

Radical Ions, 51¹⁾**Oxidative Rearrangement of Diphenyl Disulfides to Thianthrenes***Judith Giordan and Hans Bock**

Institut für Anorganische Chemie der Universität Frankfurt,
Niederurseler Hang, D-6000 Frankfurt (M) 50

Received November 13, 1981

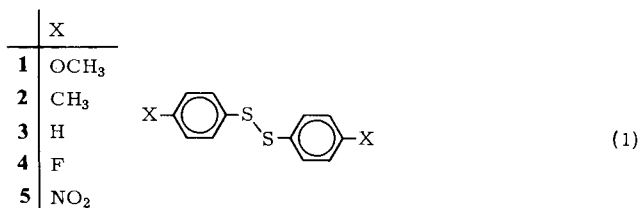
para-Substituted diphenyl disulfides **1**–**5** with low gas phase ionization energies of about 8 eV react with AlCl₃ in CH₂Cl₂ to form radical cations of the corresponding thianthrenes (Table 2, Figure 2). Warming of these solutions produced a second ESR signal which is attributed to a benzodithiete radical cation (Table 2, Figure 3). This is possibly the reactive intermediate in the S₈ or S₂Cl₂ catalyzed Friedel-Crafts chlorination of benzene.

Radikationen, 51¹⁾**Oxidative Umlagerung von Diphenyldisulfiden in Thianthrene**

para-Substituierte Diphenyldisulfide **1**–**5** mit niedrigen Ionisierungsenergien um 8 eV reagieren mit AlCl₃ in CH₂Cl₂ zu Radikationen der gleichartig substituierten Thianthrene (Tab. 2, Abb. 2). Beim Aufwärmen der Lösungen beobachtet man ein zweites ESR-Signal, das einem Benzodithiet-Radikalkation (Tab. 2, Abb. 3) zugeordnet wird. Dies ist möglicherweise das reaktive Zwischenprodukt der S₈- oder S₂Cl₂-katalysierten Friedel-Crafts-Chlorierung von Benzol.

An efficient method to generate radical cations from compounds with first gas phase ionization energies of approximately 8 eV or less, as determined from PE spectroscopy, uses the selective oxygen-free system of AlCl₃ in CH₂Cl₂¹⁾. The resulting radical cations that have been studied by ESR include compounds such as main-group substituted hydrazines^{1,2)}, various organometallic compounds³⁾, and, recently, strained disulfides⁴⁾ as well as open chain amino disulfides⁵⁾.

Often, structural changes have been observed during „adiabatic“ one-electron oxidation in solution that provide additional stabilization of the forming radical cation, e. g., planarization of the disulfide bridge^{4,5)}. Therefore, a series of *para*-substituted diphenyl disulfides **1**–**5** was studied in an attempt to generate other stable disulfide radical cations and determine the effects of donor and acceptor substituents.



A. Photoelectron Spectra

Although many sulfur compounds such as diphenyl sulfide⁶⁾, alkyl substituted phenyl sulfides^{7,8)}, and various disulfides^{7,9)} have been investigated by PE spectroscopy, no study of *para*-substituted diphenyl disulfides has appeared. The PE spectrum of bis-(4-methylphenyl) disulfide (**2**) is shown in Figure 1 as an example of the general appearance of ionization patterns in **1**–**5**. Their vertical ionization energies and those of the parent mono-substituted benzenes are presented in Table 1.

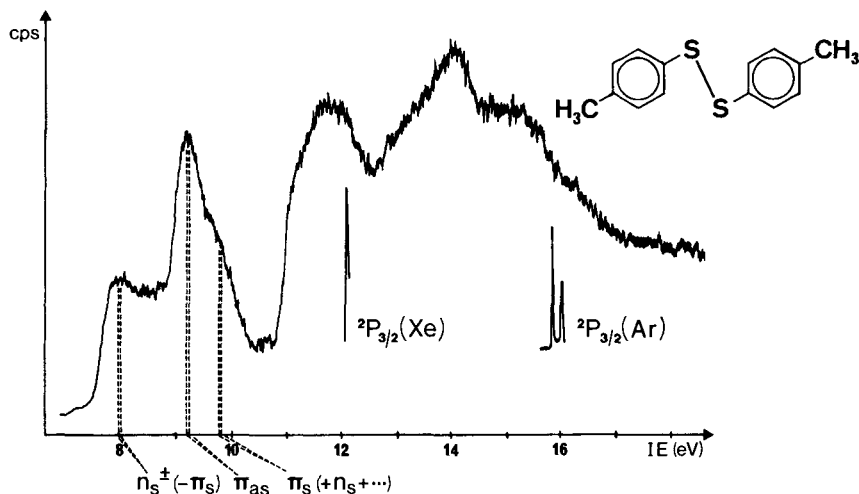


Figure 1. He(I) PE spectrum of bis(4-methylphenyl) disulfide (**2**), calibrated by the $^2P_{3/2}$ peaks of Xenon (12.13 eV) and Argon (15.76 eV)

