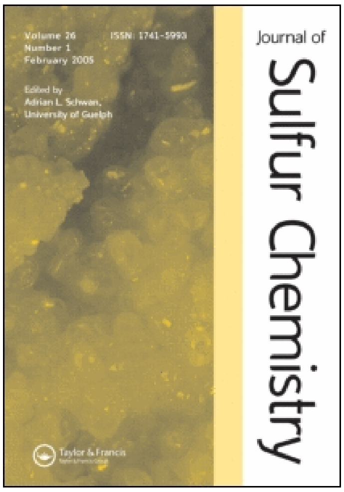

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THE PHYSICAL CHEMISTRY OF 1,2-DITHIOLE COMPOUNDS – THE QUESTION OF AROMATICITY

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The parent compound, the 1,2-dithiolylium ion, can by successive addition of vinylenethio groups give rise to higher polycyclic systems each composed of 1,2-dithiole rings with the sulfur atoms in a row. Until now, however, it has only been possible to extend the system to compounds with 3 (1,6,6aλ^4-trithiapentalene), 4 and 5 sulfur atoms in a row. The discussion of the structure of these systems has been based on results obtained by use of X-ray crystallography, electron diffraction, ^{1}H NMR-, ^{13}C NMR-, ESR-, Infrared-, microwave-, ESCA-, photo-electron spectroscopy and mass spectrometry. The results from other physico-chemical studies such as photo- and electrochemical studies have also been used in the discussion of bonding and structure. Physico-chemical data from the period 1970-1979 are included.

Based on these physico-chemical studies the 1,2,dithiolylium system seems to be an aromatic 6π-electron system. 1,6,6aλ^4-trithiapentalenes in all respects behave as bicyclic aromatic 1oπ-electron systems, which are much alike naphthalene.

These carbon-sulfur systems can be modified by replacing one or more sulfur atoms by selenium, tellurium, oxygen or nitrogen. A further modification can be made by substitution of one or more carbon atoms by nitrogen. Very few physico-chemical data are known for such systems. It is for most of these systems impossible to draw any conclusion concerning the electronic structure. In a few cases available data suggest a trithiapentalene-like structure.

I. GENERAL INTRODUCTION

The term aromatic is a rather diffuse description which has been defined in modern theoretical treatments in many different ways[1-3]. In this review the term aromatic is not used in any sophisticated way. As aromatic systems, we will consider systems which show electron delocalization, which have an electron organization like that of benzene and obey the Hückel 4*n* + 2 rule.

The classes of compounds which will be treated here are: 1,2-dithiolylium salts, trithiapentalenes, extended structures derived from these two classes of compounds, 1,2-dithiol-3-ylidene ketones and aldehydes and analogous to the trithiapentalenes with other heteroatoms in the ring system.

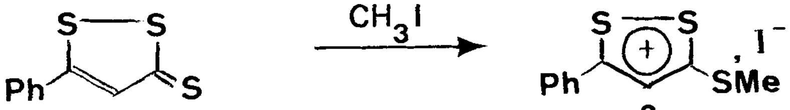
As many reviews concerning these classes of compounds have appeared during the sixties[4–10] we will mainly concentrate on literature from the period 1970-1979 in this paper. Only physico-chemical aspects will be dealt with. New aspects in synthesis and reactions can be found in[11–15].

II. 1,2-DITHIOLYLIUM SALTS

1. Introduction

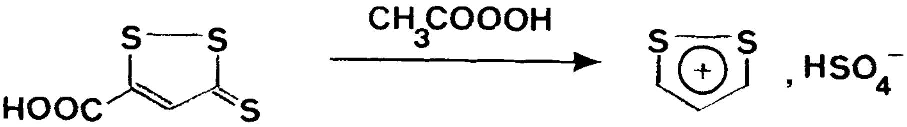
It should be noted that most neutral dithiole derivatives may be written as mesoionic compounds with a dithiolylium nucleus. Although these mesoionic formulas give account of some properties of the compounds, we will not deal with them in this presentation. Only compounds with a full positive charge on the dithiole nucleus will be treated in this chapter.

The first 1,2-dithiolylium salt 2 was prepared by Böttcher and Lüttringhaus in 1947[16] from the corresponding 1,2-dithiole-3-thione 1.



1 2

The parent compound 4 was prepared by Klingsberg in 1960[17] by oxidation of 3 with peracetic acid under spontaneous decarboxylation of the 3-carboxylato-1,2-dithiolylium hydrogen sulfate.



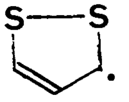
3 4

The 1,2-dithiolylium system is formally analogous to the tropylium ion system 5. Each of the two ring sulfur atoms can contribute with its free pair of 3p electrons to give an aromatic 6π electron system 6. *cf.* p. 14.

5

6

The ion has been given the following names in the literature: dithiolium, dithiylium, dithiolyl and dithiolylium. The last name, which will be used in this review, is in accordance with the IUPAC rule C-83,1[18] as the ion is formally formed by loss of an electron from the free valence position in the corresponding 1,2-dithiolyl radical 7.



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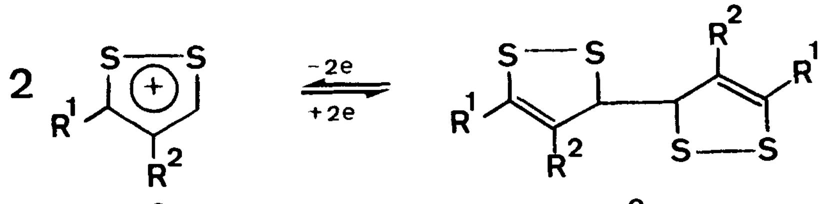
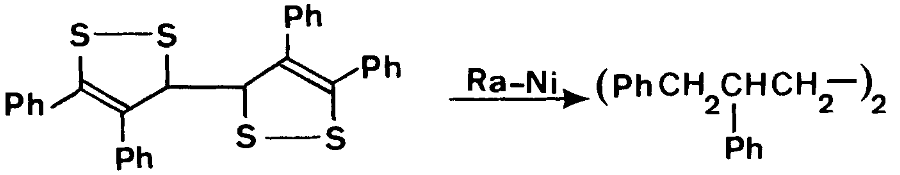
2. *Electrochemistry*

Cathodic reduction of 1,2-dithiolylium salts 8 in dry acetonitrile on a platinum electrode results in the formation of dimers 9[19] probably via a short-lived radical. The structure of the dimer was proved by Raney-nickel desulfurization[20] of 9 ($R^1=R^2=Ph$) which resulted in the formation of 1,2,5,6-tetraphenyl hexane



8 9



$$(PhCH_2\underset{Ph}{C}HCH_2-)_2$$

Figure 1 shows a typical cyclic voltammogram for a 3,4-diaryl substituted 1,2-dithiolylium salt and its dimer.

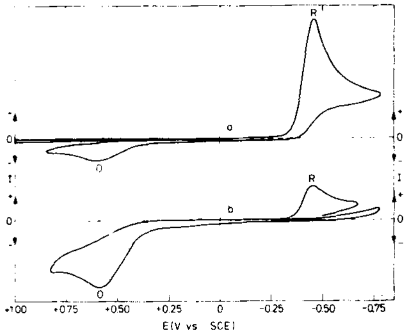


Figure 1. Cyclic voltammograms of (a) reduction of 8 ($R^1=R^2=Ph$) and (b) oxidation of 9 ($R^1=R^2=Ph$) in acetonitrile.[19] Voltage sweep rate=150 mV per second.[Courtesy of Pergamon Press.]

TABLE I

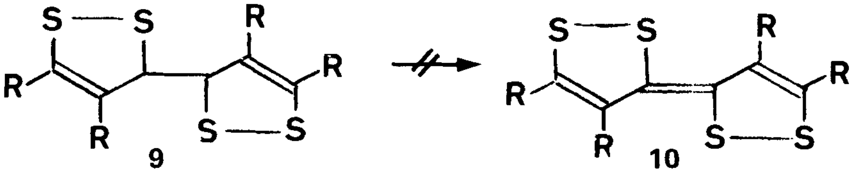
Peak Potentials for the Electrochemical Interconversion: 2 Dithiolylium Ion + 2e ⇄ Bis-(1,2-dithiole-3-yl)[19]
8 9

R_1	R_2	$E_R{}^a$	$E_O{}^b$
Ph	Ph	-0.46	+0.59
Ph	H	-0.45	+0.70
An^c	H	-0.46	+0.72
An^c	An^c	-0.33	+0.70

a. Peak potential for reduction of 8, b. Peak potential for oxidation of 9, c. *p*-Anisyl group.

The electrochemical data for a series of aryl substituted 1,2-dithiolylium salts is given in Table I.

It was found impossible to convert the dimer **9** to the corresponding tetrathiafulvalene **10**[20]. This is different from what is observed for the corresponding 1,3-dithiole derivative where the tetrathiafulvalene **11** is easily formed.[21-23]



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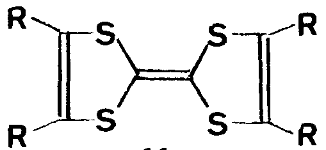

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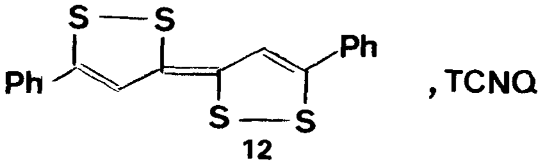
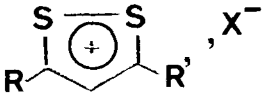


12

Compounds of type **10** have been prepared by reduction of 3-chloro-1,2-dithiolylium salts with zink in acetonitrile or methylene chloride.[24] The physico-chemical properties were not studied. Reduction of 3,4-diphenyl-1,2,dithiolylium bromide under the same conditions gave the dihydro derivative **9**. **10** (R=Ph) gave a 1:1 donor-acceptor complex with tetracyanoethylene. A corresponding complex **12** with tetracyanoquinodimethane had an electrical conductivity of 3-5 Ω^{-1} cm^{-1}. (Ref. 23 p. 74).

Cyclic voltammograms of 1,2-dithiolylium salts of type **13** where R and R′ are aryl



13

groups or *tert*-butyl are quite different from the one shown in Figure 1.[25-26] The voltammogram of 3,5-diphenyl-1,2-dithiolylium perchlorate is shown in Figure 2.

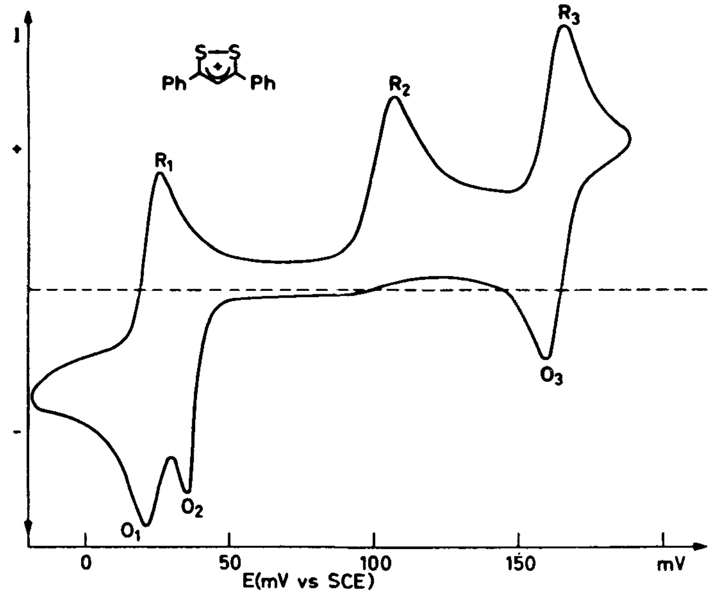
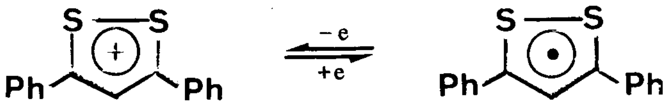


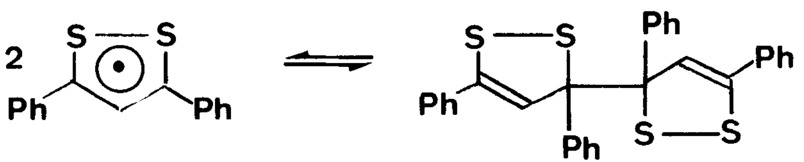
FIGURE 2. Steady-state cyclic voltammogram of **14** in CH_3CN containing Bu_4NBF_4(0.2M), sweep rate = 300 mV/sec. The initial scan shows all the peaks present in the steady-state voltammogram (ref. 26). [Courtesy of The American Chemical Society.]

The first couple R^1–O^1 approaches electrochemical reversibility on a platinum electrode and corresponds to the process **14** ⇄ **15**.



14 **15**

The existence and stability of such radicals as **15** has also been predicted by theoretical studies.[27,28] By exhaustive coulometric reduction precisely 1.0 Faraday pr. mole was consumed resulting in a grass green solution with λ_{max} = 400 nm and 650 nm. By exclusion of water and oxygen a solution of the radical could be stored for months. On cooling the color faded due to the dimerization to **16**.



15

16

The following temperature dependence of the equilibrium constant was obtained:

TABLE II

Temperature Dependence of the Equilibrium Constant, K[a,b] 26

$$\underset{16}{\text{dimer}} \overset{K}{\rightleftarrows} 2\ \underset{15}{\text{monomer}}$$

Temp, °C	+25	+20	+15	+10	+5	0	-5
K(M) $\times 10^5$	57	37	25	16	9.7	5.7	3.2

[a] Total concentration 2(15) + (16) was 1.0×10^{-3} M.

[b] Measured in dichloromethane containing $(n\text{-Bu})_4NBF_4$(0.2M)

The radical/dimer equilibrium was found to be dependent on the substituents R and R′ as seen from Table III.

TABLE III

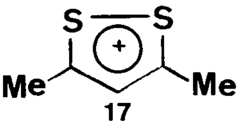
Estimate of Relative Equilibrium Constants for Dimer Dissociation in Dichloromethane at Room Temperature[26]

Compound 13	(Monomer)[a] $\times 10^{-3}$ M	(Dimer)[a] $\times 10^{-3}$ M	K_x/K_3[b]
(p-An, p-An)	0.38	0.43	0.06
(p-An, Ph)	0.51	0.37	0.13
(p-An, p-DMAPh)	0.65	0.30	0.26
(p-Tol, p-Tol)	0.80	0.22	0.54
(p-Tol, Ph)	0.81	0.22	0.55
(Ph, Ph)	0.93	0.16	1.0
(p-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 the reaction 15 ⇄ 16.

Bulky substituents must be present in the 3- and 5-positions as shown by the observation that **17** gives irreversible electrochemistry of the same type as **8**, indicating that the corresponding radical is only short-lived.



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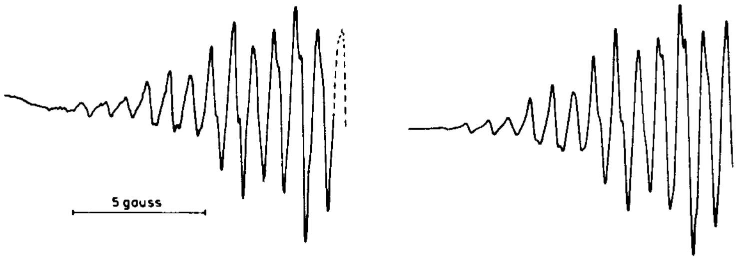
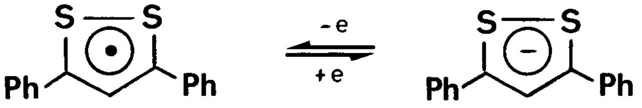


FIGURE 3. Experimental (left) and simulated esr spectra of **15** (ref. 26). [Courtesy of The American Chemical Society.]

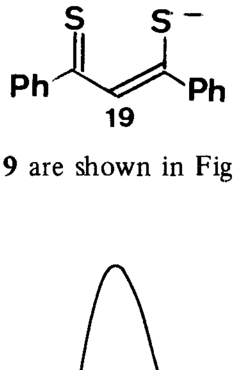
The isotropic *g* value of **15** was found to be 2.003, very close to the spin-only value of 2,0023.

The second couple R^2–O^2 in Figure 2 which is completely irreversible corresponds to the process **15** $\rightleftarrows$ **18**.



15 **18**

The irreversibility is probably due to the chemical transformation of **18** into the dithioketonate anion **19**.



19

The visible spectra of **15** and **19** are shown in Figure 4.

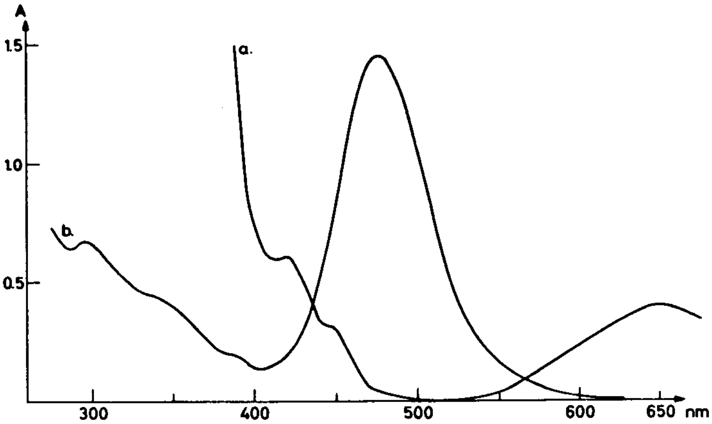
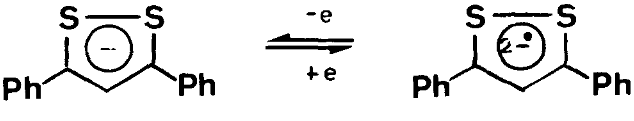


FIGURE 4. (a) Visible spectrum of **15** + dimer (total concentration 3.3×10^{-4} M) in CH_3CN containing Bu_4NBF_4 (0.1 M). (b) Uv and visible spectrum of **19** (total concentration 5.6×10^{-5} M) in CH_3CN containing Bu_4NBF_4 (0.1 M) (ref. 26) [Courtesy of The American Chemical Society.]

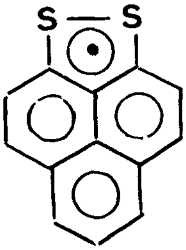
Further reduction resulted in the reversible couple R^3–O^3 which corresponds to the process **18** ⇄ **20**.



18 **20**

However, the dianion radical **20** was only stable during the times scale of cyclic voltammetry, it was not possible to prepare it by exhaustive reduction.

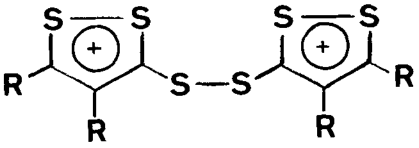
The phenaleno[1,9-cd]dithiolyl radical **21** has been shown to be monomeric at room temperature.[29] No dimerization was observed down to –95 °C. A well-resolved 36-line esr spectrum was obtained. Comparison with the esr spectrum of the phenalenyl radical showed that approx. 20% of the spin density was removed from the phenalenyl nucleus on disulfide substitution.



21

Fabian *et al.*[30] have studied the polarography of a series of alkyl substituted 1,2-dithiolylium salts and have found a linear relationship between the polarographic half-wave potentials and the energy of the lowest unoccupied orbital.

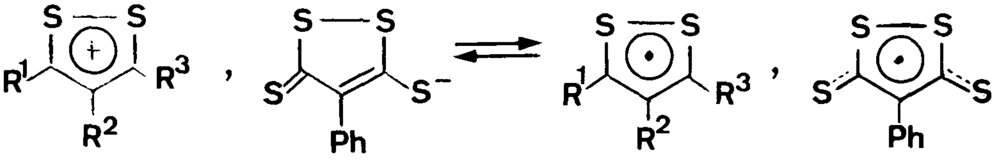
Bis-dithiolylium ions such as **22** have been reported from the anodic oxidation of 1,2-dithiol-3-thiones.[31]



22

1,2-Dithiolylium salts are found to form charge-transfer salts which have interesting electrical properties.[32–35]

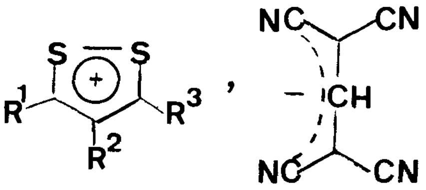
Pedersen *et al.* observed that salts of type **23** were charge-transfer complexes.[32] The electronic spectra were given for a series of complexes and the single crystal conductivity for **23** (R^1=R^3=Ph, R^2=H) was found to be 0.17×10^{-12} ohm^{-1}cm^{-1} along the



23

crystallographic *b* axis. X-Ray studies showed that the donor and acceptor were mixed in stacks, which explains the low conductivity.[33]

Catel and Mollier have studied charge-transfer salts with the tetracyanopropenide anion **24**.[35] For a series of complexes they have observed a charge-transfer band in the region 460-530 nm. They have found a linear correlation between the position of this charge-transfer band and Kosower's Z index for the solvent. The conductivity of these complexes was of the order 10^{-12} ohm^{-1} cm^{-1}.[35]



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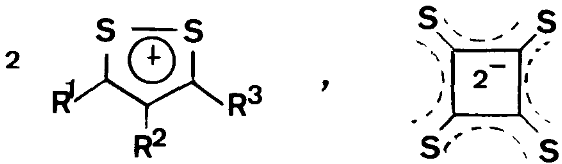
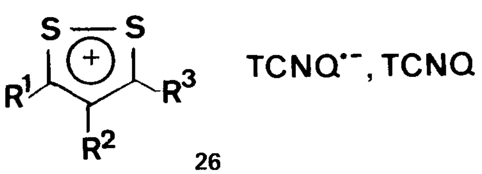
The tetrathiosquarate anion forms 2:1 complexes **25** with dithiolylium salts.[35] These complexes have a conductivity of approx. 10^{-12}ohm^{-1}cm^{-1}.



