preliminary communication: H. Bock and U. Stein, Angew. Chem. **92**, 863 (1980); Angew. Chem., Int. Ed. Engl. **19**, 834 (1980).

[16] *Cf. e. g.* R. V. Lloyd and D. E. Wood, J. Am. Chem. Soc. **99**, 8269 (1977).

[17] *Cf. e. g.* S. F. Nelson, G. R. Weisman, P. J. Hintz, D. Olp, and M. R. Fahey, J. Am. Chem. Soc. **96**, 2916 (1974).

[18] B. L. Chenard and T. J. Miller, J. Org. Chem. **49**, 1221 (1984). For temperature-dependent conformation studies as well as for calculations *cf.* ibid. **52**, 2411 (1987).

[19] The ^{33}S coupling constant is reproduced on reaction of benzene with 48.46% ^{33}S enriched sulfur and $SbCl_5$ in H_2CCl_2 (Ph. D. Thesis U. Stein).

[20] M. Breitenstein, R. Schulz, and A. Schweig, J. Org. Chem. **47**, 1979 (1982); *cf.* also R. Schulz, A. Schweig, K. Hartke, and J. Köster, J. Am. Chem. Soc. **105**, 4519 (1983) and l.c.

[21] On warming $AlCl_3/H_2CCl_2$ solutions of 1,2-benzo-dithiete radical cations, slowly the ESR signals of the well-known thianthrene radical cations develop at higher field (g values ~ 2.0080) [2–4, 8, 10], indicating a possible, yet mechanistically mysterious pathway to larger and, due to the extensive delocalization of the positive charge, more stable products.

[22] K.-D. Asmus, D. Bahnemann, C.-H. Fischer, and D. Veltwisch, J. Am. Chem. Soc. **101**, 5322 (1979) and the preceding literature quotations given, *e.g.* [23].

[23] W. K. Musker, T. L. Wolford, and P. B. Rausch, J. Am. Chem. Soc. **100**, 6416 (1978) as well as **98**, 3055 (1976).

[24] H. Bock, W. Kaim, A. M. Semkow, and H. Nöth, Angew. Chem. **90**, 308 (1978); Angew. Chem., Int. Ed. Engl. **17**, 286 (1978) or J. Am. Chem. Soc. **102**, 4421 (1980) and l.c.

[25] S. F. Nelson, W. C. Hollinsed, C. R. Kessel, and J. C. Calabrese, J. Am. Chem. Soc. **100**, 7876 (1978).

[26] *Cf. e.g.* the review by R. J. Gillespie and J. Passmore, Adv. Inorg. Radiochem. **17**, 48 (1975) and l.c.

[27] *Cf. e.g.* the summary by W. Kaim; Nachr. Chem. Techn. Lab. **32**, 436 (1984) and l.c.

[28] B. Milligan, B. Saville, and J. M. Swan, J. Chem. Soc. [London] **1965**, 2901.

[29] H. J. Backer and N. Evenhuis, Rec. Trav. Chim. Pays-Bas **56**, 174 (1937).

[30] B. L. Chenard, R. L. Harlow, A. L. Johnson, and S. A. Vladuchik, J. Am. Chem. Soc. **107**, 3871 (1985).

[31] *Cf. e.g.* A. Hudson and G. R. Luckhurst, Chem. Rev. **69**, 191 (1969) and l.c.

[32] M. J. S. Dewar and W. Thiel, J. Am. Chem. Soc. **99**, 4899 (1977).