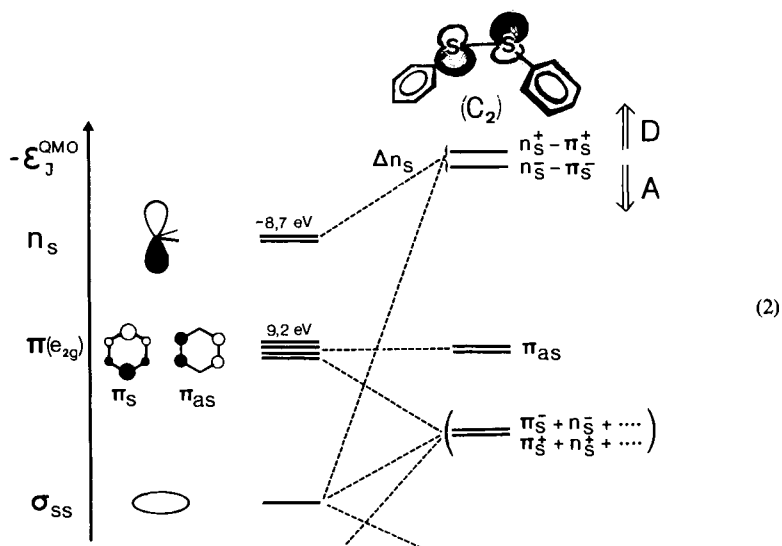
Table 1. Vertical ionization energies, IE_n^x (eV), in the low energy region of *para*-substituted diphenyl disulfides and the corresponding phenyl derivatives

X	X- <chem>c1ccc(cc1)SSc2ccc(cc2)X</chem>			<chem>c1ccc(cc1)X</chem>		Lit.
	$\overline{IE}_{1,2}^a$	$\overline{IE}_{3,4}^a$	$\overline{IE}_{5,6}^a$	IE_1^c	IE_2	
OCH ₃	(7.6) ^{b)}	9.2	() ^{c)}	8.42	9.23	8)
CH ₃	8.0	9.2	(9.8) ^{b)}	8.88	9.15	10)
H	8.3	9.35	10.1	9.24	9.24	
F	8.4	9.75 ^{d)}	() ^{c)}	9.20	9.81	11)
NO ₂	8.98	10.3	11.2	9.92	10.3	11)

a) Average value. – b) Shoulder. – c) Unresolved overlapping bands. – d) Additional shoulder at 9.2 eV. – e) Assigned π_s from the benzene (e_{2g}) pair.

The dominant feature in Figure 1 is the large hill of extensively overlapping bands which makes individual assignments in this region impossible. In the He(I) spectrum of the parent compound, diphenyl disulfide, C₁₂H₁₀S₂, the 70 valence electrons are expected to result, according to a useful rule-of-thumb¹²⁾, in approximately 21 ionizations.

Of these only those in the low energy region are sufficiently resolved to be assigned. The ordering of these ionization energies is best explained using Koopman's theorem, $IE_n^v = -\epsilon_j^{\text{SCF}}$, in conjunction with the qualitative molecular orbital scheme (2).



Forming the appropriate linear combinations from 2 sulfur lone pair orbitals n_s , 4 π -type benzene orbitals and 1 σ_{ss} bonding orbital and mixing them according to overlap in C_2 symmetry results in

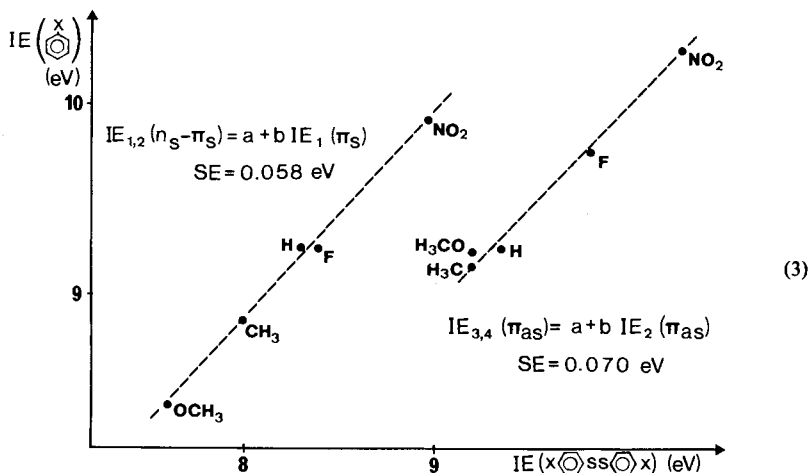
i. a pair of strongly mixed sulfur lone pair and benzene π_s orbitals, denoted $n_s^+ - \pi_s^+$, $n_s^- - \pi_s^-$ in (2), which are slightly split (Δn_s) by additional contributions from lower lying orbitals, e. g. σ_{ss}^9 . These essentially degenerate sulfur lone pair ionizations are a result of the approximately perpendicular arrangement of the sulfur lone pairs (93° dihedral angle, CSSC)¹³.

ii. a pair of nearly degenerate benzenoid (π_{as}) orbitals with a nodal plane through the substitution centers, which remain at about the same energy as in benzene (9.2 eV)¹¹.

iii. the complementary bonding combination of benzene π_s and sulfur lone pair orbitals which, according to CNDO calculations, mix strongly with other low lying orbitals. This mixing prevents a clear-cut orbital assignment for the corresponding radical cation states.

The effects of donor and acceptor *para*-substituents on diphenyl disulfides become manifest by comparison of the ionization energies along the series 1–5 with respect to each other and the corresponding mono-substituted benzene (Table 1). To facilitate discussion a diagram of these data is presented in (3).