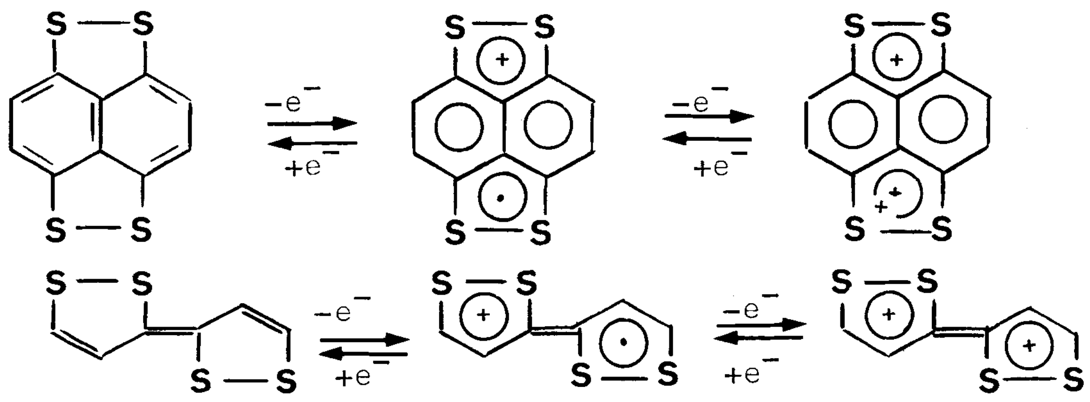
25

It was also observed that 1:2 complexes **26** were formed with tetracyanoquinodimethane (TCNQ).[35] These complexes were found to have a conductivity of the order 1 ohm^{-1}cm^{-1}.

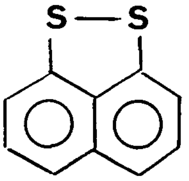


26

Neutral 1,2-dithiole derivatives may also form charge-transfer complexes in which the dithiole nucleus is transformed into a dithiolylium ion. *e.g.*

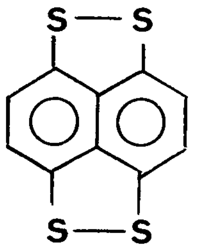


Charge-transfer complexes of the following neutral dithiole derivatives have been studied.



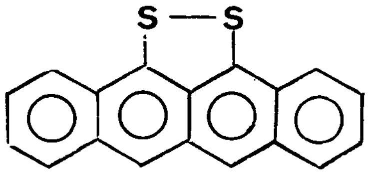
DTN

Naphtho [1,8-*cd*] -1,2,-dithiole



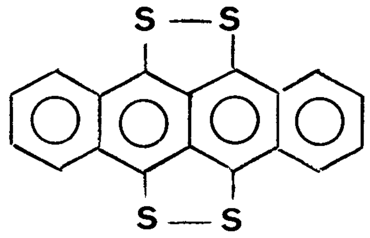
TTN

Naphtho [1,8-*cd*:4,5-*c'd'*] bis [1,2] -dithiole



DTT

Naphthaceno [5,6-*cd*] -12-dithiole



TTT

Napthaceno [5,6-*cd*: 11, 12-*c'd'*] bis [1,2] -dithiole

DTN forms a 1:1 complex with TCNQ. This complex exhibited a conductivity of 10^{-10}ohm^{-1}cm^{-1}. The UV photoelectron spectrum of DTN was studied and PMO and CNDO/S2 calculations were carried out.[36] It was found that the highest occupied molecular orbital structure is determined by interaction between sulfur lone pairs and naphthalene π levels. A PPP calculation has also been carried out on DTN.[37]

Complexes between the selenium and tellurium analogues of DTN and TCNQ have been studied;[38] they exhibit a room temperature conductivity of 10^{-7}ohm^{-1}cm^{-1} and $2x10^{-2}$ohm^{-1}cm^{-1}, respectively.

TTN forms a 1:1 complex with TCNQ.[39] This has a room temperature single crystal conductivity of 40 ohm^{-1}cm^{-1}cm^{-1}. The cyclic voltammogram of TTN exhibits two reversible oxidation steps consonant with two one-electron processes.

DTT gives a 1:1 complex with TCNQ. The room temperature single crystal conductivity is $3x10^{-6}$ohm^{-1}cm^{-1}. The differential pulse polarogram of DTT exhibits one reversible oxidation step.[40]

The conductivity of a series of TTT salts has been measured on compressed-powder pellets.[41,42] The results are summarized in Table IV.

TABLE IV

Conductivity of TTT Salts

Salt	Conductivity (ohm^{-1}cm^{-1}	ref.
(TTT)Cl, H_2O	3 X 10^{-4}	41
(TTT)Br	2 X 10^{-2}	41
(TTT)I	140 X 10^{-2}	41
(TTT)(SCN)	23 X 10^{-2}	41
(TTT)(HSO_4)	1 X 10^{-2}	42
(TTT)$(HSO_4)_2$	3 X 10^{-8}	42

A complex of special interest is $(TTT)_2I_3$ which has properties that are quite different from (TTT)I.

The reaction of iodine with TTT in nitrobenzene leads to single crystals of both iodides.[43] X-ray crystal structure determinations were carried out for both. The single crystal conductivity along the *c*-axis at room temperature was for (TTT)I 30-70 ohm^{-1}cm^{-1}. For $(TTT)_2I_3$ values of 600-1200 ohm^{-1}cm^{-1} were found and it was observed that the conductivity increased with decreasing temperature.

The temperature dependence has been studied in detail[44] and it exhibited a broad maximum of about 3000 ohm^{-1}cm^{-1} in the region 40-80°K. The temperature dependence was also studied by Hilti *et al.*[45] in connection with a study of the structure of these complexes. They gave crystallographic data which differ from those given in ref. 44.

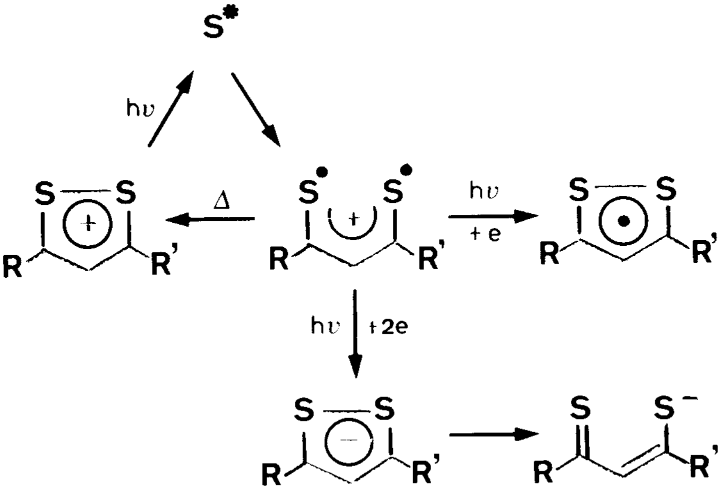
Single crystals of the TTT 1:1 complex with TCNQ have been studied between room temperature and 2K. The room temperature conductivity of this complex was 1 ohm^{-1}cm^{-1}.[46]

A single complex **12** of a bis(1,2-dithiol-3-ylidene) has been studied (*cf.* page 4).

3. *Photochemistry*

The photochemistry of 1,2-dithiolylium salts has been studied by Pedersen and Lohse[47,48] who have shown that the irradiation of dithiolylium salts in ethanol gives rise to formation of dithiolyl radicals and dithioketonate anions as found for the electrochemical reduction of the same salts.[25,26]

They have proposed the following mechanism for the reaction



In Table V are given the rate constants for the lst order decay of 1,2-dithiolyl radicals in absolute ethanol.

TABLE V

Rate Constants for the 1st Order Decay of 1,2-Dithiolyl Radicals. (ref. 48)

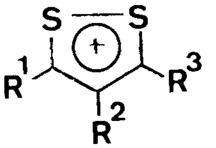
R	R^1	k (sec^{-1})
Ph	Ph	903
Ph	4–$CH_3OC_6H_4$	2020
Ph	4–$CH_3C_6H_4$	895
Ph	4–Br C_6H_4	735
4–$CH_3C_6H_4$	4–$CH_3C_6H_4$	880
4–$CH_3OC_6H_4$	4–$CH_3OC_6H_4$	2300
tert-Bu	*tert*-Bu	252
Ph	CH_3	2040
Ph	SCH_3	2480
CH_3	CH_3	4270
H	H	754

The general trend in the lifetimes is the same as that found electrochemically for the dimerization of dithiolyl radicals[26] although the radicals here decay by reaction with the ethanol.

The unsubstituted radical is surprisingly stable, there has been given no explanation for this, but the same was observed by thermolytic studies of 1,2-dithiolylium salts in the ion source of the mass spectrometer.[49]

4. *Mass Spectrometry*

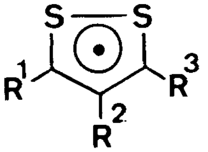
Although 1,2-dithiolylium salts **27** are true salts, and as such not volatile, reproducible mass spectra are obtained on introduction in the ion source of the mass spectrometer.[49]



27

The mass spectra obtained correspond to thermolysis products which can be rationalized if it is supposed that the primary thermolysis products are radicals or carbenes which give rise to the mass spectra either *per se* or *via* secondary transformation products.

If R^1 and R^3 are different from hydrogen the primary products are radicals **28** which, when R^1 and R^2 are phenyl, *tert*-butyl or hydrogen, give rise to the molecular peaks in the spectra.



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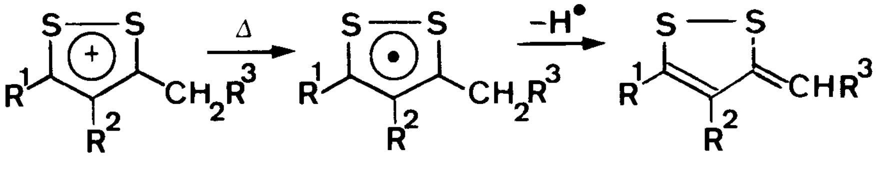
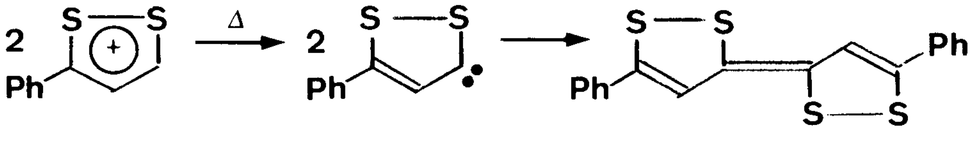
If one of the substituents has a hydrogen in the α-position the radical stabilizes itself by loss of a proton under formation of **29**.

In the case where one of the substituents R^1 and R^3 is hydrogen the primary pro-



29

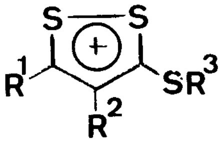
cess is the formation of a carbene **30** which dimerizes with formation of the tetrathiafulvalene **31**.



30 31

The pyrolytic behavior of the 1,2-dithiolylium salts is analogous to that reported for the iso-π-electronic pyrylium and thiapyrylium salts.[50]

3-Alkyl or aryl-thio-1,2-dithiolylium salts **32** have also been subject to thermolytic studies in the mass spectrometer.[51]



32

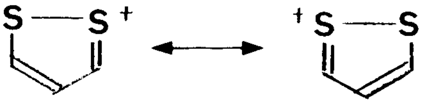
These salts have been found to behave in most respects like the simple 1,2-dithiolylium salts.

Only in the mass spectrum of 3-phenylthio-5-phenyl-1,2-dithiolylium salts were peaks corresponding to the formation of a tetrathiafulvalene observed.

There seems to exist an analogy between the electrochemical, photochemical and thermolytical behavior of 1,2-dithiolylium salts as radicals are the primarily formed products in all three kinds of fragmentation.

5. ESCA and photoelectron spectroscopy

The S2p binding energies obtained from 1,2-dithiolylium salts are situated halfway between that of 1,2-dithiolane and sulfonium sulfur.[52] This indicates that the normal charge of a sulfonium sulfur atom is shared between two sulfur atoms in accordance with the two canonical structures **33** and **34**.



33 34

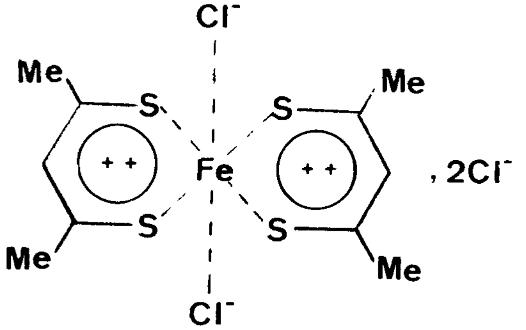
6

Schneller and Swartz[53] have studied the binding energies of both the S2p electrons and the Cls electrons in a series of 1,2-dithiolylium salts and conclude from their studies that the dithiolylium salts are best presented by the fully delocalized structure **6**.

6. *Structure determinations*

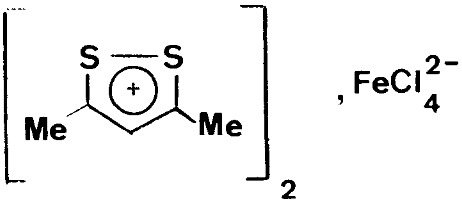
X-ray structure determination of 1,2-dithiolylium salts has been reviewed by Hordvik.[54]

A compound obtained by introducing hydrogen sulfide in acetylacetone containing ferric chloride was originally ascribed to the structure **35**.[55]



35

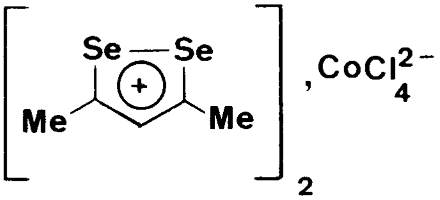
Later it was shown by electronic, infrared, Mössbauer spectra[56] and X-ray structure determination[57,58] that the structure was actually **36**.



36

Compounds with other metals such as Mn,Fe, Co,Ni and Cu have been prepared[56] and so have salts with the 3,5-diphenyl-1,2-dithiolylium ions.[59]

Heath *et al.*[60] have prepared analogous 1,2-diselenolylium salts *e.g.* **37** for structural comparison.

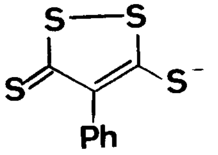


37

Some representative S—S bond lengths are given in Table VI.

TABLE VI

S–S Bond Lengths in 1,2-dithiolylium Salts 27

R^1	R^2	R^3	X^-	S–S Å	ref.
Me	H	Me	$\frac{1}{2}\ [(Fe^{II}Cl_4)^{2-}]$	2.019	57
Me	H	Me	$\frac{1}{2}\ [(Co^{II}Cl_4)^{2-}]$	2.020	60
H	Ph	H	Cl^-	2.021	61
Ph	H	Ph	$\frac{1}{2}\ [(Hg^{II}Cl_4)^{2-}]$	2.020	59
Ph	H	Ph	$\frac{1}{2}\ [(Fe^{II}Cl_4)^{2-}]$	2.010	59
Ph	H	Ph	$\frac{1}{2}\ [(Fe^{III}Cl_4)^-,Cl^-]$	2.023	62
Ph	OH	Ph	ClO_4^-	2.004	63
Ph	O^-	Ph		2.005	63
MeS	MeS	MeS	I^-	2.024	64a
Ph	H	Ph		2.065	33

Menabue *et al.*[64b] have studied electronic spectra, magnetic moments, electric conductivity and polarographic properties for a series of 3,5-diamino- and 3,5-bis(methylamino)-1,2-dithiolylium salts.

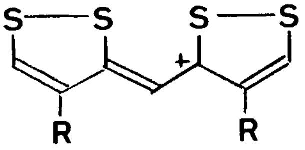
7. *Theoretical Studies*

Palmer and Findlay have in a study of a series of sulfur heterocycles[65] studied 1,2-dithiolylium salts using a linear combination of gaussian orbitals (LCGO) with 10 s and 6 p orbitals for sulfur which were augmented with a single gaussian for each of the five 3d orbitals where appropriate. Their conclusion from the calculation which include thiophene, 1,2- and 1,3-dithiolylium salts, thiapyrylium salts and 1,6,6aλ^4-trithiapentalenes, is that the d orbitals only play a minor role.

Pfister *et al.*[66] have studied the electronic spectra of unsubstituted, 3- and 4-methyl-, 3- and 4-phenyl-1,2-dithiolylium salts and compared the experimental spectra with calculated spectra using CNDO/S methods. They find that they obtain a better agreement when d orbitals are included in the calculations although the d orbitals do not contribute much to the total energy.

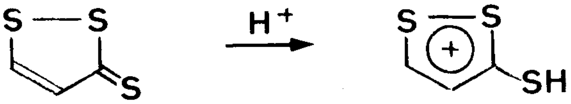
Electronic spectra of 1,2-benzodithiolylium salts, 3-mercapto-1,2-benzodithiolylium salts, 1,2-dithiolylium salts and 3-mercapto-1,2-dithiolylium salts have been interpreted by Fabian *et al.*[67] by PPP methods, and results which fit with experimental spectra are obtained.

Among other polymethine dyes in the 1,2- and 1,3-dithiolylium series Fabian *et al.* have studied compounds of type **38** by PMO and PPP methods and have obtained good agreement between calculated and experimental data.[68,69]



38

Pfister *et al.* have been able to explain the modification of the electronic spectrum of 1,2-dithiole-3-thione upon protonation[70] forming the mercaptodithiolylium ion **39** by CNDO/2 methods.



39

Further examples of calculation of 1,2-dithiolylium salts are given by Fabian.[71,72]

Pfister *et al.*[28] have examined the electrochemical reduction of 1,2-dithiolylium salts by CNDO/2 methods. The experimentally observed formation of dithiolyl radicals **15** and dithioketonate anions **19** is in agreement with the calculations.

Fabian *et al.*[30] have studied the effect of alkyl groups on the UV spectrum, the charge-transfer spectrum with iodine, and the polarographic behavior of a series of 1,2- and 1,3-dithiolylium salts and have compared the observed data with the results obtained by SCF-LCI calculations.

8. NMR Spectroscopy

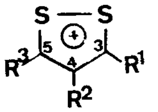
No general studies of ^1H NMR spectra have been published. Representative proton chemical shifts can be found in ref. 5.

Some ^{13}C NMR data are found in the literature. The data are summarized in Table VII.

The values given in Table VII fall in the same region as values recently published for 1,3-dithiolylium salts.[76]

TABLE VII

^{13}C Chemical Shifts of 1,2-Dithiolylium Salts



			C-3	C-4	C-5	
R^1	R^2	R^3		p.p.m.		ref.
H	H	H	176.72	142.68	176.72	73[a]
MeS	H	H	197.97	134.95	170.61	-[a]
Me	H	Me	195.49	143.19	195.49	-[a]
Ph	H	H	176.01	134.63	190.17	74[b]
4-$MeOC_6H_4$	H	H	194.65	136.05	171.79	73[a]
H	Ph	H	170.83	144.21	170.83	-[a]
Et	Ph	H	192.19	157.95	173.35	-[a]
Ph	H	MeS	181.33	132.03	195.63	74[b]
Ph	Ph	H	191.08	154.70	173.67	73[a]
4-$MeOC_6H_4$	4-$MeOC_6H_4$	H	190.85	152.94	172.18	-[a]
Ph	H	Ph	193.03	138.03	193.03	-[a]
Ph	H	4-$MeOC_6H_4$	190.63[x]	137.61	191.93[x]	-[a]
Ph	H	4-BrC_6H_4	191.41[y]	138.26	193.49[y]	-[a]
t-Bu	O^-	t-Bu	172.4	171.6	172.4	75[c]
t-Bu	O^-	Ph	177.5	170.7	153.8	-[c]
MeS	O^-	Ph	172.2	167.7	142.5	-[c]
EtS	O^-	Ph	170.3	167.9	142.4	-[c]
PhS	O^-	Ph	173.5	167.1	144.5	-[c]
t-Bu	OH	t-Bu	192.3	156.9	192.3	-[c]
t-Bu	OEt	t-Bu	195.4	158.0	177.2	-[c]
MeS	OEt	Ph	189.6	153.7	169.0	-[c]

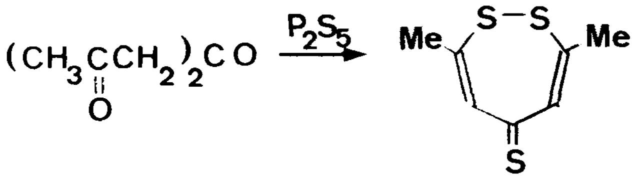
Solvent: *a.* CF_3COOD, *b.* DMSO-d_6, *c.* $CDCl_3$

The values marked x may be interchanged. The same applies to the values marked y.

III. 1,6,6aλ^4-TRITHIAPENTALENES

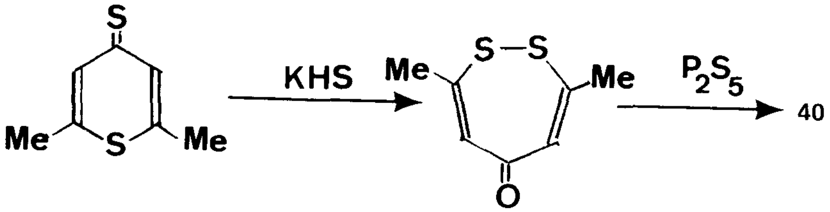
1. Introduction

In 1925 Arndt *et al.*[77] treated 2,4,6-heptanetrione with phosphorous pentasulfide and obtained a compound to which they ascribed the structure **40**, which remained unquestioned



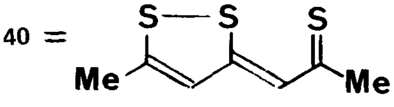
40

for many years. In 1953 Traverso and Sanesi treated 4-thiapyranthiones **41** with potassium hydrogen sulfide and isolated a compound which they formulated as **42**[78] as it was converted to **40** by reaction with phosphorus pentasulfide.



41 42

In 1958 a new structure was proposed simultaneously by Guillouzo by means of IR-spectroscopic studies[79] and by Bezzi and Carbuglio[80] on the basis of X-ray studies. The structures proposed were **43** and **44**.