The plot of $IE_{3,4}$ of the disulfide versus IE_2 of the parent substituted benzene exhibits a slope of nearly 1 and thereby indicates that, as expected, only a first order perturbation effect is operative; due to the nodal properties of the π_{as} benzene orbital, substituents in *para*-positions are anticipated to affect the energy of the orbital and, there-



fore, its corresponding radical cation state only through an inductive and not a π -type interaction. Therefore, addition of a disulfide group at the *para*-position of the benzene ring perturbs the π_{as} orbital only slightly with the dominant effect being that from the substituent, X. The second plot of $\overline{IE}_{1,2}$ of the disulfides, denoted as $n_S - \pi_S$, versus $IE_1(\pi_S)$ of the appropriate substituted benzene, also has a slope of nearly 1. This unexpected correlation between sulfur lone pair ionization energies and the first IE of the corresponding substituted benzenes shows that the mixture between the benzene π_S orbital and the sulfur lone pairs is very strong, since a smaller admixture would be expected to result in a considerably smaller effect of *para*-substituents on the lone pair ionization energies. Thus, here, both first order inductive and second order π -type perturbations are required for interpretation of the data.

B. Electron Spin Resonance Spectra

From the vertical ionization potentials (Table 1), it would be expected that only the donor-substituted diphenyl disulfides, **1** and **2**, would be easily oxidized in $\text{AlCl}_3/\text{CH}_2\text{Cl}_2$ to their radical cations in contrast to **3**–**5** whose first ionization energies are above 8 eV^{1-3} . The ESR spectra observed (Figure 2) indicate, however, that all derivatives, with the exception of the *p*-nitro compound, **5**, can be oxidized to the corresponding 2,7-disubstituted thianthrene radical cations. With **5**, the ESR spectrum of thianthrene $^{\oplus}$ itself was obtained (Figure 2). This is not exceptional since it is known that reactions between nitro benzene and AlCl_3 sometimes result in loss of the nitro group 14,15 .

The formation of thianthrenes from disulfides was somewhat surprising since oxidation to radical cations using the $\text{AlCl}_3 + \text{CH}_2\text{Cl}_2$ method does not usually result in rearrangements involving bond breaking 2 . However, AlCl_3 catalyzed rearrangements in aromatic systems occur frequently 16,17 . At elevated temperatures reaction between AlCl_3 and diphenyl disulfide has been reported to result in benzene evolution and polymer formation containing thianthrene structural units 18 . At slightly lower tem-

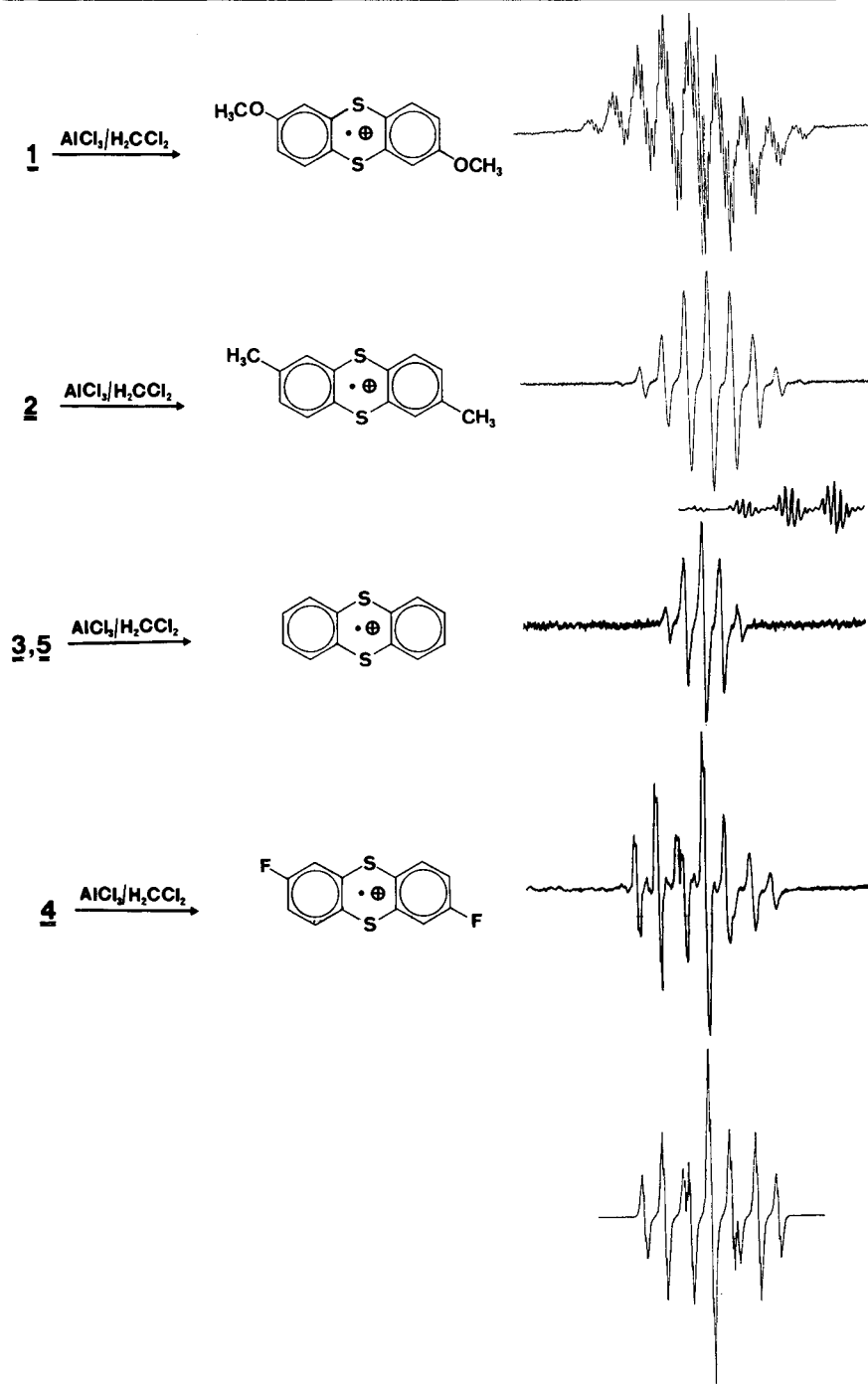
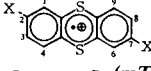
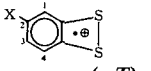


Figure 2. ESR spectra of the thianthrene radical cations produced via $\text{AlCl}_3/\text{CH}_2\text{Cl}_2$ treatment of the corresponding disulfides, 1–5, and computer simulation of the ESR spectrum of 4^{\oplus} (below)

peratures, it has been found using ^{14}C labelled diphenyl sulfide that this reaction produced thianthrene, benzene, and label-scrambled starting material¹⁹⁾.

Table 2 summarizes the ESR data obtained for all the compounds studied. Rationale for assigning the initially observed ESR signals to substituted thianthrene radical cations is based on known data from thianthrenes $^{\bullet\oplus}$. In these ESR spectra, only substituents in the 2,3,7, and 8 positions manifest themselves, thereby indicating, that with the exception of the sulfur centers²⁰⁾, the largest spin density is on the β -positions of the thianthrene ring.

Table 2. ESR data, coupling constants, a_x (mT), and g values, from diphenyl disulfides **1**–**5** by $\text{AlCl}_3/\text{CH}_2\text{Cl}_2$ oxidation (numbering according to²⁰⁾)

X	Nuclei				
		g	a_x (mT)	g	a_x (mT)
OCH ₃	H (CH ₃)	2.0071	.019	– b)	– b)
	H (3/8)		.245		– b)
	H (6/1) ^{a)}		.148		– b)
	H (4/9) ^{a)}		.133		– b)
CH ₃	H (CH ₃) ^{c)}	2.0080	.168	2.0150	.151
	H (3/8) ^{c)}		.168		.151
H	H (2/3/7/8)	2.0084	.130	2.0150	.115
F	F	2.0083	.330	2.0160	.330
	H (3/8)		.145		.120
	H (?) ^{d)}		.012		– e)

a) Assignment based on donating effect of methoxy group. – b) Thianthrene overlap too great for determination. – c) Equivalent nuclei. – d) Coupling of 2 hydrogen, not assigned. – e) Not resolved.

In light of known thianthrene $^{\bullet\oplus}$ spectra²⁰⁾, the ESR signals observed for **1** $^{\bullet\oplus}$ –**5** $^{\bullet\oplus}$ are readily interpreted. Oxidation of bis(4-methoxyphenyl) disulfide (**1**) resulted in the formation of the 2,7-dimethoxythianthrene radical cation. Unlike with **2** $^{\bullet\oplus}$ –**5** $^{\bullet\oplus}$, only here do the 1,4,6, and 9 protons contribute to the observed ESR spectrum exhibiting nine major lines (Figure 2). Previous ESR studies on **1** $^{\bullet\oplus}$, generated by H_2SO_4 oxidation of the disulfide, reported an unassigned nine line spectrum but no resolution of the splittings from the methyl groups were observed²¹⁾. In bis(4-methylphenyl) disulfide (**2**), the thianthrene signal is a normal nonet as previously described²⁰⁾ for 2,7-dimethylthianthrene, due to the accidental equivalence of the six methyl and two ring protons in the 3 and 8 positions. Oxidized diphenyl disulfide (**3**) exhibited only a quintet, as is expected from the parent unsubstituted thianthrene²⁰⁾. Bis(4-fluorophenyl) disulfide (**4**) results in the radical cation of 2,7-difluorothianthrene, which is presented with a computer simulation in Figure 2. Here, the high resolution ESR spectrum reveals contributions from both the fluorine substituents and the 3,8 hydrogens. Bis(4-nitrophenyl) disulfide (**5**), as mentioned above, resulted in the spectrum of parent unsubstituted thianthrene due to loss of the nitro groups via reaction with AlCl_3 .

Surprisingly, upon warming the samples of the radical cations, **1** $^{\bullet\oplus}$ –**5** $^{\bullet\oplus}$, to either 300 or 380 K (cf. Exp. Part) and replacing them in the ESR cavity, in each case a second

ESR signal developed downfield from that of thianthrene^{•+}, with a rather large g value of approximately 2.015 (Table 2, Figure 3). This second radical species is attributed to a benzodithiete radical cation^{6,22,23}. Parametrized Hückel/McLachlan calculations (c. f. Exp. Section) on the proposed dithiete structure show that, with the exception of the sulfur centers, the highest spin density is on the 2,3 position (cf. Table 2) – just as with thianthrene^{•+}^{6,20,22,23}. Therefore the ESR spectra of benzodithiete radical cations would be expected to contain contributions from hydrogens or substituents in these positions.