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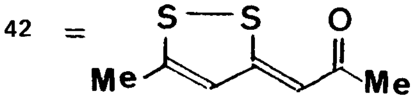
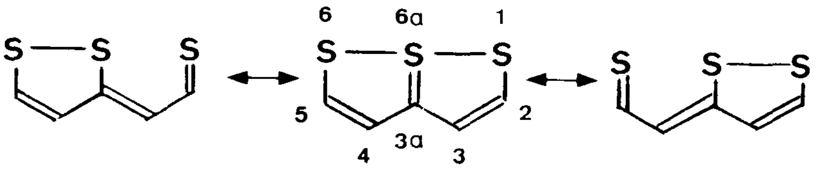


44

The structure **43**, however, was not in accordance with the observation that the two sulfur distances were equal[80] and that the ^{1}H NMR spectrum showed that the methyl groups were identical.[81] These problems were solved by the introduction of the concept of no-bond-single-bond resonance as described by the three canonical structures **45**, **46** and **47**.[81]

The no-bond-single-bond resonance problem has recently been reviewed by Gleiter and Gygax.[82]



45 46 47

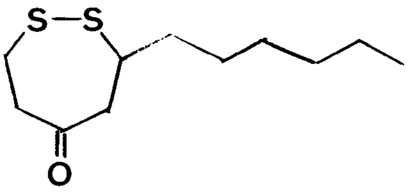
The fact that we have to deal with resonance structures where not the same atoms are bonded in the different structures has given serious problems in finding a correct nomenclature for these compounds.

The following names have been used for the system: meribicyclo-3, 5-epidithio-2, 4-pentadienethione, thiothophthene, thiathiophthene, [1,2]dithiolo[1,5-b][1,2]dithiole, α-(1,2-dithiol-3-ylidene)thioacetaldehyde, 1,6,6a$^{\mathrm{IV}}$S-trithiapentalene and 1,6,6aλ^4-trithiapentalene.

The last two names are the best as they are in accordance with the IUPAC rules. The symbol $^{\mathrm{IV}}$S is used in inorganic chemistry to indicate the oxidation state of the element. It is therefore proposed that λ^4 is used instead, as λ is the number of bonds to an atom.[83]

Compounds with structures **40** and **42** have never been prepared and it has been suggested by Zahradnik that for theoretical reasons **35** must be unstable.[84]

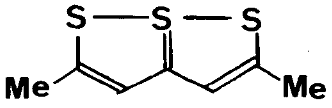
A compound with the structure **48** has recently been isolated from the Hawaiian algae *Dictyopteris plagiogramma* and *D. australis.*[85,86]



48

2. *Electrochemistry*

The electrochemical reduction of the 1,6,6aλ^4-trithiapentalenes **49** - **53** to the corresponding anion radicals has been described.[87,88] The chemistry of the anion radicals was not studied, it was only noticed that the stability of the anion radicals increases in order **49**<**50**<**51**<**52**<**53**. The half-lifetime of **49**$^{-\cdot}$ is only a few minutes at 20°C, whereas **53**$^{-\cdot}$ is stable over a period of several hours. The ESR spectra of the anion radicals were



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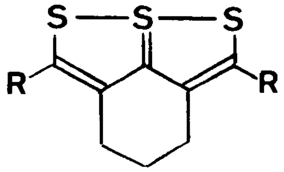
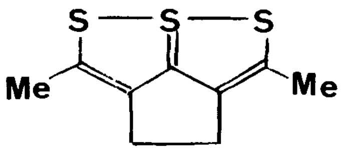


51 R : Me
52 R : Et
53 R : i-Pr

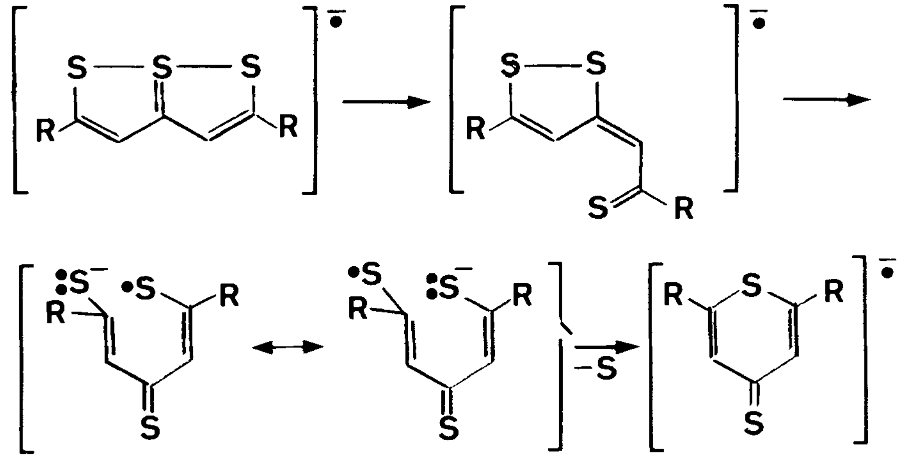


50

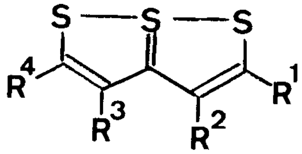
studied in the temperature range +25 – −40°C and the radical anions were found to retain a mirror plane passing through C(3a)–S(6a) indicating that the system is symmetrical.

The ESR spectra of $51^{-\cdot}$, $52^{-\cdot}$ and $53^{-\cdot}$ displayed a marked temperature dependence due to inversion of the 3,4-trimethylene chain and the restricted rotation of the 2,5-alkyl groups.[88]

An electrolytic reduction under more controllable conditions[89] revealed that the anion radicals previously described[87,88] underwent a *cis-trans* isomerization to 4*H*-thiapyranthiones, probably via the same intermediate assumed for the photochemically induced *cis-trans* isomerization.[90] More data concerning the ESR spectra were given.

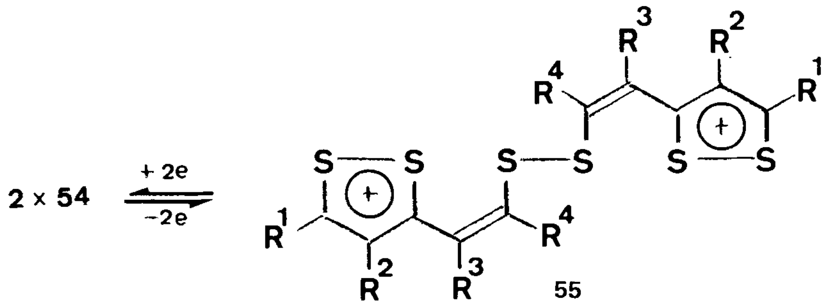


Voltammetric studies of **54** showed that the oxidation was electrochemically irreversible, indicating that no stable cation radicals were formed.[91] This is consistent with



54

the lack of an ESR signal from the resulting solution. The electrochemistry was consistent with the formation of the dimeric β,β′-dithio-bis(3-styryl-5-phenyl-1,2-dithiolylium) dication **55**. (R^1=Ph, R^2=R^3=H)



55

Reduction of the dimers resulted in regeneration of **54**. **54** (R^1=R^4=Ph, R^2=R^3=H) has λ_{max} 258 and 511nm whereas **55** (R^1=R^4=Ph, R^2=R^3=H) showed absorption at 258nm and 494, indicating that the trithiapentalene system is no longer present in the oxidized product.

The voltammetric and coulometric data for a series of substituted 1,6,6aλ^4-trithiapentalenes are shown in Table VIII.

TABLE VIII

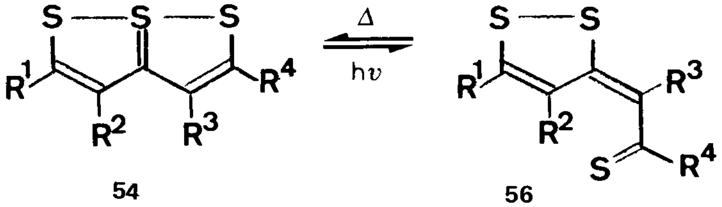
Voltammetric and Coulometric Data for Oxidation of 54 and Reduction of 55[91]

R^1	R^2	R^3	R^4	E_p^O/V	E_p^R/V	n^O	n^R	% Recovery
Ph	H	H	Ph	+0.87	+0.32	1.0	0.8	100
Ph	Ph	H	Ph	+1.16	-0.03	1.0	1.0	87
Ph	H	H	An	+0.73	+0.42	1.0	0.7	84
An	H	H	An	+0.69	+0.30	1.0	0.7	100
An	An	H	An	+0.80	+0.29	1.0	0.8	86
An	An	An	An	+0.84	-0.35	1.0	1.1	97
An=4–$MeOC_6H_4$								

Peak potentials refer to the aq.satd.calomel electrode and are for oxidation or reduction at a platinum electrode.

3. *Photochemistry*

In the same way as 1,2-dithiolylidene ketones are converted to *trans* isomers upon irradiation (*cf.* page 43), **54** has been reported to be transformed to the *trans* isomer **56** photochemically.[90,92]



The kinetic data shown in Table IX were obtained.

That the photoproducts formed are *trans* isomers is suggested by the fact that the kinetic data and the activation parameters are very much like those of 1,2-dithiolylidene ketones, and by the observation that the compounds **57** and **58** are photostable.

As seen from Table IX, unsymmetrically substituted compounds exhibit two decays corresponding to the break of one or the other of the two S–S linkages.

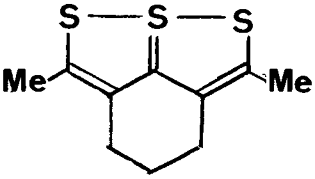
TABLE IX

Rate Constants for the Dark Reaction 56 → 54

R^1	R^2	R^2	R^4	k* (EtOH)/s^{-1}	k*(Ch)/s
H	H	H	H	2 090	
Me	H	H	H	82 (s), 2 000 (f)	
Ph	H	H	H	46 (s), 690 (f)	
H	Me	H	H	800 (s), 9 800 (f)	
H	Ph	H	H	530 (s), 11 500 (f)	
Me	H	H	Me	1 030	
Ph	H	H	Ph	360	
4-MeO·C_6H_4	H	H	4-MeO·C_6H_4	400	
4-MeO·C_6H_4	H	H	Ph	290	
Ph	H	H	Me	360	
H	Me	Me	H	1 480	
H	$CH_2{\cdot}CH_2{\cdot}CH_2$		H	Stable	
Ph	Me	H	H	570	
Ph	Ph	H	H	950	
Ph	H	Ph	H	250 (s), 8 500 (f)	
α-Thienyl	H	Ph	H	330 (s), 11 500 (f)	
Ph	Ph	H	Ph	260	
4-MeO·C_6H_4	4-MeO·C_6H_4	H	4-MeO·C_6H_4	210	
Ph	Ph	H	4-MeO·C_4H_4	320	
$CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2$		H	4-MeO·C_6H_4	10 500	
$CH_2{\cdot}CH_2{\cdot}CH_2$		H	4-MeO·C_6H_4	5.17	0.0
Ph	Ph	Ph	H	20 000	54
Ph	Ph	Ph	Ph		19 300
4-MeO·C_6H_4	4-MeO·C_6H_4	4-MeO·C_6H_4	4-MeO·C_6H_4		8 500
Me	$CH_2{\cdot}CH_2$		Me	Stable	
Me	$CH_2{\cdot}CH_2{\cdot}CH_2$		Me	Stable	
Ph	$CH_2{\cdot}CH_2{\cdot}CH_2$		Ph	Stable	

* 10^{-3} M-Solutions in 96% EtOH at 25°C [or in cyclohexane (Ch)]; s = slow; f = fast.

The activation energies (3-15 kcal mol^{-1}) and the entropies of activation (-30 - +5 cal mol^{-1}K^{-1}) are given for some representative compounds.



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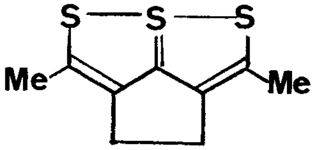

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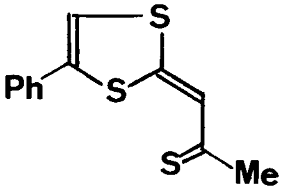
It has been claimed that *trans*-1,6,6aλ^4-trithiapentalenes should be stable compounds,[93] but a compound which has been described as a stable *trans*-trithiapentalene has been shown to be a 1,3-dithiolylidenethione **59**.[94]



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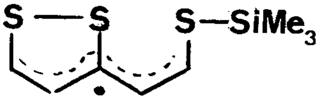
Photolysis of a mixture of **49**, di-t-butyl peroxide and trimethylsilane gave rise to radicals which were detected by their ESR signals.[95]

The ESR spectra are in accordance with radicals of type **60**. Analysis of the ESR spectra indicates a significant delocalization of unpaired spin onto sulfur.



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Analogous radicals could be detected from the irradiation of **49** and hexa-n-butylditin.

4. *Mass spectrometry*

Although mass spectra of trithiapentalenes have been used in many cases as structural proof in connection with new synthesis mechanistic studies are rare.[96,97]

The general feature of the mass spectra is that the trithiapentalenes behave as aromatic compounds giving rise to intense molecular ions.[96] The spectrum of 1,6,6aλ^4-trithiapentalene given in Figure 5 is representative of the group.

Other prominent peaks in the spectra are due to the loss of hydrogen and SH from

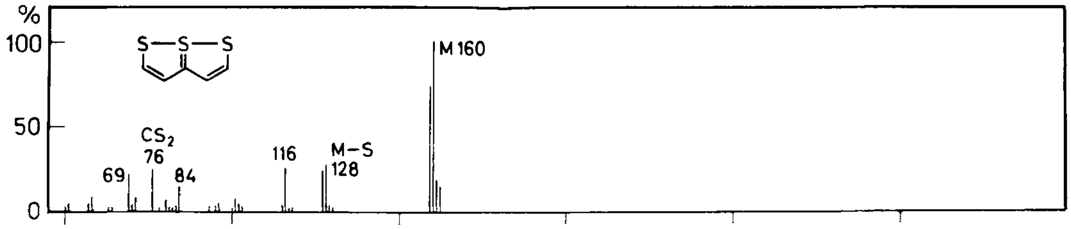
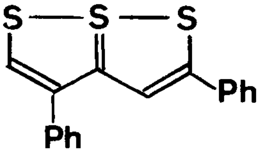


FIGURE 5. Mass Spectrum of 1,6,6aλ^4-Trithiapentalene. [Courtesy of Acta Chemica Scandinavica.]

the molecular ions. The M–SH peak derived from **61** has been ascribed to the 1,2-dithiolonaphthalene structure **62**, which is analogous to the structure of the photoproduct



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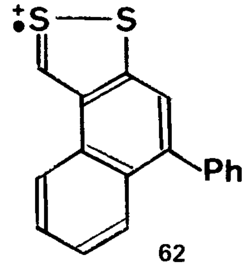
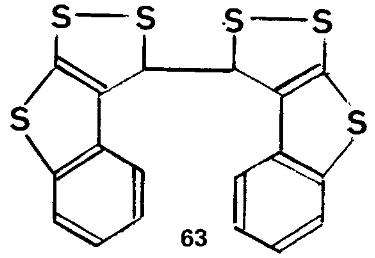


62

63 obtained from 4-phenyl-1,2-dithiol-3-thione,[98] and the M–H ion **64** derived from 1,2-dithiol-3-thiones[99] as ring closure to a phenyl substituent occurs in all cases.



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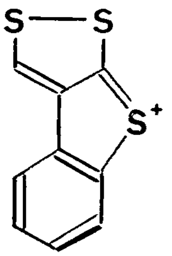
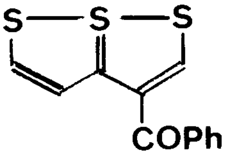


64

It was observed that if the mass spectrometer was contaminated with sulfur compounds, intense peaks due to the loss of sulfur were present.[96] This is probably due to a catalytic effect.

Surprisingly the substitution pattern in aryl substituted trithiapentalenes had only a small influence on the fragmentation.[96] If the trithiapentalene was substituted with functional groups such as in **65** and **66** a greater dependence on the substitution was observed.[97] In **66** the base peak is *m/e* 159 corresponding to loss of [PhCO + S], this peak is in the spectrum of **65**, only 30%. In **65** the base peak is due to *m/e* 77, which is Ph^+, this peak is only 15% in the spectrum of **66**.



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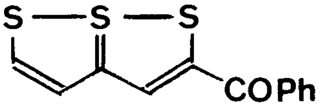
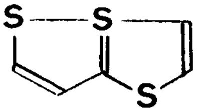


66

The reaction of activated acetylenes with 1,2-dithiole-3-thiones gives rise to compounds which can either be formulated as 1,3aλ^4,4-trithiapentalenes **67** or as 1,3-dithiolylidenethiones **68**.[100–102]



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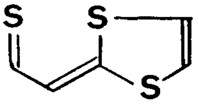

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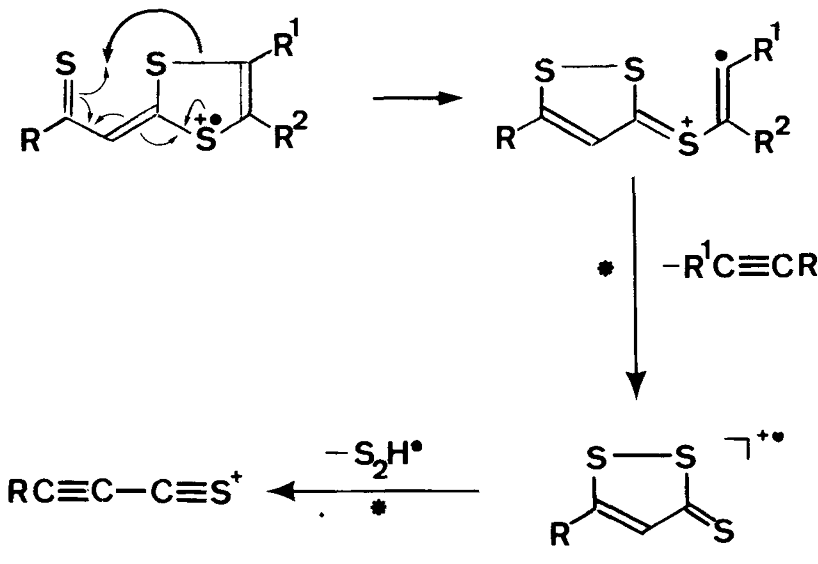
Mass spectrometric studies of these compounds, however, show, that they do not behave like an aromatic bicyclic system as **67**.[94,103] The principal fragmentation of the compounds is a retro-cycloaddition with loss of acetylenes and reformation of the 1,2-dithiole-3-thione **69**.



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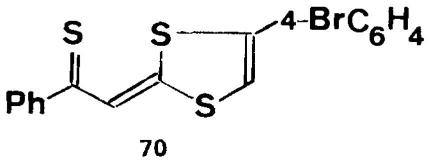
This is also in accordance with the observation that the distance between the two "disulfide" sulfur atoms in **90** is 2.91 Å, which is the same value as the Huggins "constant-energy" distance, the distance reported between presumably non-bonded, but adjacent sulfur atoms. This is longer than that found in 1,6,6aλ^4-trithiapentalenes.[104] (*cf.* Table X).



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5. ESCA and photoelectron spectra

Electron binding energies of the three sulfur atoms in trithiapentalenes should, *a priori*, be considered as a good indication of symmetry or absence of symmetry in the trithiapentalene system. If the compounds are symmetrical, two signals with the intensity ratio 2:1 should be found in the ESCA spectrum, whereas an unsymmetrical structure should give rise to three signals with the intensity ratio 1:1:1.

If we have to deal with a system of fast interconverting valence tautomers, it should be possible to see the different tautomers even in a rapid equilibrium, since the X-ray absorption-photoelectron ejection process occurs in 10^{-14} – 10^{-16} sec.

Clark *et al.*[105] have studied the core binding energies of the S2p electrons in a series of trithiapentalenes and have come to the conclusion that unsubstituted and symmetrically substituted trithiapentalenes have a symmetrical structure.

Lindberg *et al.* have reached the opposite conclusion.[52] It has hitherto been a serious problem that the ESCA spectra could not be fully resolved, and broad lines corresponding to the unresolved $S2p_{1/2,3/2}$ complex line pattern were used. Lindberg *et al.* have used the line width of elemental sulfur as a standard for the mathematical deconvolution of the experimental spectra and they can only make a satisfactory deconvolution if they use a 1:1:1 model.

Recently a gas-phase ESCA spectrum of the parent 1,6,6aλ^4-trithiapentalene with a monochromator which is able to resolve the $S2p_{1/2,3/2}$ doublet was reported.[106-108] The spectrum shown in Figure 6 was obtained.

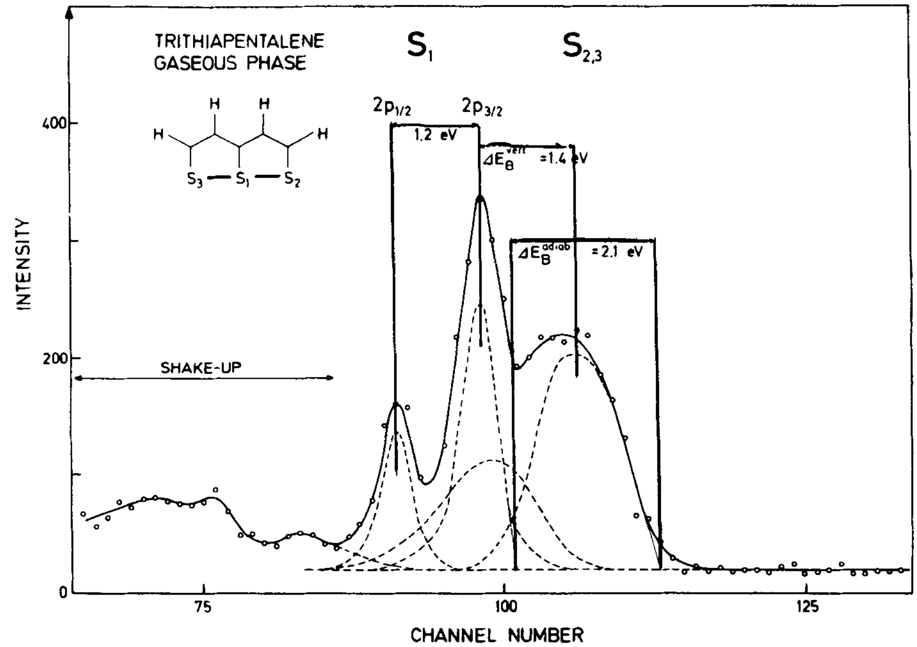


FIGURE 6. Spectrum of the S2p Lines of Trithiapentalene Recorded in the Gaseous Phase.[106] [Courtesy of Elsevier Scientific Publishing Company.]

The broad $S2p_{1/2,3/2}$ line to the right which has twice the area of the two lines to the left is ascribed to the outer sulfur atoms S(1) and S(6) whereas the doublet corresponds to S(6a).

It has not been possible to resolve the signal from the outer sulfur atoms further. The strong broadening of this signal is caused by the loss of symmetry when the photoionization takes place from one of the outer sulfur atoms whereas the symmetry is preserved when the ionization takes place at the central sulfur atom.[108]

The result obtained in these studies is thus in agreement with a symmetrical structure.

A gas-phase ESCA spectrum has also been obtained from the 2,5-dimethyl derivative. This spectrum is also in accordance with a bicyclic symmetrical structure.[108]

Coffey has obtained an ESCA spectrum of 2,5-diphenyl-1,6,6aλ^4-trithiapentalene[109,110] which is interpreted in the way that the compound is unsymmetrical, but there is some evidence that this spectrum should be taken with some reservation.[111]

Gleiter *et al.*[112] have studied the He-584 Å photoelectron spectra of a series of trithiapentalenes. They find that EH and CNDO/2 calculation of the orbital energies for an unsymmetrical structure gives energies which are very close to the energies obtained from the photoelectron spectra, although serious problems are present, due to limitations in the assumptions of Koopman's theorem.[82]

Thus it seems impossible at present to come to any definite conclusion about the structure of trithiapentalenes on the basis of photoelectron spectroscopy.

6. *Structure determination*

Since it was shown by X-ray crystallography that the structure originally proposed by Arndt was wrong,[77] structure determination by X-ray has been the most used method to obtain new information concerning the trithiapentalene system.[113,114]

In Table X the two sulfur distances in a series of trithiapentalenes are given.

It can be seen from Table X that the two sulfur distances S(1)-S(6a) and S(6a)-S(6) are normally equal when the system is symmetrically substituted and unequal in unsymmetrically substituted systems.

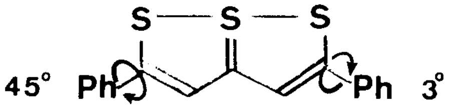
There has been some discussion whether the fact that the equal sulfur distances found in *e.g.* 2,5-dimethyl-1,6,6aλ^4-trithiapentalene can be taken as evidence that the system is really symmetrical or whether the equivalence of the two bonds is the result of the solid phase being a statistically disordered combination of compounds with a long and a short sulfur distance.[139] This last possibility was ruled out by Leung and Nyburg[119] in a re-examination of the structure. In disordered crystals of such compounds a doubling of the peaks on the electron density distribution should be observed, but such a doubling was not found.

It can be seen from Table X that not all symmetrically substituted trithiapentalenes have equal sulfur distances, it is *e.g.* not the case for 2,5- and 3,4-diphenyl-1,6,6aλ^4-trithiapentalene. This lack of symmetry is caused by a torsion of the phenyl groups in the crystals, the phenyl groups are not situated in the plane of the trithiapentalene part

TABLE X

S–S Distances in Trithiapentalenes 54

R^1	R^2	R^3	R^4	S(1)–S(6a)	S(6a)–S(6)	Ref.
H	H	H	H	2.363	2.363	115,116
Me	H	H	H	2.425	2.301	117
				2.4311	2.3076	118
Me	H	H	Me	2.358	2.358	119
Me	H	Ph	H	2.481	2.242	120
Ph	H	H	H	2.356	2.365	121
Ph	H	H	Ph	2.362	2.304	122,123
Ph	H	Ph	H	2.499	2.218	124
H	Ph	Ph	H	2.232	2.434	125
				2.236	2.430	126
4-$Me_2N–C_6H_4$	H	Ph	H	2.348	2.350	127,128
Ph	Me	H	Ph	2.255	2.398	129
SMe	NH_2	H	Ph	2.375	2.266	130,131
4-BrC_6H_4	H	PhCO	SMe	2.168	2.454	132
				2.163	2.561	
Ph	Ph	Ph	H	2.270	2.375	133
Ph	Me	Me	Ph	2.303	2.303	134
Ph	$–CH_2–CH_2–$		Ph	2.351	2.351	135
Ph	$–CH_2–CH_2–CH_2–$		Ph	2.329	2.288	136,137
Ph	Ph	Ph	Ph	2.312	2.312	138



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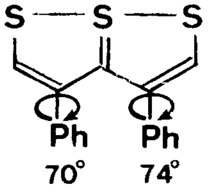


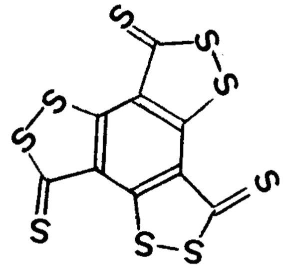
72

as seen from **71** and **72**. The observed effect of this torsion on the sulfur distances is consistent with CNDO calculations carried out by Hordvik *et al.*[140]

Hordvik *et al.* have also found that there is agreement between the calculated influence of methyl and phenyl substituents on the S–S bond length and experimental data. A 2-methyl group causes a lengthening of the S(1)–S(6a) bond whereas a 3-methyl group has the opposite effect. A 2-phenyl group has a lengthening effect on the sulfur distance dependent on the twist angle of the phenyl plane. The effect is near zero at an angle of 0° and most pronounced at 90°. A 3-phenyl group shortens the same bond, but the effect is only small and independent of the twist angle of the phenyl group.

It is obvious from this discussion that there are great problems in using X-ray data from crystal structure determinations in the discussion of the structure of the isolated trithiapentalene molecule. The anomalies observed may be caused by crystal packing. It is therefore of great importance that a structure determination by electron diffractometry in the gas phase of the unsubstituted trithiapentalene has been made.[141] Calculated radial distribution curves fit nicely with the experimental curves if a symmetrical model is used for the calculation, whereas calculation based on an unsymmetrical model is in poorer agreement with the observed results. These observations indicate that 1,6, 6aλ^4-trithiapentalene has C_{2v} symmetry in the gaseous state where there is little interaction between the molecules.

A compound prepared by Brown[142a] and originally ascribed the thione structure 73



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has by X-ray studies been found to be more correctly described as the condensed trithiapentalene Figure 7,[142b] which is a thiaanalogue of coronene.

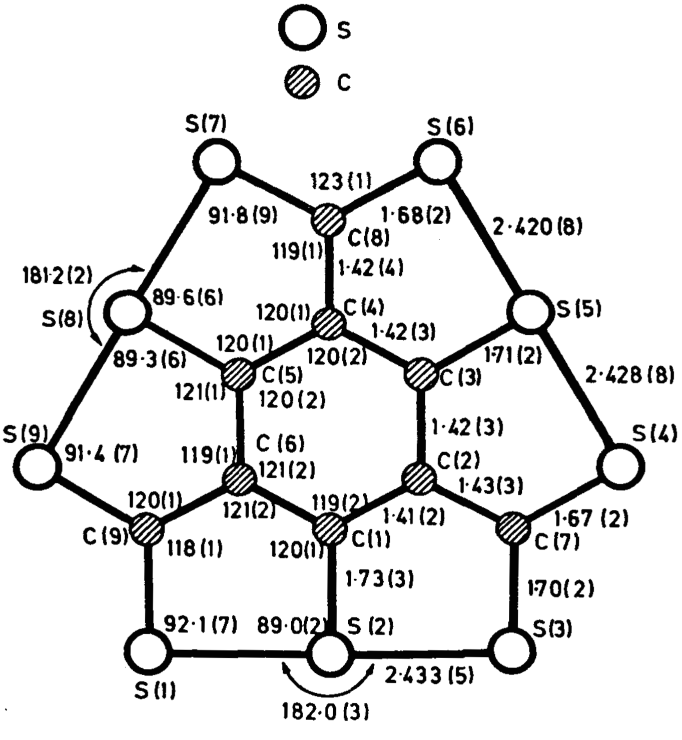
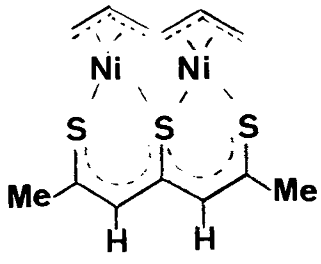
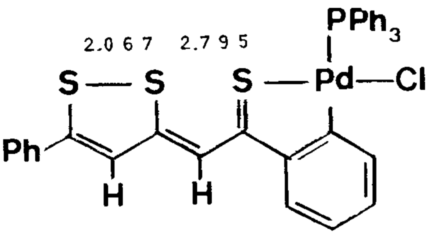


FIGURE 7. Bond Lengths (Å) and Bond Angles (°) in S_9C_9.[142b] [Courtesy of The Chemical Society.]

The structure of two metal complexes **74A** and **74B** derived from valence tautomers of trithiapentalenes has been described.[143a,143b]



74A



74B

In both complexes the geometry of the trithiapentalene moiety has been changed. In **74A** the original symmetry of the molecule with a sulfur-sulfur distance of 2.358 Å has been changed to an unsymmetrical structure with sulfur-sulfur distances of 3.361 Å and 3.342 Å, which means that there is no bonding between the sulfur atoms in the complex.

The ^1H chemical shifts of the methyl and methine protons have been changed, too.

	δMe	δCH
2,5-Dimethyl-trithiapentalene:	2.64 ppm	7.56 ppm
74A	2.41 –	6.98 –

which is in accordance with a lowering of the aromaticity of the trithiapentalene system.

The trithiapentalene can be regenerated from the complex upon reaction with carbon monoxide.

In **74B** the original sulfur-sulfur distances of 2.362 Å and 2.304 Å are changed to 2.067 Å, which is in the range found for dithiolylium salts, and 2.795 Å. The last value is close to the sulfur-sulfur distances found in compounds of type **68**.

The two complexes are together with the analogous oxygen compounds, bis(η^3-allylnickel)-1,3,5-triketonates[143c] of great interest as model substances with the same atom arrangement as found in trithiapentalenes, but without or with diminished resonance stabilization.

7. *Theoretical Studies*

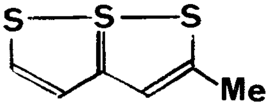
If we try to explain the properties of trithiapentalenes outlined hitherto by classical theories using classical structure with normal σ and π bonds, serious difficulties arise as pointed out by Johnstone and Ward.[144]

Johnstone and Ward have used a description for the trithiapentalenes which includes the intervention of the 3d orbitals of S(6a) which they consider to be p^2d hybridized. They found that the π-π transitions as well as the ionization potential of trithiapentalene could be predicted from SCF LCAO calculations with PPP approximation on the basis of their hypothesis.

Yamabe *et al.*[145] have calculated the electronic structure and the electronic transitions of the unsubstituted trithiapentalene and 2,5-dimethyl-1,6,6aλ^4-trithiapentalene using the semi-empirical ASMO SCF method and have obtained satisfactory agreement between predicted and experimental electronic spectra.

Clark and Kilcast[146] have made a CNDO/2 calculation on the parent trithiapentalene as well as on the 2- and 3-methyl derivatives. Whereas earlier studies have been centered around the electronic structure of the trithiapentalenes Clark and Kilcast have tried to calculate reactivities, too. The results obtained by them indicate that the 3-position should be the preferred position for electrophilic substitution, which is in accordance with experimental evidence for *e.g.* bromination[147] and formylation.[148] Further, some tendency to react on S(1) and S(6) should be present. This is in agreement with the observation that these sulfur atoms can be methylated with methyl iodide[149] or trimethyloxonium tetrafluoroborate.[150] The 2-position is predicted to be the favored position for nucleophilic attack. Nucleophilic attack has not been much studied experimentally, but attack by $C_2H_5O^-$ has been described.[151]

Clark and Kilcast have also tried to estimate the acidities of the methyl protons in **75** and **76**. The calculations show that **75** should be more acidic than **76** in accordance with the observation that **75** condenses readily with benzaldehyde to give the styryl substituted **77**[152] whereas **76** does not condense.



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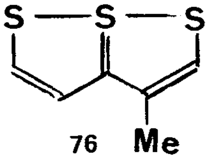

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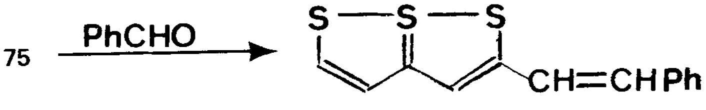

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Gleiter and Hoffman[153] have treated the trithiapentalene problem as a special case in an analysis of electron-rich 3-center bonds. They consider the three sulfur atoms a linear system where three orbitals are occupied by four electrons for σ-bonding, and π-bonding is superimposed. The stabilization obtained in this way is not expected to be great since the p_π–p_π overlap is still small when the equilibrium distance for a three-center bond involving second-row elements is reached. The potential energy of the S(1)–S(6a)–S(6) system as a function of the displacement of S(6a) from an equilibrium location between S(1) and S(6) shows a very flat minimum corresponding to a symmetrical structure if d orbitals are included in the calculation; if d orbitals are not included an unsymmetrical structure is favored.

Hansen *et al.*[140] have calculated the energies of a series of trithiapentalenes by using

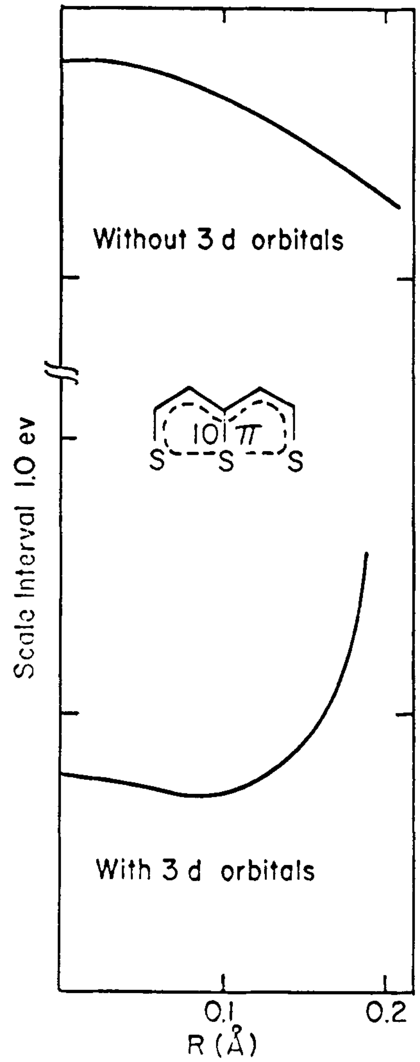
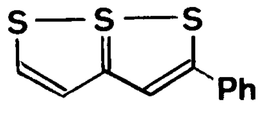


FIGURE 8. Potential energy curves for horizontal displacement of the central sulfur atom of 1,6,6aλ^4-trithiapentalene with and without 3d orbitals on S. The horizontal axis measures displacement of the central sulfur atom from the symmetrical position. (ref. 153) [Courtesy of Pergamon Press.]

the CNDO/2 method, and they have correlated these energies with X-ray data for the compounds **75**, **76**, **78** and **79** and have found a close correlation with the potential curve Figure 9. Figure 10 shows the effect of twisting a phenyl substituent.



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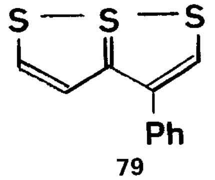

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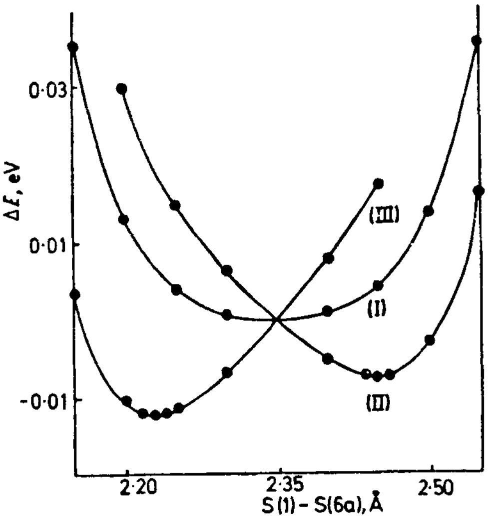


FIGURE 9. The change ΔE in CNDO/2 total energy for compounds (I)=46, (II)=75 and (III)=76 as a function of the S(1)–S(6a) bond length. [Courtesy of The Chemical Society.]

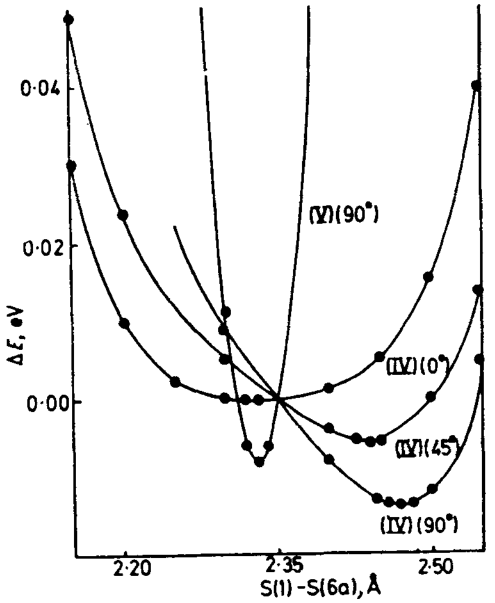
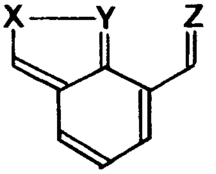


FIGURE 10. The change ΔE in CNDO/2 total energy for (IV)=78, (V)=79 as a function of the S(1)–S(6a) bond length. The twist angle of the phenyl group is indicated. [Courtesy of The Chemical Society.]

The energy curve for 1,6,6aλ^4-trithiapentalene is roughly the same as the one obtained by Gleiter and Hoffmann from extended Hückel calculations Figure 8.

Fabian[154] has by using HMO-LCI methods studied the absorption spectra of a series of trithiapentalenes.

Klingsberg[155] has pointed out that the no-bond resonance scheme used to describe the trithiapentalenes can be considered as a degenerate case of a rearrangement described by Katritzky and Boulton[156] who have studied the general rearrangement **80** → **81**.



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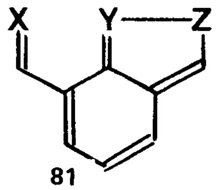

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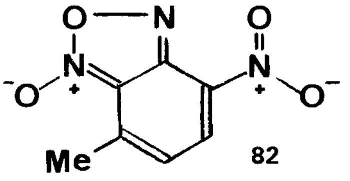
An example of such a rearrangement is **82** → **83** in nitrobenzofuroxane chemistry.



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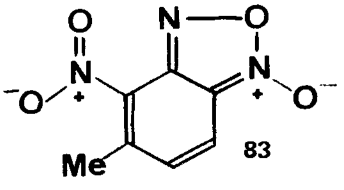


83

The symmetrical structure in the trithiapentalenes corresponds to the transition state in the Katritzky-Boulton rearrangement in contrast to the nitrobenzofuroxane case where it is the unsymmetrical structure which is stable.

So far there are no reports of the isolation of a system with C_{2v} symmetry where the central atom is a first-row element. This does not necessarily mean that participation of empty d orbitals is essential. It could be due to the fact that the overlap provided by the 2p orbitals of the central atom is not sufficient for a stabilization of the three-center bond.

Clark *et al.*[111,157] have calculated by *ab initio* methods the total energies for trithiapentalene in the symmetrical and the unsymmetrical case.

Symmetrical	-1368.220680 au
Unsymmetrical	-1368.220676 au

On the basis of this he proposes that the concept of no-bond resonance ought to be given up as there is no drastic change in the bonding pattern on distorting a symmetrical system to an unsymmetrical one within the range of S. .S distances encountered in trithiapentalenes. Clark finds it more realistic to discuss the bonding problem in terms of a single or a double minimum energy curve for the S. .S. .S system, but we need more experimental and theoretical data before we know if we have to deal with a single or a double minimum. There may also be serious problems in using different spectroscopic techniques since questions of time-scale of measurement arise, and also the question whether the property investigated is essentially a ground state property or not needs to be asked.

Clark has also discussed the d orbital participation on sulfur and he has found only a small contribution of d orbitals as seen from Table XI.

Palmer and Findlay[65,158] have by use of gaussian orbital (LCGO) approach to the Hartree-Fock method on 1,6,6aλ^4-trithiapentalene and some oxa- and aza-derivatives come to the conclusion, that the molecules have only little resonance energy and that the 3d orbitals on the central sulfur atom are not heavily involved in the bonding in these compounds.

TABLE XI

Valence electron populations in 46[111]

	σ		π		d		Total	
Atom	Ab initio	CNDO	Ab initio	CNDO	Ab initio	CNDO	Ab initio	CNDO
S6a	4.308	4.282	1.870	1.753	0.598	0.682	6.178	6.035
S1,S6	4.407	4.319	1.761	1.803	0.220	0.345	6.169	6.122
C3a	3.039	3.059	0.786	0.830	–	–	3.825	3.889
C2(C5)	3.096	3.097	0.820	0.862	–	–	3.916	3.959
C3(C4)	2.957	2.949	1.091	1.044	–	–	4.048	3.993

Palmer and Findlay[159] have by non-empirical calculations of the electronic structure of some trithiapentalenes and isosteric compounds with oxygen and nitrogen reassigned the photoelectron spectra of these molecules, and have shown substantial differences from those previously reported.[82,112]

Nyburg *et al.*[160,161] have made a conformational *ab initio* MO study on trithiapentalene and the related model compounds dithiomalonaldehyde and its anion. The results of the calculations showed that the *cis-cis* planar conformation is the most stable, in agreement with experimental observations. An energy cross section is shown in Figure 11.