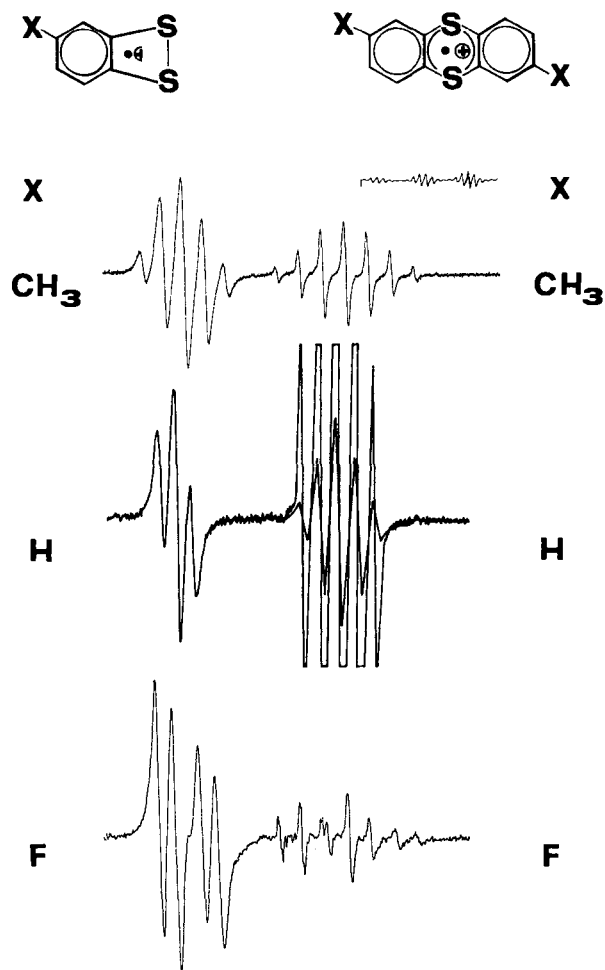
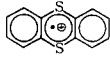

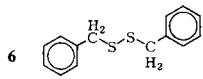

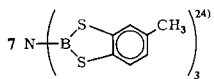


Figure 3. ESR spectra of thianthrene and benzodithiete radical cations from the reaction of diphenyl disulfides with $\text{AlCl}_3/\text{CH}_2\text{Cl}_2$

In bis(4-methoxyphenyl) disulfide (1), the ESR signal attributed to the dithiete species overlaps strongly with the original thianthrene signal. Although clearly present, the

radical cation is difficult to characterize and, therefore, the ESR spectrum is not presented. A radical cation of a benzodithiete arising from **2** would be expected to exhibit a quintet ESR signal since four equivalent hydrogens are present; three from the methyl group and the ring proton in position 3; Figure 3 shows exactly that. A triplet signal is seen in the ESR of the unsubstituted dithiete radical cation from diphenyl disulfide (**3**), due to the two protons in the 2,3 positions. The doublet of doublets ESR signal arising from the 2-fluorodithiete radical cation results from one fluorine and one hydrogen in the 2 and 3 positions, respectively, of the benzene ring. In addition to $1^{\oplus} - 5^{\oplus}$, the radical cations formed by $\text{AlCl}_3/\text{H}_2\text{CCl}_2$ oxidation of dibenzyl disulfide (**6**), tris(5-methyl-1,3,2-benzodithiaborol-2-yl)amine (**7**)²⁴ and thianthrene in the presence of S_2Cl_2 were investigated to further elucidate the scope of this rearrangement ((cf. (4) and Table 3).

Table 3. Splitting parameters a_x (mT) and g values for radical cations generated via $\text{AlCl}_3/\text{CH}_2\text{Cl}_2$ oxidation of thianthrene in the presence of S_2Cl_2 , dibenzyl disulfide (**6**), and of tris(5-methyl-1,3,2-benzodithiaborol-2-yl)amine (**7**)²⁴