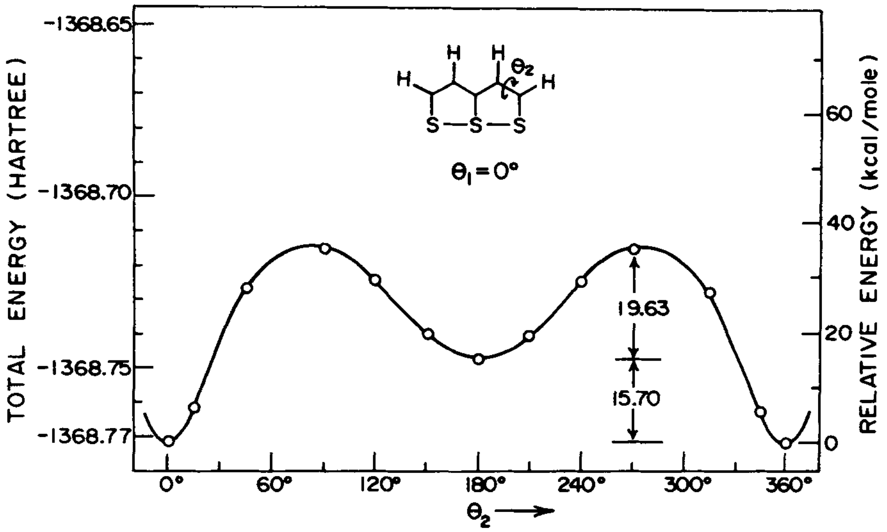


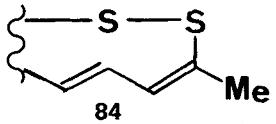
FIGURE 11. The energy cross-section for the 1,6,6aλ^4-trithiapentalene molecule along $\theta_1=0$.[161] [Courtesy of Springer Verlag.]

Two more general studies of sulfur bonding have been published. Calzaferri and Gleiter have performed calculations on various thiocarbonyl systems related to trithiapentalenes.[162] Steudel has discussed the S–S bond.[163]

8. *NMR Spectroscopy*

Although ^1H chemical shifts are given in many papers dealing with synthesis and reactions of trithiapentalenes (for a collection of characteristic chemical shifts *cf.* ref. 9), only few papers dealing with the analysis of the NMR spectra have been published.

By comparison of the chemical shift of the methyl protons in 2,5-dimethyl-1,6,6aλ^4-trithiapentalene and 2-methylnaphthalene and the hypothetical model **84** it was con-



84

cluded[164] that the aromaticity of the trithiapentalene was 65% of that of naphthalene. Dingwall *et al.*[165] also conclude on the basis of ^{1}H chemical shifts, that trithiapentalene is an aromatic system. ^{1}H chemical shifts and coupling constants for 1,6,6aλ^4-trithiapentalene are given in Table XII.[166]

TABLE XII

^{1}H NMR Data for 1,6,6aλ^4-Trithiapentalene[166] and for Naphthalene

	41	Naphthalene exp.	Naphthalene[c,d] calc.
δH(2)	549.29 Hz		
δH(3)	476.42 Hz		
^{3}J(H–2H–3)	+6.31 Hz	8.28[a]	
^{5}J(H–2H–4)	+0.08 Hz	+0.21[b]	+ 0.54
^{6}J(H–2H–5)	$|0.345^e|$	-(0.2-0.3)[a]	0.02
^{4}J(H–3H–4)	$|0.299^e|$	unobserved	- 0.58

[a] J. B. Pawliczek and H. Günther, *Tetrahedron* **26**, 1755 (1970).

[b] M. W. Jarvis and A. G. Moritz, *Australian J. Chem.* **24**, 89 (1971).

[c] G. F. Adams, *J. Phys. Chem.* **75**, 3765 (1971).

[d] INDO finite perturbation calculation.

[e] This value may be interchanged.

The problem whether the trithiapentalene system has to be considered as a mixture of the rapidly interconverting valence tautomers **45**, **46** and **47** or whether these formulas should only be considered as canonical structures of the same compound has been discussed by Pedersen and Schaumburg[166] on the basis of ^{13}C chemical shifts and relaxation times for the carbon skeleton in unsubstituted and substituted 1, 6, 6aλ^4-trithiapentalenes. If we had to deal with a 1,2-dithiolylidenethione structure such as **45** or **47**, one should expect C(3a) to have a chemical shift near that of C(2) in 2-methylthiophene, but the chemical shifts observed are quite different:

$C(3a)_{\text{trithiapentalene}}$: δ = 177 ppm

C(2) 2-methylthiophene : δ = 139.2 -

If an interconversion between **45** and **47** takes place, we would expect the relaxation time for C(2) and C(3) in trithiapentalene to be different as this interconversion should be equivalent to a fast averaging of C(2)'s chemical shift over two very different values. This process, if operating, would contribute through chemical shift modulation to the relaxation process of C(2), whereas this effect will not be operative in the case of C(3). The following relaxation times have been observed:

C(2) : T_1 = 7.2 sec

C(3) : T^1 = 10.1 -

These are both close to other data for small aromatic systems. This seems to be in accordance with the formulation of trithiapentalenes as aromatic bicyclic systems.

If the ^{13}C chemical shifts in trithiapentalenes are correlated with the charge of the respective carbon atoms a straight line is obtained which is in accordance with corresponding plots carried out for naphthalene. Figure 12.

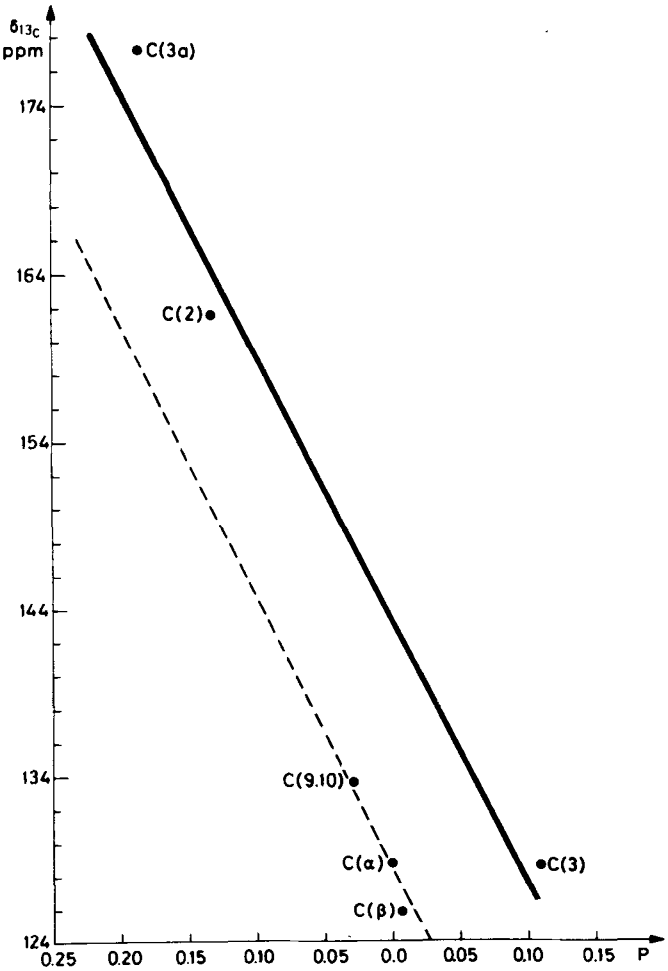


FIGURE 12. Correlation of charge densities calculated using CNDO/2 and C-13 chemical shifts. The dotted line is the correlation for substituted benzenes from G. L. Nelson *et al. J. Amer. Chem. Soc.* 94, 3089 (1972). C-α, C-β and C-9, 10 are naphthalene data taken from A. J. Jones *et al. J. Amer. Chem. Soc.* 92, 2386 (1970). The solid line is the correlation for 1,6,6aλ^4-trithiapentalene (ref.[166]). [Courtesy of Heiden and Son Ltd.]

Lapper and Pool[167] have reached the same conclusion concerning the structure of trithiapentalenes by a study of the substituent chemical shift effect. In Table 13 are given some characteristic ^{13}C chemical shifts of substituted trithiapentalenes.

The ^{1}H NMR spectrum of the parent trithiapentalene in a nematic phase has recently been analyzed and published.[168]

The interpretation of the spectrum is in accordance with the assumption that the molecule possesses C_{2v} symmetry. From the dipole-dipole coupling constants obtained

TABLE XIII

^{13}C Chemical Shift and ^{1}J(CH) Coupling Constants Observed in 1,6,6aλ^{4}-Trithiapentalenes. 81[166]

Substituent					^{13}C Chemical Shift					^{1}J Coupling constants
R_1	R_2	R_3	R_4	Ref.	C–2	C–3	C–4	C–5	C–3a	
H	H	H	H	114	161.69	128.64	128.64	161.69	177.45	C–2: 176.16 C–3: 165.3
CH_3	H	H	CH_3	–	176.78	126.94	126.94	176.78	178.91	C–3: 160.0
CH_3	H	H	H	115	176.6	126.4	128.9	161.5	177.9	
Ph	H	H	CH_3	114	177.0	124.14	128.48	176.9	179.70	
Ph	H	H	Ph	–	175.66	124.84	124.84	175.66	177.0	
H	Ph	H	Ph	–	158.48	142.57	126.19	176.48	177.65	C–2: 176.16 C–4: 163.74
H	H	Ph	Ph	–	168.7	127.65	140.8	168.9	177.30	
Ph	H	Ph	Ph	–	–	127.37	–	–	–	
$PhOCH_3$	H	$PhOCH_3$	$PhOCH_3$	–	180.92	125.90	138.84	180.92	179.11	
Ph	Ph	Ph	Ph	–	–	139.42	139.42	–	–	
Ph	H	H	H	115	176.1	125.5	127.4	160.9	177.9	
CH_3	H	Ph	H	–	176.3	127.6	141.4	158.7	178.6	
Ph	H	H	SCH_3	–	165.6	122.1	124.2	190.9	174.0	
SC_2H_5	H	H	SC_2H_5	–	177.6	122.4	122.4	177.6	174.0	

from the spectra, the relative distances between the protons can be evaluated. The data obtained are found in Table XIV.

TABLE XIV

Dipole-Dipole Coupling Constants and Relative Distances in 46

D_{23}	-1678.5 ± 0.8
D_{24}	-350.6 ± 1.1
D_{25}	-140.0 ± 0.8
D_{34}	-2862.2 ± 0.9
r_{23}/r_{34}	1.013 ± 0.006
r_{24}/r_{34}	1.939 ± 0.003
r_{25}/r_{34}	2.734 ± 0.003

D_{xy} is the dipole-dipole coupling constant in Hz and r_{xy} the distance between proton x and y. The spectrum was recorded in N-(4-ethoxybenzylidene)-4-butylaniline (EBBA).

The H–H distance ratios are in agreement with those obtained in an electron diffraction study.[141] The X-ray structure[116] deviates to a small extent from the combined electron diffraction and NMR structure, probably as a result of the distortion of the molecule in the crystalline phase.

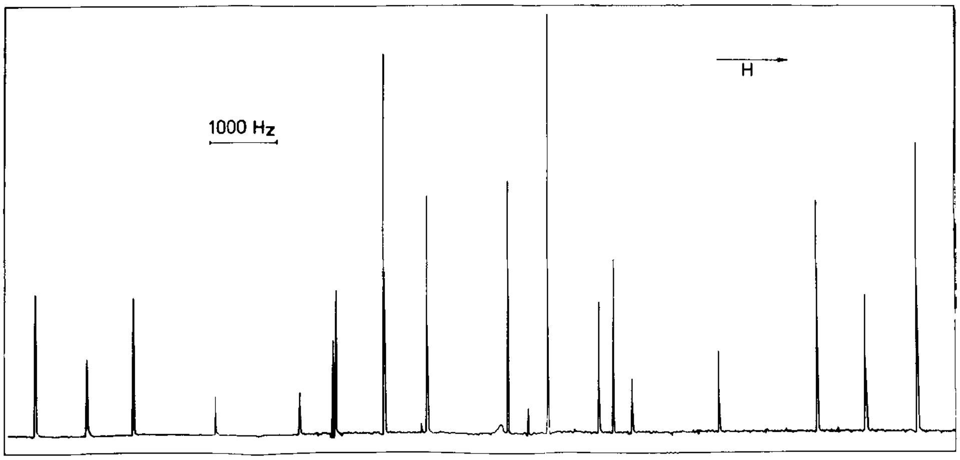


FIGURE 13. ^{1}H NMR spectrum of 1,6,6aλ^4-Trithiapentalene in EBBA.[168] [Courtesy of The Chemical Society.]

9. *Dipole Moments*

Dipole moments have been used for structural assignments. Representative data can be found in ref. 9.

Lumbroso *et al.*[169] have discussed the problem of C_{2v} versus C_s symmetry on the basis of dipole moments, and find that the recorded moments are in agreement with a bicyclic structure with tetracoordinated sulfur.

10. *Microwave Spectroscopy*

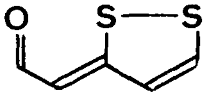
As the problem of whether trithiapentalenes have C_{2v} or C_s symmetry is equivalent to whether the central sulfur atom lies in a single or a double potential minimum, microwave spectroscopy should be well suited to solve the problem.

Due to the low vapor pressure of the parent compound it is not possible to record MW spectra with normal techniques at room temperature.[170] Attempts to record spectra at higher temperature failed, too. Only the spectrum of thiapyran-4-thione was obtained although mass spectrometrical analysis of the contents of the cell showed only the presence of a few percent thione, the rest was the original trithiapentalene.[171] This may be due to a very flat minimum with many near-lying energy levels. The formation of thiapyran-4-thione from trithiapentalene has been observed in other cases.[89,98]

IV. α-(1,2-DITHIOL-3-YLIDENE) KETONES AND ALDEHYDES

1. *Introduction*

Dithiolylidene ketones can in the same way as trithiapentalenes be considered as hybrids of several canonical forms such as **85**, **86**, and **87**.



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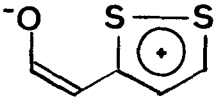

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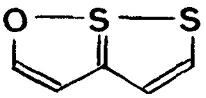
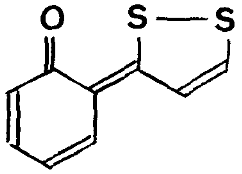


87

The compounds can be given different names corresponding to these resonance forms, *e.g.* **88**, **89** and **90**.



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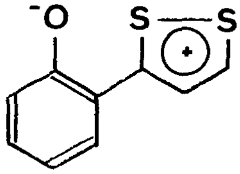

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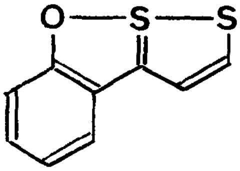


90

88 : 6-(1,2-dithiol-3-ylidene)-2,6-cyclohexadien-1-one.

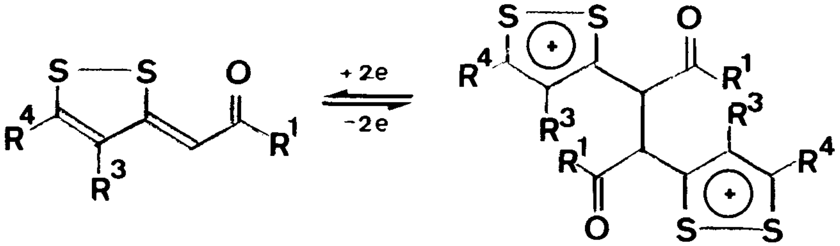
89 : 2-(1,2-Dithiol-3-ylio)phenolate.

90 : 8-oxa-1,8aλ^4-dithiacyclopenta[a]indene.
The name furothiophthene is also used in the literature.

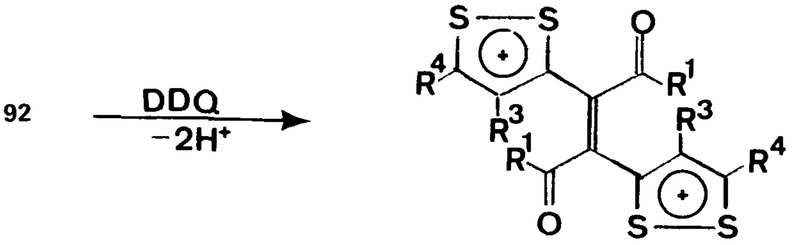
In this review we will use names corresponding to **88**.

2. *Electrochemistry*

One-electron oxidation of **91** gave the dimeric cation **92**.[172,173] **92** was not capable of undergoing further electrochemical oxidation, but treatment with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) gave rise to a new dication **93**, which upon electrochemical reduction gave the dimer **94** of the original dithiolylidene ketone **91**.



91 **92**



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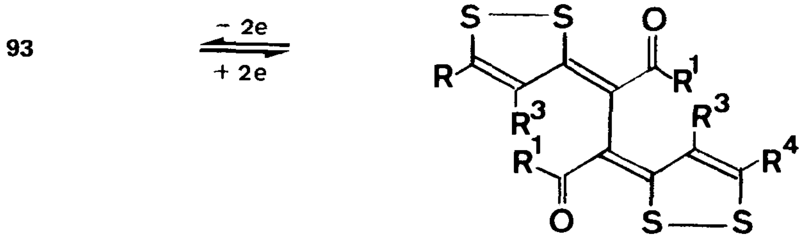

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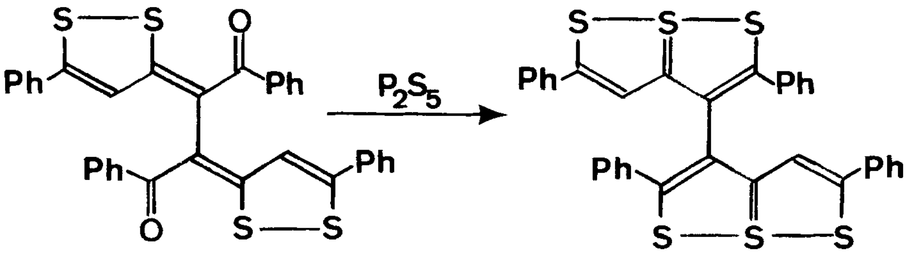
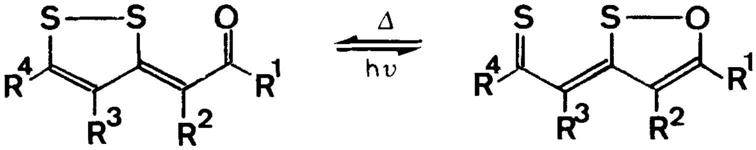
The dimer **95** could be converted into the dimeric 1,6,6aλ^4-trithiapentalene **96** by reaction with phosphorus pentasulfide.



95 96

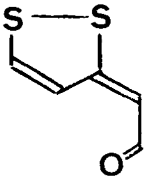
3. *Photochemistry*

It was observed by Gleiter *et al.*[174] that 1,2-dithiolylidene ketones **97** were transformed into a photoproduct upon irradiation. The photoproduct reverted to starting material by a dark process. Gleiter ascribed the O-S bonded structure **98** to the photoproduct.



97 98

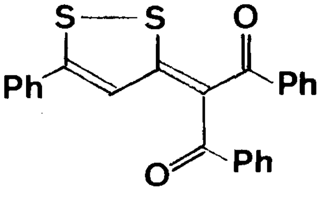
It has, however, later been shown[175-177] that the product formed is in fact the isomeric *trans*-dithiolylidene ketone **99**, which is in accordance with the HSAB principle.[178]



99

When the dithiolylidene ketones were irradiated in a methacrylic matrix they were converted into a photoproduct, but they only reverted to starting material upon prolonged heating. This is consistent with the formation of a *trans*-form as the conversion from *trans* to *cis* is a drastic geometric change and therefore it should be strongly dependent on the viscosity of the solvent.

The formation of a *trans*-form was further confirmed by the observation that no photoisomerization was observed upon irradiation of **100**[176] as the *cis*-form in this case is identical with the *trans*-form.



100

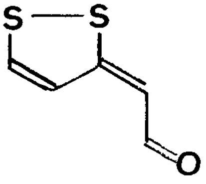
Calzaferri *et al.*[177] have studied the NMR and IR spectra of the photoproducts. They have found the following values for the carbonyl vibration.

TABLE XV

Carbonyl Vibration in *cis*- and *trans*-Dithiolylidene Ketones[177]

	ν_{CO} start.	ν_{CO} photopr.
α-(5-Methyl-1,2-dithiol-3-ylidene)acetone	1595 cm^{-1}	1645 cm^{-1}
α-(5-Phenyl-1,2-dithiol-3-ylidene)acetophenone	1552 cm^{-1}	1635 cm^{-1}

There may be several possibilities **99**, **101** and **102** for the structure of the S–S bonded photoproducts.



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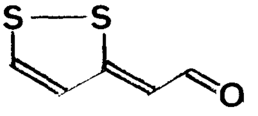

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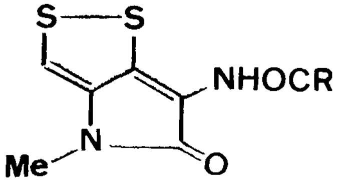


103

The ^{1}H NMR data and the substituent effect are consistent with the conformation **102**. The conformation **101** is found in a "frozen form" in a series of antibiotics, thiolutin, aureothricin, isobutyropyrrothine and holomycin[179-183] isolated from various *Streptomyces* species. They all have the general formula **103** with various R groups.

Comparison of IR carbonyl vibrations of ^{16}O and ^{18}O enriched compounds shows that in the *cis*-form there is only 20% ketonic contribution due to polar forms whereas the contribution is as high as 57% in the photoproduct.[177]

The electronic spectra of the *cis*-and *trans*-forms are very similar.[177,184]

The rate constants for a series of compounds are given in Table XVI.