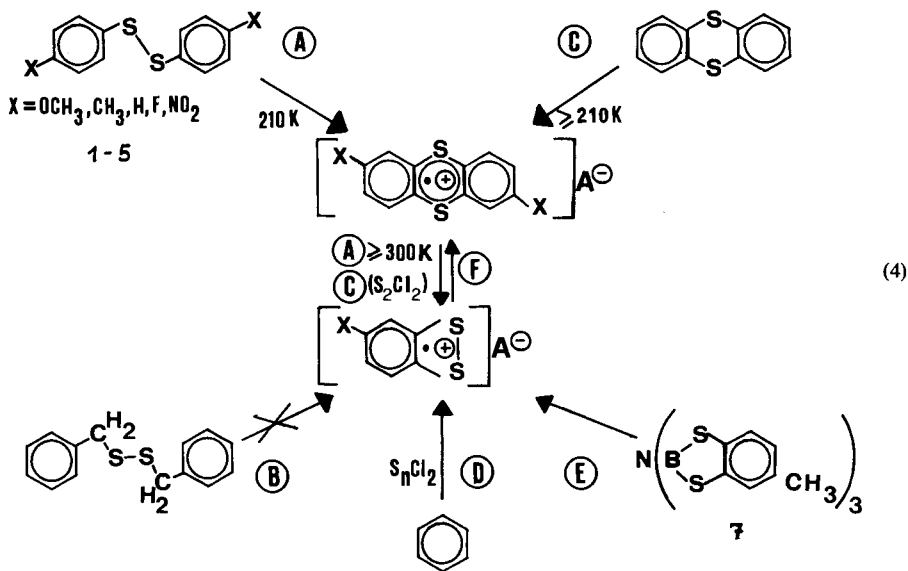
Redox Component (+ $\text{AlCl}_3/\text{H}_2\text{CCl}_2 \rightarrow$)				
	g	$a(\text{mT})$	g	$a(\text{mT})$
6 	————— ^{a)}		————— ^{a)}	
 + S_2Cl_2	2,0082	0,132	2,0150	0,120
7 N  ²⁴⁾	2,0080	0,161	2,0150	0,150

^{a)} The ESR quintet observed ($g = 2.0075$, $a_{\text{H}} = 0.143$ mT) belongs presumably to dibenzyl disulfide radical cation.

Dibenzyl disulfide (**6**) was chosen as a control system since, although it contains a disulfide bridge and phenyl rings, one would anticipate that the intervening methyl groups could hinder isomerization to a thianthrene. The ESR of oxidized 6^{\oplus} shows a g value of 2.0075 and only a quintet with hydrogen coupling constant $a_{\text{H}} = 0.143$ mT, inconsistent with that of thianthrene, but consistent with reduced spin density on sulfur and increased density in the adjacent methylene groups. Surprisingly, the borolyamine **7**²⁴ reacted immediately to give a quintet ESR signal identical to the proposed dithiete structure for **2**. After remaining at 0°C for 9 hrs. a second ESR signal developed attributable to the 2,7-dimethylthianthrene radical cation. Reaction between thianthrene and S_2Cl_2 , $\text{AlCl}_3/\text{CH}_2\text{Cl}_2$ resulted in the same ESR spectrum, whether all three components in CH_2Cl_2 as solvent were reacted together or whether a radical cation of thianthrene was first generated and S_2Cl_2 was added to the solutions. In both cases, an ESR spectrum of the radical cation of thianthrene as well as a second signal similar to that of diphenyl disulfide (Figure 3) and assigned to the benzodithiete radical cation were observed.

C. The Diphenyl Disulfide → Thianthrene Radical Cation Rearrangement and Its Implications

A reaction scheme summarizing the ESR results obtained from $\text{AlCl}_3/\text{CH}_2\text{Cl}_2$ oxidation of the phenyl/sulfur containing systems studied is presented in (4).



Although it must be emphasized that the mechanisms for these reactions are as yet unknown, from the ESR spectra of the radical cations generated from compounds 1–7 under $\text{AlCl}_3/\text{H}_2\text{CCl}_2$ reaction conditions the following oxidations and rearrangements are inferred:

A. Cold solutions of diphenyl disulfides undergo facile rearrangement to thianthrenes. Further heating of the radical cations $1^{\oplus} - 4^{\oplus}$ resulted in the formation of another radical cation species assigned the structure of a benzodithiete $^{\oplus}$.

B. If there are intervening methylene groups, as with dibenzyl disulfide (6), formation of the thianthrene is hindered and the ESR of what appears to be the parent disulfide $^{\oplus}$ is observed.

C. Thianthrene radical cations from $\text{AlCl}_3/\text{CH}_2\text{Cl}_2$ oxidation of the neutral species may be further reacted in the presence of S_2Cl_2 to obtain the ESR signals assigned to a benzodithiete $^{\oplus}$ (Figure 3).

D. Reaction of benzene and SCl_2 or S_2Cl_2 in the presence of $\text{AlCl}_3/\text{CH}_2\text{Cl}_2$ results first in the ESR signal of a benzodithiete $^{\oplus}$ followed after further reaction by that of a thianthrene radical cation.

E. Other compounds, such as the tris(benzodithiaboroly)amine 7, also react with $\text{AlCl}_3/\text{CH}_2\text{Cl}_2$ to form a benzodithiete $^{\oplus}$ followed by a thianthrene radical cation.

F. ESR spectra containing signals from both the known thianthrene radical cation and the unknown benzodithiete radical cation are observed from both reactions C and D.