TABLE XVI

Rate Constants for Thermal *trans-cis*-Isomerization of Compounds 97[176]

R_1	R_2	R_3	R_4	$k_{EtOH/s^{-1}}$*
Ph	H	H	Ph	3.1×10^{-3}
Ph	H	H	4–$MeOC_6H_4$	9.6×10^{-3}
Me	H	H	Ph	5.7×10^{-3}
Ph	H	Me	Me	3.1×10^{-3}
Me	H	H	Me	9.5×10^{-3}
Ph	H	Ph	H	3.6×10^{2}
Ph	H	Ph	Ph	5.0×10^{2}
4–MeC_6H_4	H	Ph	Ph	2.9×10^{2}
4–BrC_6H_4	H	Ph	Ph	10.6×10^{2}
Ph	Ph	Ph	Ph	2.6
Ph	Ph	Ph	H	2.5
Ph	Ph	4–$MeOC_6H_4$	4–$MeOC_6H_4$	10.3
4–$MeOC_6H_4$	4–$MeOC_6H_4$	Ph	Ph	0.35
H	Ph	Ph	Ph	45
H	H	Ph	Ph	4.3
H	Ph	H	Ph	2×10^{-2}

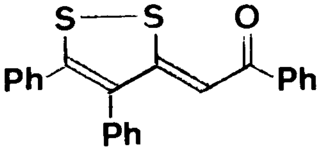
*Rate constants for the thermal back reaction from 10^{-5}M solutions in absolute ethanol.

Calzaferri[177] has from kinetic measurements estimated that there should be a difference in stability of 15 kcal/mole between the *cis*-and the *trans*-isomer. This is in good agreement with CNDO/2 calculations[185] which give a value of 20 kcal/mole for this difference if d orbitals are taken into consideration.

In a series of α-(1,2-dithiol-3-ylidene)-cycloalkanones[186] it was observed that a correlation exists between the 13–C chemical shift of the carbonyl carbon and the half-lifetime of the *trans*-form.

4. *Mass Spectrometry*

1,2-Dithiol-3-ylidene ketones and aldehydes normally give mass spectra with intense molecular ions.[187] Other intense peaks are due to the loss of acylium ions. In some cases, *e.g.* **104**, it was observed that neutral acyl radicals were expelled with charge retention on the dithiole moiety, probably due to the great ability of the dithiole nucleus to stabilize a positive charge.



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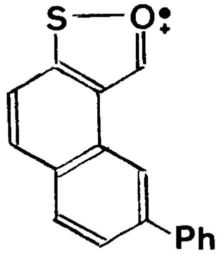
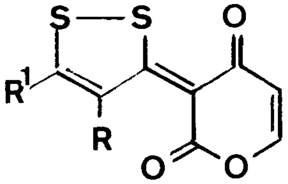
Loss of OH gives rise to ions with the same structure as **62**, which is derived from trithiapentalenes by expulsion of SH. Loss of SH from dithiolylidene ketones and aldehydes gives rise to the analogous ion **105**.



105

No definite conclusions concerning the contribution of O–S bonded structures such as **87** could be drawn from the mass spectra.

The mass spectra of a series of dithiolylidene ketones where the carbonyl group is part of a 4-pyrone system, **106**, **107** have been studied.[188,189]



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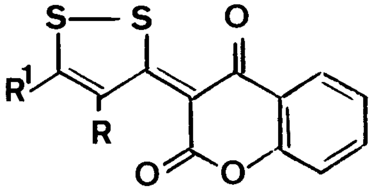


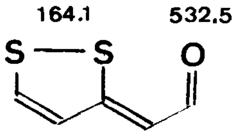
107

In both series of compounds the primary fragmentation is related to the pyrone part of the molecule. Thus the incorporation of the carbonyl group in the pyrone ring and the resulting change in charge distribution does not in principle change the fragmentation modes observed for simple dithiolylidene ketones.[187]

5. *ESCA and photoelectron spectroscopy*

Lindberg *et al.*[52] have studied the ESCA spectra of a series of 1,2-dithiolylidene ketones and aldehydes.

Calculated core binding energies in eV for sulfur and oxygen in structures which may be considered for this class of compounds are given below. The average sulfur shift observed for a series of compounds is 164.1 eV and the average oxygen shift is 531.1 eV, which means that the oxygen is considerably more negative than normal carbonyl oxygen. The negative character of the oxygen seems inconsistent with any considerable pπ-dπ bonding interaction between oxygen and sulfur. The shifts observed are in good agreement with those calculated for the structure **109**.



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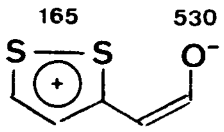

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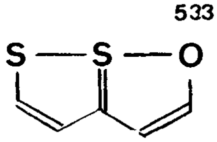

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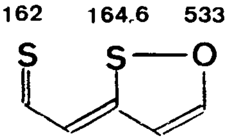

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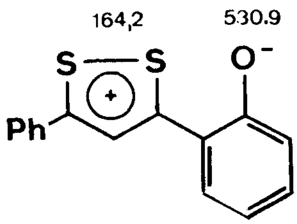
The average shifts are also very close to those observed for the true zwitter-ionic compound **112**.



112

Photoelectron spectra have been recorded and discussed for a few dithiolylidene ketones.[159,190] From the electronegativity, it could be anticipated that substituting oxygen for sulfur in trithiapentalene should yield a simpler pattern in the photoelectron spectra. This was, however, not observed.

6. *Structure Determinations*

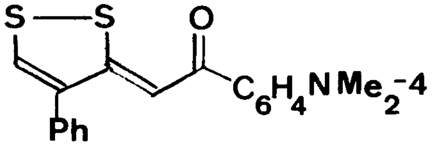
Relatively few structure determinations have been carried out on 1,2-dithiolylidene ketones and aldehydes; *cf.* Table XVII.

TABLE XVII

S–S and S–O Distances in 1,2-Dithiolylidene Ketones 97

R^1	R^2	R^3	R^4	S(1)–S(2)	S(2)–O	Ref
Me	H	H	Me	2.12	2.41	180
Ph	H	Ph	H	2.106	2.382	191
4–Me_2NPh	H	Ph	H	2.1045	2.441	192,193
				2.1101	2.287	
–$CH_2CH_2CH_2CH_2$		H	Ph	2.126	2.255	194

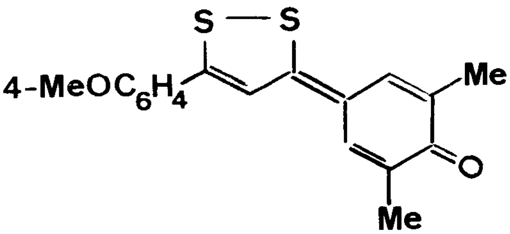
In all compounds S. .O distances of less than the sum of the van der Waal radii are observed. Pinel and Mollier[194] have discussed the correlation between the IR spectra (carbonyl vibration) and S. .O distances and have concluded that the S. .O distance is an intrinsic molecular property rather than a consequence of crystal forces. In this connection it has to be noticed that the S. .O distances in the two crystallographically independent molecules of **113** are different.[192,193]



113

Leung and Nyburg[195] have pointed out that there is a correlation between the differences in the electronegativity of S and X in the system S. .S. .X and the S. .S bond length in such a way that the S. .S distance decreases as the difference in electronegativity increases.

The structure of the vinylogous dithiolylidene ketone **114** has been discussed.[196,197]



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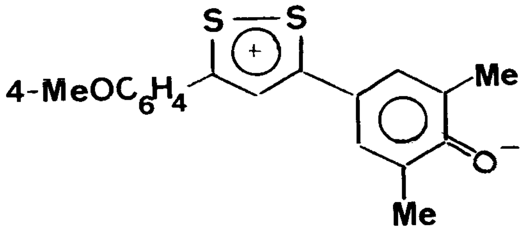


115

On the basis of the X-ray structure determination it is concluded that the structure is described well by the two resonance hybrids **114** and **115**. The hybrid **114** predominates in the ground state.

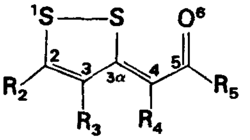
7. NMR Spectoscopy

Lindberg *et al.*[198] have studied the correlation between $\delta^{19}F$ values and the S2p binding energies obtained from ESCA spectra and have found a linear correlation for **116**, **117** and some other 1,2-dithiole derivatives. This shows that the ^{19}F chemical shifts in the case of 1,2-dithiole derivatives constitute a convenient evaluation of the charge. ^{19}F chemical shifts have been used to discuss charge separation between the dithiole ring and oxygen in compounds of type **106** and **107**.[74] The shifts observed are in agreement with a rather polar structure.

A detailed study of ^{13}C NMR spectra of dithiolylidene ketones and aldehydes has been published.[199] The results obtained from ^{1}H and ^{13}C data in this study are in agreement with a structure which is a hybrid between **85** and **86**, whereas no evidence was found for a contribution from **87**.

TABLE XVIII

Carbon-13 Chemical Shifts Observed in 1,2-Dithiol-3-ylidene Ketones and Aldehydes in ppm Relative to TMS[199]



R_2	R_3	R_4	R_5	C-2	C-3	C-3a	C-4	C-5
H	H	H	H	145.71	126.72	172.04	109.89	181.12
Me	H	H	Me	160.23	124.55	171.34	109.14	190.84
Me	Me	H	Ph	154.82	130.34	173.38	104.91	183.77
Ph	H	–CH=CH–CH=CH–		174.06	122.23	178.10	124.19	170.38
H	Ph	H	Ph	143.00	134.43	170.17	107.13	182.39
Ph	H	H	Ph	161.72	122.08	172.06	106.41	182.58
Ph	Ph	H	Ph	159.25	136.16	173.78	108.41	184.14
Ph	H	Ph	Ph	163.74	123.09	173.65	123.43	183.54
H	Ph	Ph	Ph	149.40	141.93	168.60	124.92	184.91
Ph	Ph	H	H	159.67	136.27	172.05	111.15	181.88
Ph	Ph	Ph	H	162.46	136.97	167.63	125.79	184.57
Ph	H	Ph	H	163.61	182.10	169.35	124.50	181.83

It has been shown that a correlation exists between the 13–C chemical shift for trithiapentalene and the calculated electron population.[166] In the case of dithiolylidene ketones the correlation is less convincing in view of the monocyclic nature of these compounds.

The difference in chemical shift between *ortho*-and *meta*-carbon atoms in phenyl substituted compounds has been used to study the coplanarity of the substituents with the dithiole ring. In the non-coplanar case this difference is increased by 3-5 ppm compared to the coplanar case. It seems in this way possible to monitor stereochemical problems concerning coplanarity in solution.

Frandsen and Jacobsen have studied the carbon spectra of a series of compounds with structure **106** and **107** and conclude from the carbon chemical shifts that these compounds are relatively polar and best represented by polar formulas such as **86**.[74]

The proton data for the unsubstituted 1,2-dithiol-3-ylidene acetaldehyde is given in Table XIX.[199] The proton spectrum is given in Figure 14.

TABLE XIX

^{1}H NMR Data for 1,2-Dithiol-3-ylidene Acetaldehyde 85

δ(H–5)	564.29 Hz	9.405 ppm
δ(H–4)	414.57 Hz	6.909 ppm
δ(H–3)	435.73 Hz	7.262 ppm
δ(H–2)	480.45 Hz	8.008 ppm
^{3}J(H–4,H–5)	+1.68 Hz	
^{5}J(H–5,H–3)	+0.13 Hz	
^{6}J(H–5,H–2)	⩽0.05 Hz	
^{4}J(H–3,H–4)	-0.40 Hz	
^{5}J(H–4,H–2)	+0.19 Hz	
^{3}J(H–2,H–3)	+6.00 Hz	

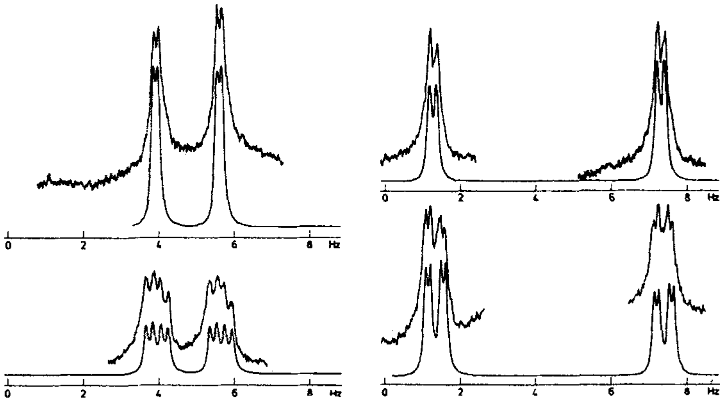
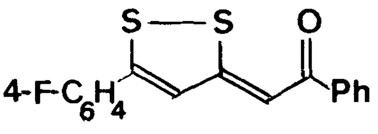


FIGURE 14. The proton spectrum of 85.[199] The experimental spectrum corresponding to the four protons is in each case shown as the upper trace, while the theoretical spectrum is shown below. H–5 top left, H–2 top right, H–4 bottom left and H–3 bottom right. [Courtesy of Heiden and Son Ltd.]

The proton data are also in agreement with a monocyclic structure.

Chemical shift reagents such as Eu(dpm)$_3$ have been used for the analysis of proton spectra from dithiolylidene ketones.[200]



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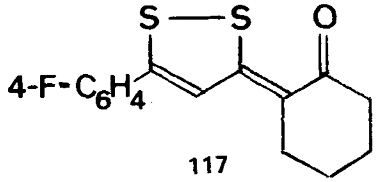


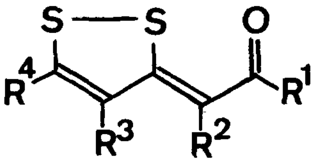
117

8. *Infrared Spectroscopy*

It was already observed by Guillouzo[79] that 1,2-dithiolylidene ketones did not display a normal carbonyl vibration in the region 1610-1750 cm^{-1} where most carbonyl compounds absorb.

The infrared spectra of dithiolylidene ketones have been studied intensively by Mollier and collaborators.[201-204]

By comparison of the IR spectra of ^{16}O compounds with those of ^{18}O enriched compounds it was possible to locate the carbonyl vibration.



118	R^1:Ph,	R^2:CN,	R^3:H,	R^4:Bu^t
119	Ph	CN	H	4-$Me_2NC_6H_4$
120	Me	H	H	Ph

118: ν_{CO} = 1554 cm^{-1}

119: ν_{CO} = 1549 cm^{-1}

120: ν_{CO} = 1574 cm^{-1}

By this method it could be shown that a band at 1460 cm^{-1} originally ascribed to the carbonyl vibration[205] had nothing to do with the carbonyl group.

From the isotopic displacement of the carbonyl vibration the contribution of true ketonic structure in the dithiolylidene ketones could be calculated. The values obtained are found in Table XX.

As can be seen there is a relatively important difference between the calculated and observed displacement. This is due to the contribution of polar forms such as **86**.

The values found for the carbonyl vibration in *trans* dithiolylidene ketones **99** have been reported.[177,184]

TABLE XX

Observed and Calculated Isotopic Displacements[201]

Ketone	Δν(cm^{-1}) obs.	Δν(cm^{-1}) calc.	% Participation of ν_{CO}
ω-Cyanoacetophenone.	32	41	78
α-(4-Phenyl-[1,2-dithiol-3-yl])acetone.	30	41.4	73
α-(4-Phenyl-[1,2-dithiol-3-ylidene])acetone.	12	37.3	34
α-(5-*t*-Butyl-[1,2-dithiol-3-ylidene]) cyanoacetophenone.	14	37.4	38
α-(5-*p*-Totyl-[1,2-dithiol-3-ylidene]) cyanoacetophenone.	10	37.3	27

Analogous sulfur-oxygen interaction has been discussed in hexahydro-9-thiaantracene as well as Se–O and Te–O interaction in the corresponding selena and tellura analogues.[206]

9. *Theoretical studies*

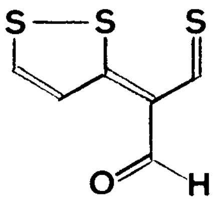
Whereas the structure of $1,6,6a\lambda^4$-trithiapentalenes has been the subject of several theoretical papers, the corresponding oxygen analogues have only received little attention.

In connection with extended Hückel calculations on compounds with a short S. .O distance the charge densities in α-(4-methyl-1,2,-dithiol-3-ylidene)acetone have been calculated.[207] It was the result of this study that if present the covalent bonding between oxygen and sulfur is only weak and there is some doubt about the direct correlation of short interatomic distances between formally nonbonded atoms and partial single bonds.

These conclusions are not in accord with the calculations by Pfister-Guillouzo[185,208,209] who has used CNDO/2 methods with inclusion of d orbitals on sulfur. These calculations show a great contribution of sulfur d orbitals. The result of these calculations is that there has been created a bond between sulfur and oxygen as if a pair of electrons had been transferred from oxygen to the d orbitals of the central sulfur atom. The pπ- dπ interaction, however, is only small between sulfur and oxygen.

The relative stability of **121** and **122** has also been calculated by CNDO/2 methods and the results obtained are shown in Table XXI.

As can be seen structure **121**, which corresponds to the trithiapentalene structure **123**, is strongly favored over the dithiolylidene aldehyde structure.



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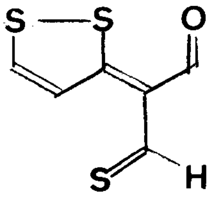

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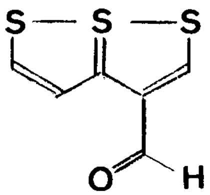


123

TABLE XXI[209]

Compound	Conformation	Method	Electronic energy (a.u.)	Total energy (a.u.)	ΔE Tota energy (kcal mole
121	CO *trans*	without d orbitals	-331.5065	-96.1038	-12.5
122	CS *trans*	without d orbitals	-333.2862	-96.0665	
122	CS *cis*	without d orbitals	-329.5726	-96.0837	
121	CO *trans*	with d orbitals on central sulfur	-331.8526	-96.4499	-44.5
122	CS *trans*	with d orbitals on central sulfur	-335.5858	-96.3611	
122	CS *cis*	with d orbitals on central sulfur	-329.8675	-96.3785	

These observations are in accord with the rate constants observed for the thermal reversal of the photoproducts formed from 1,2-dithiolylidene ketones[176,177] and trithiapentalenes.[90,92]

For α-(1,2-dithiol-3-ylidene)acetaldehyde it has been calculated[185] that the *cis*-form is favored by 20 kcal/mole if d orbitals are included and by 4.4 kcal/mole if d orbitals are omitted.

Yamabe *et al.*[145] have made ASMO SCF calculations on α-(4-methyl-1,2-dithiol-3-ylidene)acetone, but the calculated electronic transition energies do not match the experimental values particularly well.

In connection with calculations on trithiapentalenes, calculations have also been carried out on analogous oxygen systems.[158,159]

V. EXTENDED STRUCTURES

1. Introduction

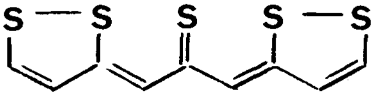
The trithiapentalene system embodies a structural principle that is capable of indefinite extension. Repetition of the vinylenethio group –CH=CH–S gives rise to a succession of higher polycyclic systems each composed of dithiole rings. The members of this family with an even number of sulfur atoms will be cations and those which have an odd number of sulfur atoms will be neutral compounds.

Until now, however, it has only been possible to extend the system to compounds with four and five sulfur atoms. Only few papers dealing with the physico-chemical aspects of these classes of compounds have been published.

It is not possible to draw any definite conclusions concerning the aromaticity of these compounds based on the data published.

The bonding in these extended structures has been discussed.[82,162]

The energy difference between the three structures **124**, **125** and **126** has been calculated.



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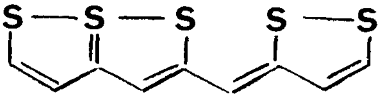

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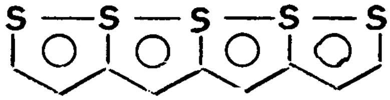


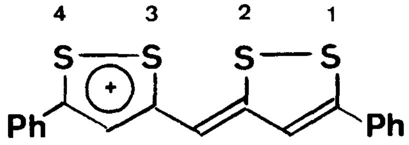
126

EH calculations predict that **126** should be approximately 2 eV less stable than **124** and **125** 0.9 eV less stable than **124**. This means that the creation of the electron-rich five-center bond in **126** cannot compensate for the breaking of two S–S single bonds in **124**. This is contrary to what is predicted for the couple dithiolylidenethione-trithiapentalene, where the formation of the electron-rich three-center bond in trithiapentalene compensates for the breaking of one S–S single bond in the dithiolylidene structure.

The bonding and structure in linear multisulfur systems has been discussed by Sletten.[210]

2. *3-(1,2-Dithiol-3-ylidenemethyl)-1,2-dithiolylium salts*

The first member **127** of this class was synthesized by Klingsberg.[211] The structure has been determined by Hordvik[212] who found the S. .S distances:



127

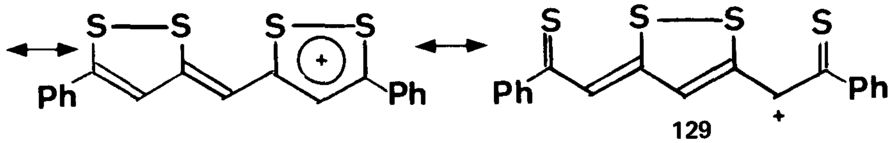
S(1)–S(2)=2.03 Å

S(2)–S(3)=2.93 Å

S(3)–S(4)=2.00 Å

(*cf.* ref. 215). Several resonance structures, *e.g.* **127**, **128** and **129**, can be written for these compounds. The X-ray data, however, show that there can only be a weak interaction between the two central sulfur atoms which means that structures such as **129** have only little weight. The identical sulfur distances between the outer sulfur atoms and the observation that the two dithiole protons are equivalent in the NMR spectra,[213] show the symmetrical nature of the system, which can be explained by structures such as **130**.

128



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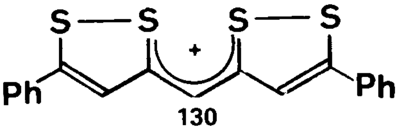
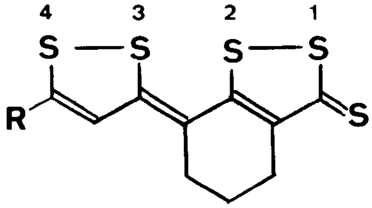


130

3. *7-(1,2-Dithiol-3-ylidene)-4,5,6,7-tetrahydro-1,2-benzodithiole-3-thiones*

Compounds of type **114** were synthesized by Stavaux and Lozac'h.[214]



131

132 R: $\mathrm{Bu^t}$

The cyclohexane ring is a prerequisite for the synthesis of compounds of this type.

The structure has been determined by Sletten[215] who has found the following sulfur distances in **132**:

S(1)–S(2)=2.062 Å

S(2)–S(3)=2.863 Å

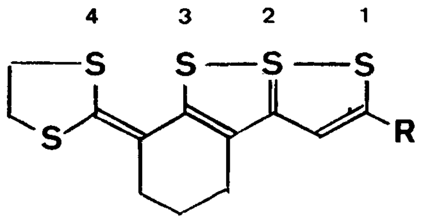
S(3)–S(4)=2.063 Å

S(1)–S(2)–S(3) is approximately linear while the fourth sulfur atom deviates significantly from this line, the angle S(1), S(2), S(3)/S(3), S(4) being 163°. The two outer sulfur distances are not significantly different from those in isolated disulfide rings. 3-Phenyl-1,2-dithiolylium iodide[216] for instance has a S. .S=2.00 Å. From the C–S bond lenghts in **132** it can be judged that there is a comparable π–conjugation in the two dithiole rings.

The mass spectra of compounds of type **131** are dominated by strong molecular ions which are the base peaks.[217]

4. 4,5-[1-(1,3-Dithiolan-2-ylidene)-tetramethylene]-1,6,6aλ^4-trithiapentalene

Compounds of type **133** have been described by Stavaux and Lozac'h.[218]



133

134 R = Bu^t

135 R = 4-$MeOC_6H_4$

A structure determination has been carried out by Sletten[219] who has found the following sulfur distances:

S(1)–S(2)=2.482 Å

S(2)–S(3)=2.209 Å

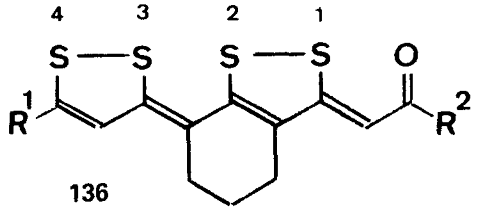
S(3)–S(4)=2.965 Å

On the basis of the S. .S bonds it is proposed that S(1), S(2) and S(3) are parts of a true trithiapentalene system whereas S(4), although S(3)–S(4) is shorter than the sum of the van der Waals radii, does not participate in σ-bonding to S(3).

The crystals of **135** are found to consist of two chemically equivalent, but crystallographically different molecules with different sulfur-sulfur distances.[220]

5. *α-[7-(1,2-Dithiol-3-ylidene)-4,5,6,7-tetrahydro-1,2-benzodithiol-3-ylidene] ketones*

The formation of the compounds **136**, which are analogous to 1,2-dithiolylidene ketones, has been described by Stavaux.[221]



136

137 R^1: Bu^t
R^2: Ph

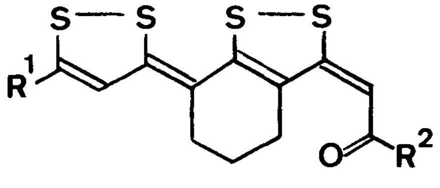
The following distances have been determined by Sletten and Velsvik[222] for **137**.

S(1)–S(2)=2.110 Å
S(2)–S(3)=2.856 Å
S(3)–S(4)=2.064 Å
S(1)–O =2.327 Å

This compound is similar to **132**, but we see that the introduction of the oxygen atom gives a pronounced lengthening of the S–S bond adjacent to the oxygen whereas the other S–S bond is not changed. This indicates that a delocalized σ-system does not include all the five atoms in the linear row. From the S(4). .O bond distance it can be estimated that a significant interaction is present between these two atoms.

The mass spectra of compounds of type **136**[217] display intense molecular ion peaks, other prominent peaks in the spectra are due to acyl ions R^2CO^+ and to ions resulting from loss of neutral acyl radicals with charge retention on the rest of the molecule.

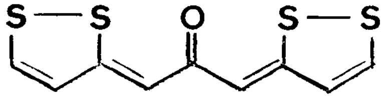
The photochemistry of **136** has been studied by Pedersen *et al.*[223] It is found that these compounds are transformed into the *trans*-form **138** upon irradiation. The *trans*-forms revert to *cis* in a dark process on the same way as observed for 1,2-dithiolylidene ketones.[175–177] Isomerization round the other exocyclic double bond could be excluded on the basis of the ^{1}H NMR spectrum of the photoproduct.



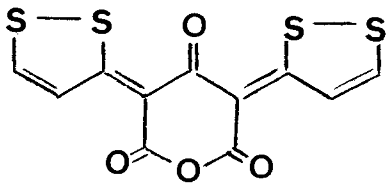
138

6. *1,3-bis(1,3-Dithiol-3-ylidene)-2-propanones*

Compounds of type **139** have been prepared by Frandsen[224] from the corresponding pyrane derivative **140**. The possibility of *cis-trans* isomers round the exocyclic double bonds is discussed on the basis of NMR and IR data. It is concluded that the sequence S–S–O–S–S is linear.



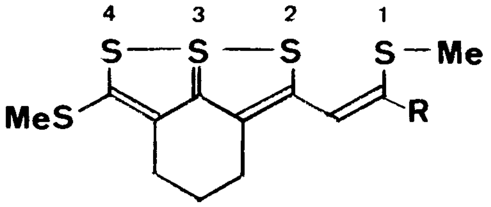
139



140

7. *2-(2-Methylthiovinyl)-3,4-trimethylene-5-methylthio-1,6,6aλ^4-trithiapentalenes*

Compounds of type **141** have been described by Stavaux and Lozac'h.[218] A structure determination has been carried out by Sletten.[225] She has found the following S. .S distances in **142**.



141

142 R=4-MeOC_6H_4

S(1)–S(2)=3.0021 Å

S(2)–S(3)=2.1563 Å

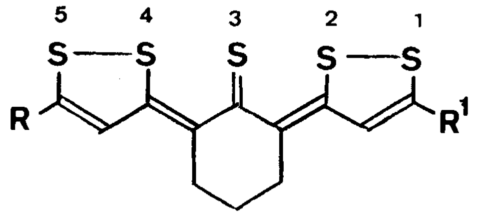
S(3)–S(4)=2.5510 Å

The values obtained for this compound are close to those found for **134** and **135**.

8. *2,6-Bis-(1,2-dithiol-3-ylidene)cyclohexanethiones*

Stavaux[221] has prepared compounds with the general formula **143**. The symmetry of the molecule is consistent with the observation that if $\mathring{R}=R^2$ as in **144**, the two substituents $\mathring{R}$ and R^2 give identical ^1H NMR signals and the dithiole protons are also identical.

Stavaux has shown that the same compound **143** is obtained from the two different oxygen analogues **147** and **148**.

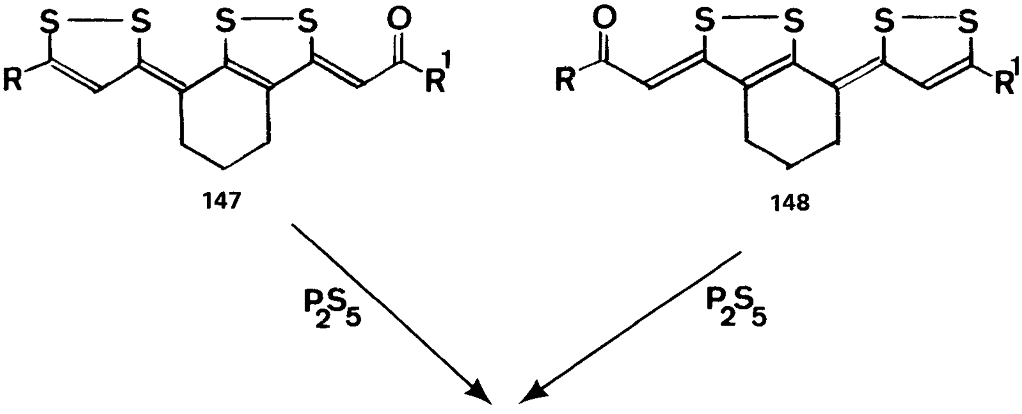


143

144 $R = R^1 = Bu^t$

145 $R = Bu^t, R^1 = Ph$

146 $R = R^1 = 4\text{-}MeOC_6H_4$



143

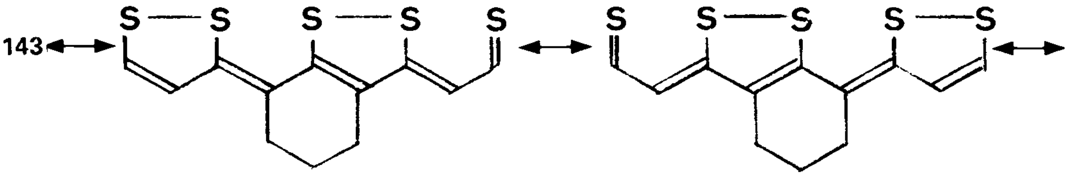
This seems to imply that a reorganization of the bonds takes place during the sulfuration with formation of a symmetrical system, which may be described with the classical formula **143**.

X-ray studies carried out by Kristensen and Sletten[226-229] show that the five sulfur atoms are approximately linear. The following S. .S distances have been found:

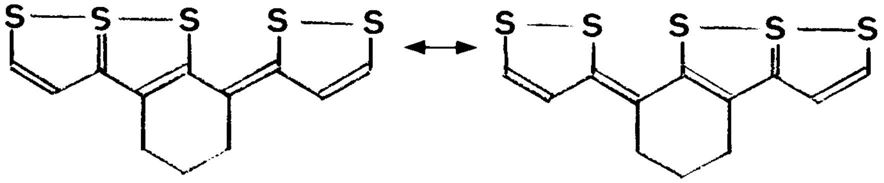
	124	125	126
S(1)–S(2)	2.183 Å	2.14 Å	2.113
S(2)–S(3)	2.580 Å	2.62 Å	2.626
S(3)–S(4)	2.583 Å	2.55 Å	2.396
S(4)–S(5)	2.172 Å	2.16 Å	2.271

The deviation in symmetry in the sulfur sequence is surprising in the symmetrically substituted compound **146**. It is probably due to the fact that the intermolecular environment in the crystal of the two halves of the molecule is quite different. This may produce a shift of electron density in the sulfur sequence.

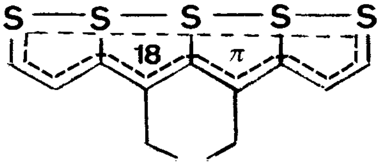
The distances observed seem to indicate that both σ- and π-delocalization over all the five sulfur atoms are present. This is consistent with the hypothesis that we have to deal with a trithiapentalene structure which can be described by the resonance forms **143**, **149** and **150** where d orbitals on sulfur are not involved and **151-153** which involve d orbital participation on sulfur.



149 **150**



151 **152**



153

The NMR data are also consistent with π-conjugation, the dithiole protons are found in the range δ 7.04 - 7.37 ppm which should be compared with the δ value for the hydrogens in benzene 7.27 ppm.

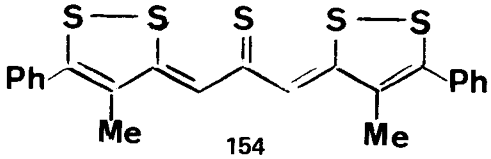
These compounds show absorptions in the visible and ultraviolet regions which are similar to those of trithiapentalenes, the absorption bands are only shifted a little towards longer wavelengths. It is possible that the visible absorption in this case, as proposed for the corresponding bands in trithiapentalenes, is due to $\pi \rightarrow \pi^*$ -transitions.[144]

Thus, in the same way as the sulfur-sulfur σ bonding in trithiapentalenes is described as a "4-electron 3-center bond",[153] the corresponding bond in this type of compound may be described as a "6-electron 5-center bond".

CNDO/2 calculations[230] predict that all S–S bonds should be longer than in dithioles, with the outer S–S bonds being the shorter ones, in good agreement with the experimental results. Furthermore it is shown that the geometrical arrangements predicted for the sulfur sequence are closely related to those predicted for the linear Cl_5^- molecule, where the outer bonds are predicted to be the shorter ones, too. However, in this case the calculations are not in agreement with experimental data as it has been shown that I_5^- is bent with two three-center systems at right angles.[231]

The mass spectra of these compounds[217] display intense molecular ions as well as peaks corresponding to thioacyl ions RCS^+. Ions corresponding to loss of 1,2,3, and 4 sulfur atoms from the molecular ion are also present.

Frandsen has described the first five-sulfur compound **154** without the cyclohexane ring annellated to the system.[232]

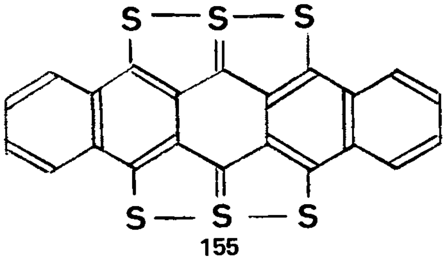


154

No structure determinations have been carried out, but the structure shown is in agreement with ^{1}H, ^{13}C NMR data as well as the electronic spectrum of the compound.

9. Pentacene Hexasulfide

Pentacene hexasulfide **155**[233] is an example of a type of trithiapentalene which can be considered as extended 1,2-dithiole derivatives, in this case the conjugation between the different 1,2-dithiole moieties is established through a carbocyclic aromatic system. The corresponding hexacene hexasulfide **156** is also known. Pentacene hexasulfide is an insulator with a conductivity of 1.2 X 10^{-13} $\Omega^{-1}cm^{-1}$, whereas hexacene hexasulfide has the unusually high electrical conductivity of 8.3 X 10^{-5} $\Omega^{-1}cm^{-1}$. This is rather surprising as **155** and **156** only differ in the annelation of a benzene ring. As the authors have not given any proof of structure it is possible that the large difference in conductivity is due to a greater variation in molecular structure *e.g.* **157** or structures with partial bonds between the sulfur atoms.



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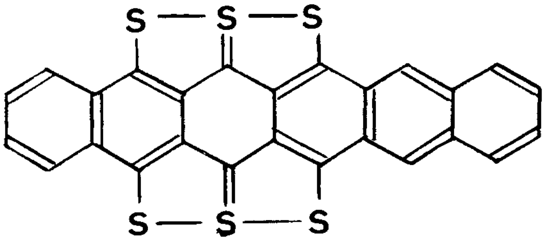

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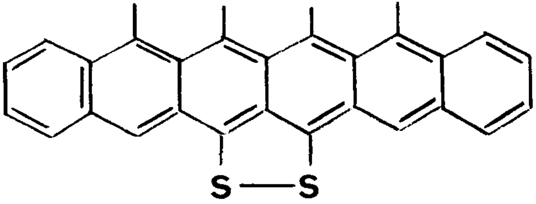
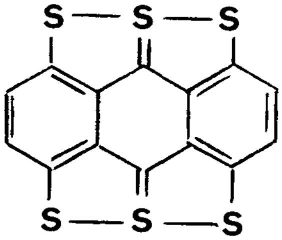


157

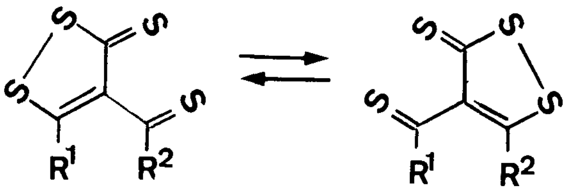
Corresponding anthracene derivatives **158** have recently been described.[233a]



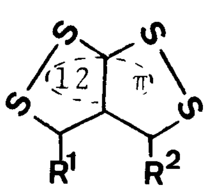
158

10. 4-Thioformyl-1,2-dithiole-3-thiones

Compounds corresponding to structure **159** have been described by Brown *et al.*[234]



159 **160**



161

These compounds are another sort of extended structures which are not directly related to trithiapentalenes.

Brown *et al.* observed two methyl singlets if they tried to prepare a compound with R^1=R^2=4–MeC_6H_4 whereas they always obtained mixtures from attempts to prepare compounds with R^1=Ph, R^2=4–MeC_6H_4 or R^1=4–MeC_6H_4, R^2=Ph. This led to the conclusion that the isomeric compounds were interconvertible, but that the tautomeric equilibrium was slowly established at room temperature based on the NMR time scale.

Theoretical studies[162] show that the transition energy in going from C_s symmetry (**159**) to C_{2v} symmetry (**161**) is approximately 35 kcal mol^{-1}, which shows that the electron-rich four-center bond in **161** is not very favorable due to the nonlinear arrangement of the four sulfur atoms.

This is also in agreement with an X-ray structure determination of **159** (R^1=R^2=4–MeC_6H_4)[234a] which shows that the thiotolyl group is twisted out of the plane of the dithiole ring by an angle of 73.8°.

VI. TRITHIAPENTALENE ANALOGUES

1. Introduction

In principle, two different types of trithiapentalene analogues exist. Compounds where one or more of the sulfur atoms have been replaced by O, Se or N–R constitute one group, another consists of compounds where one or more carbon atoms are replaced by nitrogen. A few compounds which are a mixture of these two have been described.

For the sake of brevity we will use bicyclic formulas and names analogous to trithiapentalene without any preconception of the electronic structure of these compounds, which for many of them is not known.

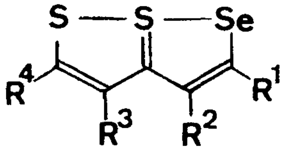
All types of known compounds will be mentioned in this chapter if they still have a group VI element as the central atom (6a), irrespective of whether anything is known concerning their aromaticity or not.

Compounds of these types have been discussed in more general terms by Boulton.[235]

The 1,2-dithiole-3-ylidene ketones belong logically to this class of compounds, but have been treated in a separate chapter because of their close relationship to the trithiapentalenes and the many papers dealing with such compounds.

2. *6-Selena-1,6aλ⁴-dithiapentalenes*

Compounds of type **162** have been prepared by van den Hende and Klingsberg[236] and Dingwall *et al.*[237] by different methods.



162

163 $R^1 = R^3 = H$

$R^2 = R^4 = Ph$

An X-ray structure determination[236] has given the following values for the S. .S and S. .Se bonds in **163**.

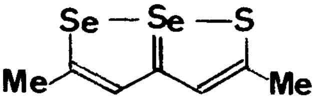
S. .S = 2.492 Å

S. .Se = 2.333 Å

The S. .Se distance is longer than the normal covalent S–Se distance (2.21 Å) but shorter than the sum of the van der Waals radii (ca. 3.7 Å). The bond lengths seem to indicate the presence of a trithiapentalene-like system. The UV–VIS spectrum of **163** is very much like the spectrum of the corresponding trithiapentalene.[236]

3. *1-Thia-6,6aλ⁴-diselenapentalenes*

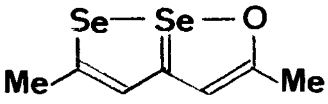
The dimethyl derivative **164** has been prepared by Traverso.[238]



164

4. *1-Oxa-6,6aλ⁴-diselenapentalenes*

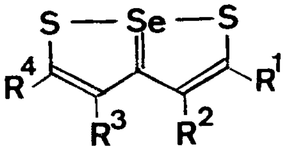
The dimethyl derivative **165** was described by Sanesi and Traverso.[239] They have determined the dipole moment to be 3.30 D.



165

5. *1,6-Dithia-6aλ⁴-selenapentalenes*

The parent compound **167** and substituted compounds have been prepared by Reid.[240]



166

167 $R^1 = R^2 = R^3 = R^4 = H$

168 $R^1 = R^4 = H$, $R^2 = R^3 = Me$

169 $R^1 = R^4 = Ph$, $R^2 = R^3 = H$

^1H NMR studies by Reid of the parent compound and substituted compounds show that the compounds in solution possess real or time-averaged C_{2v} symmetry.

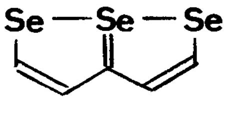
The structures of **167**, **168** and **169** have been studied by X-ray crystallography by Hordvik *et al.*[241–243] They have found the following S. .Se distances.

	167	**168**	**169**
S(1)–Se(6a) =	2.446 Å	2.414 Å	2.419 Å
Se(6a)–S(6) =	2.446 Å	2.414 Å	2.433 Å

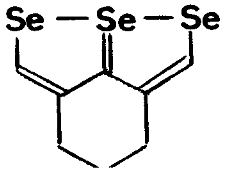
The two different S. .Se distances in **169** are caused by a torsion of the phenyl groups out of the plane of the selenapentalene of 6° and 46°, respectively.

6. *1,6,6aλ⁴-Triselenapentalenes.*

The compounds **170** and **171** have been prepared by Jackson.[244]



170



171

Hordvik *et al.*[245,246] have determined the structure of **170** and **171**. The following Se. .Se distances have been observed:

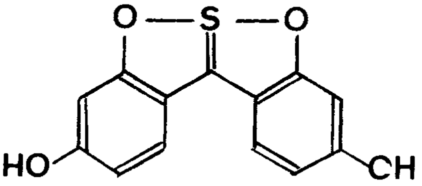
	170	171
Se(1)–Se(6a) =	2.583 Å	2.568 Å
Se(6a)–Se(6) =	2.583 Å	2.554 Å

It is obvious from the X-ray data that the triselenapentalene system is much like the trithiapentalene system.

The mass spectra of a series of substituted triselenapentalenes have been recorded.[247] The mass spectra show great similarities to those of corresponding trithiapentalenes. The main difference results from the more facile loss of selenium compared with sulfur. This gives rise to abundant hydrocarbon ions corresponding to $[M-Se_3H]^+$.

7. *1,6-Dioxa-6aλ⁴-thiapentalenes*

The first representative **172** of this class of compounds was prepared by Pomerantz *et al.*[248,249] by fusion of the fungicide "Captan" with resorcinol. They gave ^1H NMR data and mass and ultraviolet-visible spectra for **172** and some of its derivatives.

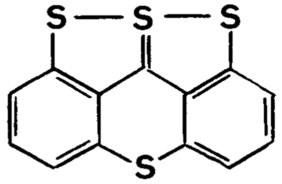


172

The structure of the dimethyl ether of **172** was determined by X-ray crystallography by Gilardi and Karle.[250]

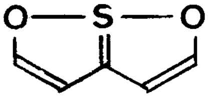
O. .S. .O forms a nearly linear system with equivalent O. .S distances of 1.879 Å which is much shorter than the shortest O. .S distance found in dithiolylidene ketones[194] (2.255 Å), but it is still ca. 0.28 Å longer than the normal S–O single bond.