The presented experimental results notwithstanding, several questions remain to be answered concerning both the structure and more importantly the formation of the intermediate species, here assigned as a benzodithiete^{•⊕}. As shown in (4), this species is formed not only during the AlCl₃ induced rearrangement of diphenyl disulfides, but also by the addition of S₂Cl₂, SCl₂, or even S₈ to solutions of benzene or derivatives and AlCl₃/CH₂Cl₂^{6,23}. Here, the question of where the hydrogens from the sulfur substitution centers are, also remains open. Corroborating evidence for the proposed radical cation structure comes from benzene/sulfur oxidation experiments using ³³S, ¹³C, and ²H isotopic labelling⁶ and various substituted benzenes²³. However, all the ESR data gathered only indicate that this radical cation must have a structure with C_{2v} symmetry, and other compounds, e. g. dithio-*o*-benzoquinones, can not be ruled out. It should be pointed out, however, that dithiete derivatives are known, have been structurally characterized²⁵, and the ESR spectra of their radical cations²⁶ and subsequent rearrangement products are known. In addition, one of the best indications that a benzodithiete radical cation is indeed formed comes from the strong initial ESR signal produced on treatment of the borolyamine **7** with AlCl₃/CH₂Cl₂. Here, a ready-made dithiete moiety is present, liberated upon the oxidative cleavage of the boron sulfur bonds [(4): Reaction E] and results, after further reaction, in a substituted thianthrene radical cation. In addition, although the reaction pathway between the thianthrene and benzodithiete radical cations is not precisely known, ESR spectra containing, simultaneously, signals from both species may be obtained from either direction, e. g., via the reaction of the borolyamine **7** with AlCl₃ [(4): Reaction E] or from thianthrene oxidation in the presence of a sulfur source [(4): Reaction D].

The scope of this reaction is not limited to the systems studied here. The halogenation of benzene is one of the longest known and most investigated reactions in aromatic organic chemistry^{17,27}. Industrially²⁷, the process is carried out in the liquid phase by the addition of gaseous chlorine to a fine suspension of about 1.5% FeCl₃, as a catalyst, in benzene held at 20 – 45 °C. The main product is usually monochlorobenzene, although, *o*- and *p*-dichlorobenzenes are also present. FeCl₃ is not the only possible catalyst for this process, SbCl₃, I₂, SbCl₅, and the Friedel-Crafts catalyst AlCl₃ are also effective^{15,27}. For the dichlorination process, the selectivity of *p*-dichlorobenzene formation is substantially increased by the addition of a sulfur containing co-catalyst such as S₂Cl₂, S₈²⁸, and even thianthrene itself²⁹. Therefore in this context, the study of the rearrangement of diphenyl disulfides to thianthrenes and, upon further reaction, to benzodithietes contributes additional information to the unknown and rather complicated sulfur-catalyzed, industrial Friedel-Crafts chlorination of benzene.

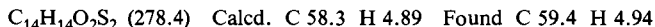
This work has been supported by *Land Hessen, Deutsche Forschungsgemeinschaft*, and *Fonds der Chemischen Industrie*. We would like to thank Miss C. Roesner for help in preparation of some of the disulfides. J. C. G. is indebted to the *Alexander von Humboldt-Stiftung* for a Fellowship during the research.

Experimental Part

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

High resolution ESR spectra of the radical cations were recorded on a Varian E 9 spectrometer. The splitting parameters and g values were determined using the perylene radical anion ($a_{\text{H}} = 0.34937, 0.30473$ and 0.04503 mT, $g = 2.0081^{20}$) and are considered correct within 1%.

Compounds used for study: Bis(4-methylphenyl) disulfide (**2**), diphenyl disulfide (**3**), and bis(4-nitrophenyl) disulfide (**5**) were purchased from EGA and recrystallized from ethanol before use, although unrecrystallized starting material gave the same results. Bis(4-methoxyphenyl) disulfide (**1**) and bis(4-fluorophenyl) disulfide (**4**) were prepared by I_2 oxidation of the parent thiols¹⁵) and recrystallized before use. Mass spectra of **1** and **4** were recorded on a Varian MAT CH 7 and NMR spectra of **1–5** on a Varian T 60. Both showed that the expected disulfides were present. Elemental analysis of **1** gave:



Radical cations were generated from **1–5** by placing AlCl_3 in the ESR tube with the parent compound and evacuating. CH_2Cl_2 that had been distilled from and stored over AlCl_3 was condensed in and the tube sealed off. Solvent was not allowed to interact with the AlCl_3 /compound mixture until immediately before the tube was placed in a pre-cooled ESR cavity at -60°C .

Generation of the second radical species was achieved by allowing the ESR tube to warm to room temperature for about 1 min or by placing it in a 80°C water bath for approximately 1 min before reinserting in the -60°C ESR probe.

Radical cations from thianthrene/ S_2Cl_2 were generated using two methods:

1) Under a stream of dry N_2 , S_2Cl_2 was added to an ESR tube, which was freeze-thaw degassed to get rid of O_2 . Still under N_2 and at -196°C , thianthrene and AlCl_3 were added and CH_2Cl_2 condensed in. The tube was sealed off and placed in the pre-cooled ESR cavity.

2) Thianthrene and AlCl_3 were added to the ESR tube under N_2 and CH_2Cl_2 was condensed in. After the development of a well resolved ESR spectrum of the thianthrene radical cation, the tube was opened under N_2 and S_2Cl_2 was added. Both procedures resulted in the formation of the same final spectrum. In all experiments the radical solutions were highly colored.

ESR spectra were simulated using the program ESPLOT, which contains some subroutines from the optimization program ESOP kindly provided to us by Prof. A. v. Zelewsky of the University of Fribourg, at the computer center of the University of Frankfurt.

¹) Part 50: H. Bock and W. Kaim, Acc. Chem. Res. **15**, 9 (1982).

²) H. Bock, W. Kaim, H. Nöth, and A. Semkow, J. Am. Chem. Soc. **102**, 442 (1980).

³) Cf. e. g. W. Kaim and H. Bock, J. Organomet. Chem. **164**, 281 (1979); M. Kira, H. Bock, H. Umino, and H. Sakurai, *ibid.* **173**, 39 (1979), or H. Bock, W. Kaim, M. Kira, and R. West, J. Am. Chem. Soc. **101**, 7667 (1979).

⁴) H. Bock, U. Stein, and A. Semkow, Chem. Ber. **113**, 3208 (1980); cf. also H. Bock, G. Brähler, D. Dauplaise, and J. Meinwald, *ibid.* **114**, 2622 (1981).

⁵) H. Bock, W. Schulz, and U. Stein, Chem. Ber. **114**, 2632 (1981).

⁶) Thesis U. Stein, Univ. of Frankfurt 1980.

⁷) Cf. the summary by R. Gleiter and J. Spanget-Larsen, Curr. Top. Chem. **86**, 139 (1979).

⁸) H. Bock, G. Wagner, and J. Kroner, Chem. Ber. **105**, 3850 (1972).

⁹) B. Solouki and H. Bock, Inorg. Chem. **16**, 665 (1977).

¹⁰) H. Bock and W. Kaim, Chem. Ber. **111**, 3552 (1978).

¹¹) K. Kimura, S. Katsumata, Y. Aohiba, T. Yamakazi, and S. Iwata, Handbook of the He(I) Spectra of Fundamental Organic Molecules, Halstead Press, New York 1981.

¹²) H. Bock and B. Ramsey, Angew. Chem. **85**, 773 (1973); Angew. Chem., Int. Ed. Engl. **12**, 734 (1973).

- 13) Cf. the review on sulfur compound structures by *P. H. Lauer* in *Sulfur in Organic and Inorganic Chemistry* (Ed. *A. Senning*), M. Dekker, New York 1972.
- 14) *A. A. Ponomarenko*, *Dopovidi Akad. Nauk Ukr. RSR* **1963** (a), 1212 [Chem. Abstr. **60**, 4035 G (1964)].
- 15) *J. March*, *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, McGraw-Hill, New York, N. Y. 1968.
- 16) *L. Brenner, Y.-H. Lai*, and *K. P. Vollhardt*, *J. Am. Chem. Soc.* **103**, 3609 (1981), and references therein.
- 17) *G. Olah*, *Friedel-Crafts and Related Reactions*, Interscience Publishers, Inc., New York 1963–1964.
- 18) *V. A. Sergeev*, *Vysokomol. Soedin., Ser. A* **1977**, **19**, 2754 [Chem. Abstr. **88**, 62635 (1978)]; *ibid.* Ser. B **1979**, **21**, 252 [Chem. Abstr. **91**, 21225 (1979)].
- 19) *O. Shigeru, Nakai, Mamoru, Furukawa*, and *Naomichi*, *Chem. Ind. (London)* **45**, 1438 (1970).
- 20) Cf. *K. Scheffler* and *H. B. Stegmann*, *Elektronenspinresonanz*, Springer-Verlag, Berlin 1970, and literature quoted. See also *A. Fava, P. B. Sogo*, and *M. Calvin*, *J. Am. Chem. Soc.* **79**, 1078 (1957); *H. J. Shine* and *P. D. Sullivan*, *J. Phys. Chem.* **72**, 13 (1968), or *H. J. Shine* and *L. Piete*, *J. Am. Chem. Soc.* **84**, 4798 (1962).
- 21) *U. Schmidt, K. Kabitzke, K. Markau*, and *G. Müller*, *Liebigs Ann. Chem.* **672**, 78 (1964).
- 22) Cf. Lecture Report from the Las Vegas ACS Meeting in *Chem. Enging. News*, Sept. 1, 1980.
- 23) Cf. Master Thesis of *P. Rittmeyer*, Univ. of Frankfurt 1981.
- 24) Unpublished results by *H. Bock, J. Giordan, H. Nöth*, and *B. Solouki*; the ESR spectrum will also be presented elsewhere.
- 25) *J. H. Hencker, O. Shen*, and *D. T. Tuck*, *J. Am. Chem. Soc.* **98**, 899 (1976), and literature quoted.
- 26) *G. N. Schrauzer* and *H. N. Rabinowitz*, *J. Am. Chem. Soc.* **92**, 5769 (1970).
- 27) Ullman's Enc. Tech. Chem., vol. 7, p. 681, Urban & Schwarzenberg, München-Berlin 1957; *ibid.*, vol. 8, p. 360, and references therein.
- 28) Cf. e. g. *E. Dibella*, US Pat. 4031145 (Cl. 260–650 R; CO7C25/04) [Chem. Abstr. **87**, 134448 g (1977)]; *Tenneco Chemicals*, US Pat. 4031146 (Cl. 260–650 R; CO7C25/04) [Chem. Abstr. **87**, 134449 h (1977)]; *Tenneco Chemicals*, US Pat. 4031146 (Cl. 260–650 R; CO7C25/28) [Chem. Abstr. **87**, 134450 b (1977)], or *Hooker Chemical Co*, Pat. Fr. 1361247 [Chem. Abstr. **87**, 13446 i (1977)].
- 29) *Dow Chemical Co*, *Netherl. Appl.* 7504410 (Cl. CO7C17/12) [Chem. Abstr. **86**, 139594 r (1977)].

[405/81]