The existence of such compounds as **172** is very interesting as it has not been possible to prepare analogous dibenzotrithiapentalenes,[251] probably because of steric interaction between the interior *ortho*-protons in the benzene rings. In **172** the distance between these two hydrogens is 2.02 Å, but if the two oxygens are replaced by sulfur the two benzene rings will be forced nearer to each other. This rationalization is also in accordance with the existence of compounds such as **173**.[252]



173

The parent system **174** has been prepared by Reid.[253]



174

Photoelectron spectra have been recorded and discussed for a few dioxathiapentalenes,[159,160] but there has been some trouble in the assignments.

The microwave spectrum of the parent system **174** has been recorded as well as that of the 3,4-dideutero compound.[254] All evidence obtained from the microwave spectrum is in accordance with the assumption that the compound has a single-minimum structure *i.e.* it has C_{2v} symmetry like trithiapentalene. The dipole moment 3.07 ± 0.04 D has been found.

Some ^1H NMR data have been given by Reid.[253] A more detailed discussion of the proton spectrum in both isotropic and nematic phases has recently been published.[168]

^{13}C NMR shifts are given in Table XXII together with coupling constants for dithiolylidene acetaldehyde **85** and trithiapentalene **46**.

TABLE XXII

^{13}C Chemical Shifts (ppm) and Coupling Constants (Hz) in 1,6-Dioxa-6aλ^4-thiapentalene (174), 85, and 46.

	174	85[199]	46[166]
δ(C−2)	167.78	161.69	181.12
δ(C−3)	104.13	128.64	109.04
δ(C−3a)	175.63	177.45	172.04
$^1J_{C-2,H-2}$	188.9	176.5	182.3
$^1J_{C-3,H-3}$	176.8	165.4	167.98
$^2J_{C-2,H-3}$	7.3	-4.6	7.19
$^2J_{H-3,H-2}$	15.6	3.6	22.3
$^3J_{H-2,H-3}$	2.6	6.31	1.68
$^5J_{H-2,H-4}$	0.2	0.08	0.13
$^6J_{H-2,H-5}$	0.0	0.35	0.0
$^4J_{H-3,H-4}$	±0.4	0.30	-0.4

From the ^1H NMR spectrum in a nematic phase the dipole-dipole coupling constants given in Table XXIII could be found. It was found that these dipole-dipole coupling constants could be related to the geometry of the molecule through two ordering parameters. If the compound had a symmetry lower than C_{2v}, the dipole-dipole coupling constants would have been related to the geometry through at least three ordering parameters.

TABLE XXIII

Dipole-Dipole Couplings [D_{ij}(Hz)] and Relative Distances in 1,6-Dioxa-6aλ^4-thiapentalene

	3.2 mol % in EBBA
D_{23}	-553.1 ± 0.4
D_{24}	-144.7 ± 0.5
D_{25}	-78.0 ± 0.4
D_{34}	-923.4 ± 0.5
r_{23}/r_{34}	0.902 ± 0.008
r_{24}/r_{34}	1.759 ± 0.004
r_{25}/r_{34}	2.279 ± 0.004

D_{xy} and r_{xy} are the dipole-dipole constant in Hz and the distance between proton x and y, respectively.

The spectrum was recorded in N-(4-ethoxybenzylidene)4-butyl-aniline (EBBA).

If the results from the NMR study in the nematic phase are combined with results from the MW study[254] and an X-ray study of the 2,5-dimethyl-1,6-dioxa-6aλ^4-thiapentelene[255] the H–H distance ratios given in Table XXIII could be rationalized in the structure given in Figure 15.

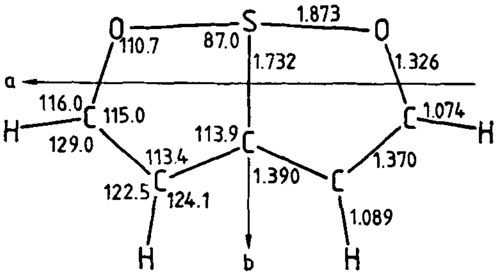


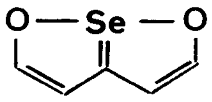
FIGURE 15. Structure of 1,6-Dioxa-6aλ^4-thiapentalene.[168] [Courtesy of The Chemical Society.]

This is the first example of a structure related to the liquid phase of this type of hypervalent sulfur compounds.

The protonation of these compounds under formation of 1,2-oxathiolium salts has been studied by means of ^{1}H NMR spectroscopy.[256]

8. *1,6-Dioxa-6aλ^4-selenapentalenes*

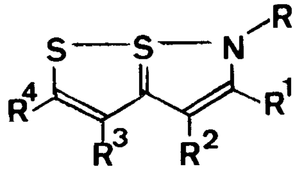
Compounds of type **175** have been studied by Reid *et al.*[253] who have given some ^1H NMR data as they have studied the protonation.[256]



175

9. *6-Aza-1,6aλ^4-dithiapentalenes*

Compounds of type **176** were first described by Klingsberg.[257]



176

177 R: 3-Quinolinyl
$R^1 = R^3 = H$, $R^2 = R^4 = Ph$

178 $R = R^2 = R^4 = Ph$
$R^1 = R^3 = H$

179 $R = R^1 = R^4 = Ph$
$R^2 = R^3 = H$

180 $R = R^1 = R^4 = Me$
$R^2 = R^3 = H$

181 $R = Ph$, $R^1 = R^4 = Me$
$R^2 = R^3 = H$

182 $R = R^1 = R^4 = Ph$
$R^2 = CN$, $R^3 = H$

The structure of **177**,[195] **178**[258] and **179**[259] has been determined. The following S—S and S—N distances have been observed:

	177	178	179
N–S(6a)	1.887 Å	1.871 Å	1.860 Å
S(6a)–S(1)	2.364 Å	2.396 Å	2.440 Å

The distance N—C(5) = 1.324 Å resembles the one found in formamide, where the C—N distance is 1.322 Å.

Ultraviolet and visible spectral data have been given by Klingsberg[257] and Behringer.[260]

Photoelectron spectra of **180** have been recorded and discussed in connection with other hypervalent sulfur compounds.[159,190]

The photochemistry of **181** and **182** has been studied.[92] The following kinetic data have been obtained.

TABLE XXIV

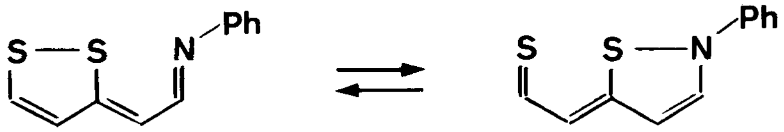
Kinetic Data for the Thermal Back Reaction[92]

Compound	Solvent	$k_{25°}$ S^{-1}	$\tau_{25°}$ S	E_a kcal/mol	$\Delta G^{\ddagger}_{25°}$ kcal/mol	$\Delta S^{\ddagger}_{25°}$ c.u.
181	toluene	322.1	2.2×10^{-3}	13.6	14.0	-3.5
181	ethanol	204.2	3.4×10^{-3}	10.8	14.3	-13.9
181	acetonitrile	550.0	1.3×10^{-3}	11.5	10.9	-9.5
182	ethanol	565.0	1.2×10^{-3}	10.2	13.7	-13.9
182	acetonitrile	550.0	1.3×10^{-3}	10.5	9.9	-12.8

On the basis of the kinetic data and the activation parameters it was concluded that the photochemical reaction which was observed was of the same nature as that observed for dithiolylidene ketones[176,177] and trithiapentalenes.[90]

Reid *et al.*[261] have prepared a series of azadithiapentalenes and recorded the ^1H NMR spectra. They find a progressive increase in deshielding of ring protons and substituents along the series 1-oxa-6,6aλ^4-dithiapentalene (dithiolylidene ketones), 6-aza-1,6aλ^4-dithiapentalenes, 1,6,6aλ^4-trithiapentalenes. It can be estimated that the delocalization increases in the same order.

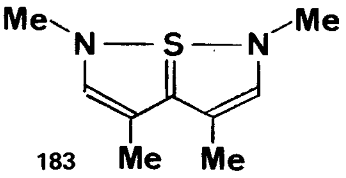
In an infrared study of ^{15}N enriched compounds (cf. ref. 259) the presence of two bands at 1400 cm^{-1} and 1550 cm^{-1} was observed. These bands could be due to the presence of a C=N and a C–N bond. This could be an indication of the tautomerism.



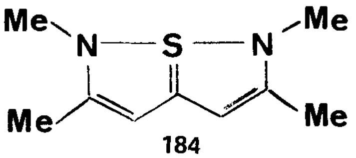
Reid has found that the azadithiapentalenes as the only class of hypervalent sulfur compounds of this type form stable charge-transfer complexes with 1,3,5-trinitrobenzene.[261]

10. 1,6-Diaza-6aλ^4-thiapentalenes

Compounds of type **183** have been prepared by Reid.[262]



183



184

The photoelectron spectrum of **184** has been studied.[159,190]

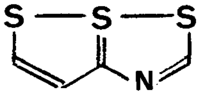
Reid has recorded the ^1H NMR spectrum of **183** and finds that the pattern of this spectrum, which shows equivalence of C–Me,N–Me as well as of dithiolic protons, remained unchanged down to $-70^\circ C$. This shows that the compound in solution has real or time-averaged C_{2v} symmetry.

Hordvik and Julshamn[263] have determined the structure of 1,6-dimethyl-3,4-trimethylene-1,6-diaza-6aλ^4-thiapentalene and found two values for the S. .N bond length (1.901 Å and 1.948 Å). The C_{2v} symmetry is probably distorted in the anisotropic crystal state by intermolecular forces.

Reid and co-workers[264] have recently prepared a series of substituted derivatives and have given ^1H NMR data. The compounds form charge-transfer complexes with 2,4,6-trinitrobenzene.

11. 3-Aza-1,6,6aλ^4-trithiapentalenes

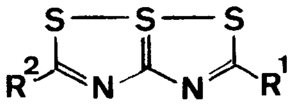
Behringer and Bender [265] have described substituted derivatives of **185**. On the basis of UV–VIS spectra they conclude that the compounds are trithapentalene-like.



185

12. 3,4-Diaza-1,6,6aλ^4-trithiapentalenes

Behringer *et al.*[266] have prepared **187** and Vialle *et al.*[267] have described other substituted derivatives. The UV and VIS spectra are given by Behringer.



186

187 $R^1 = R^2 = HNR$

188 $R^1 = R^2 = H\ NPh$

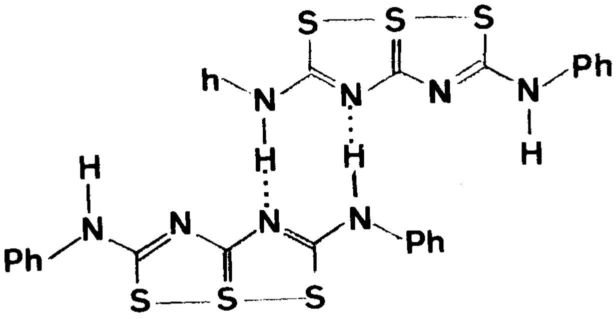
189 $R^1 = R^2 = Ph$

189A $R^1 = R^2 = NMe_2$

Hordvik has determined the structure of **188**[268] and **189**[269,270] and found the following S. .S distances:

	188	**189**	**189A**[270a]
S(1)–S(6a) =	2.225 Å	2.319 Å	2.346 Å
S(6a)–S(6) =	2.475 -	2.328 -	(2.346) -

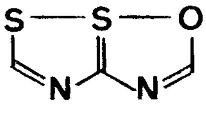
The difference in S. .S distances is caused by twisting of the phenyl groups. In **188** there is weak hydrogen bonding between the molecules in the crystal as shown in **190**.



190

13. 1-Oxa-3,4-diaza-6,6aλ^4*-dithiapentalenes*

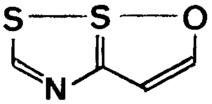
Compounds with the structure **191** have been described both by Behringer[266] and Vialle.[267]



191

14. 1-Oxa-4-aza-6,6aλ^4*-dithiapentalenes*

Derivatives with the structure **192** have been described by Behringer and Bender[265] who have reported UV and VIS spectra.

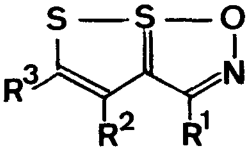


192

Leistner *et al.*[271] have given some IR and mass spectrometric data on a 2,3-benzocondensed derivative.

15. 1-Oxa-2-aza-6,6aλ^4-dithiapentalenes

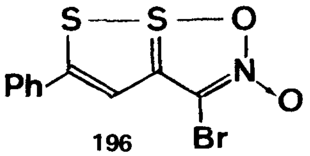
Nitrosation products of 1,6,6aλ^4-trithiapentalenes have been shown by Beer and his group to be derivatives of the ring system **193**[272,273] and structure determinations of



193

194 $R^1 = PhCO, R^2 = H, R^3 = Ph$

195 $R^1 = NO_2, R^2 = H, R^3 = Ph$



196

194-196 have been carried out by Paul and his group.[274-277] They have found the following S. .S and S. .O distances:

	194	196
S(6)–S(6a) :	2.178 Å	2.075 Å
S(6a)–O :	2.034 -	2.373 -

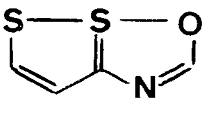
The crystals of **195** were twins, but the results obtained proved that the nitroso group rather than the nitro group is in a close contact with sulfur.

A series of compounds of this type have been described by Reid *et al.*[278] They have reported ^1H NMR data from these compounds.

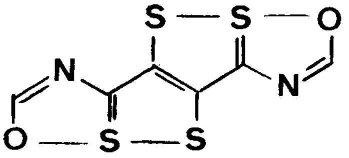
Beer *et al.*[279] have studied the mass spectra from representative compounds and have found that they fragment mostly through simple bond cleavage, in keeping with mass spectra of trithiapentalenes.[96] However, they showed evidence for rearrangement through cyclization before fragmentation.

16. 1-Oxa-3-aza-6,6aλ^4-dithiapentalenes

Compounds with structure **197** have been described by Reiter *et al.*[280] They have described both simple derivatives and compounds with the condensed structure **198**.



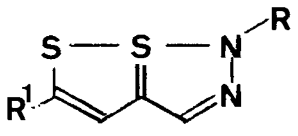
197



198

17. 5,6-Diaza-1,6aλ^4-dithiapentalenes

Reid and co-workers[281] have shown that the reaction of arenediazonium tetrafluoroborate with trithiapentalenes gave compounds derived from the ring system **199**.



199

200 R = Ph, R^1 = Bu^t

In connection with studies of the synthesis of these compounds ^{1}H NMR data were recorded.[282–284] From these proton data it was concluded that the S–S–N sequence was bonded by a four-electron three-center bond as in trithiapentalene.

From an X-ray structure determination[285] the following bond lengths for **200** were found.

S(1)–S(6a) = 2.435 Å

S(6a)–N(6) = 1.849 -

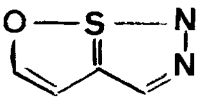
The ring system was found to be planar with the phenyl group twisted 2.5° out of the plane.

The other structural parameters were found to be in accordance with a trithiapentalene-like structure.

The mass spectrum of 1-phenyl-3,4-dimethyl-5,6-diaza-1,6aλ^4-dithiapentalene was studied in connection with analogous selenium compounds.[247]

18. 1-Oxa-5,6-diaza-6aλ^4-thiapentalenes

Compounds with the structure **201** have been described by Reid and co-workers [286,287]

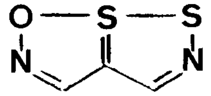


201

They have given UV, IR and ^{1}H NMR data for a series of compounds.

19. 1-Oxa-2,5-diaza-6,6aλ^4-dithiapentalenes

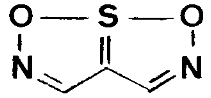
Compounds with the general structure **202** were obtained from the reaction of 1,3-dioximes with disulfur dichloride.[288] ^{1}H NMR data was given.



202

20. *1,6-Dioxa-2,5-diaza-6aλ^4-thiapentalenes*

Compounds of structure **203** were obtained together with **202**.[288]



203

The mass spectrum of the parent compound has been recorded.[289]

^1H and ^{13}C NMR data are in accordance with a bicyclic structure with C_{2v} symmetry.[288]

Ab initio MO–LCAO–SCF calculations have been carried out for the parent compound.[290] It was found that a change of 0.107 Å in the S–O distance leads to an energy increase of 5×10^{-3} a.u., whereas a corresponding bond distortion for trithiapentalene leads to an energy decrease of 5×10^{-6} a.u. The calculation for **203** thus yields a deep single minimum in the potential surface for displacement of the sulfur atom.

The gas-phase ESCA spectrum has been recorded.[291] The following energies were found:

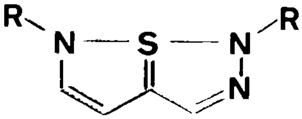
O_{1s} : 539.1 eV N_{1s} : 407.1 eV $C(3a)_{1s}$: 292.4 eV

S_{2p} : 171.8 eV

The structure for the parent compound has been determined by X-ray crystallography (*cf.* ref. 290).

21. *1,2,6-Triaza-6aλ^4-thiapentalenes*

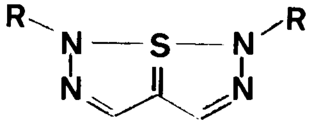
Compounds with the structure **204** were reported by Christie.[292] ^1H NMR data were given.



204

22. *1,2,5,6-Tetraza-6aλ⁴-thiapentalenes*

Compounds of the general structure **205** have been reported by two groups.[287,293]

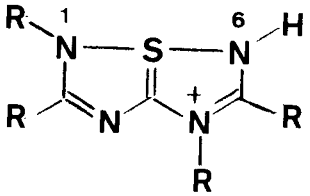


205

UV and IR spectra have been given.[287] ^1H as well as ^{13}C NMR data[287,293] are in accordance with a bicyclic structure with C_{2v} symmetry.

23. *1,3,4,6-Tetraza-6aλ⁴-thiapentalenes*

Compounds with structures related to **206** have been considered to be monocyclic.[294,295] ^1H NMR data have been given for representative derivatives.



206

The structure of the 1,2,4,5-tetramethyl derivative has been determined by X-ray crystallography,[295] the following distances have been observed.

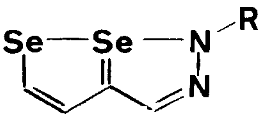
N(1)–S(6a) = 1.668 Å

S(6a)–N(6) = 2.500 Å

It was reported that bond switch often occurred at the hypervalent sulfur atom upon alkylation and protonation.

24. *1,2-Diaza-6,6aλ⁴-diselenapentalenes*

Compounds with structure **207** have been prepared by Christie and Reid.[282] They have given ^1H NMR data.

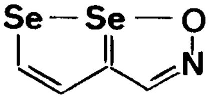


207

Mass spectral data have been recorded in connection with a study of triselenapentalenes.[247]

25. *1-Oxa-2-aza-6,6aλ^4-diselenapentalenes*

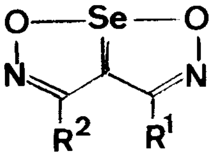
Compounds with structure **208** resulted from the nitrosation of 1,2-diselenylium salts.[278] ^1H NMR data were given.



208

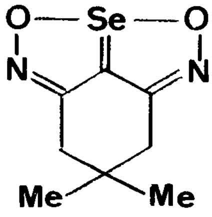
26. *1,6-Dioxa-2,5-diaza-6aλ^4-selenapentalenes*

It has been shown by Beer[296] and by Vialle[288,297,298] that the reaction products derived from selenium dioxide and 1,3-dioximes have the structure **209**.



209

210 $R^1 = R^2 = Me$



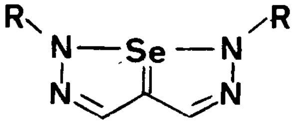
211

Vialle gives the ^1H and ^{13}C NMR data for this type of compounds and shows that the methyl groups of **210** are equivalent down to −60°C. X-ray data for **211** are reported.[296,299] The O. .Se distances have been determined as 2.017 and 2.030 Å.

The mass spectra of **209** and **210** have been recorded.[289]

27. *1,2,5,6-Tetraza-6aλ^4-selenapentalenes*

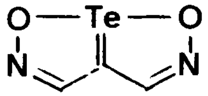
Compounds of structure **212** result from the reaction of hydrazones with selenium dioxide.[293] ^1H and ^{13}C NMR data, which are in accordance with a C_{2v} symmetrical bicyclic structure, are given.



212

28. *1,6-Dioxa-2,5-diaza-6aλ^4-tellurapentalenes*

The reaction of tellurium dioxide with 1,3-dioximes gives rise to compounds with the structure **213**.[298,288] ^1H and ^{13}C NMR data are given. They are in accordance with a symmetrical structure.[288]

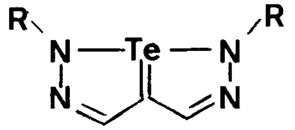


213

The mass spectra have been recorded.[289]

29. *1,2,5,6-Tetraza-6aλ^4-tellurapentalenes*

The reaction of hydrazones with tellurium dioxide results in the formation of compounds with the general structure **214**.[293] ^1H and ^{13}C NMR data are given; they are in accordance with C_{2v} symmetry. The mass spectra exhibit strong molecular peaks and abundant double-charged ions.

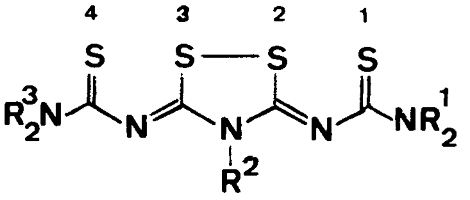


214

VII. ANALOGUES OF EXTENDED STRUCTURES

1. *3,5-Bis(thiocarbamoylimino)1,2,4-dithiazolidines*

Compounds of type **215** were originally described by Goerdeler and Ulmen[300] who proposed the different resonance forms **220** and **221**. They have also proposed non-linear no-bond resonance structures. NMR data is given for substituted derivatives. Some mass spectrometric data have been given by Oliver and Stokes.[301] Oliver and Flippen[302,303]



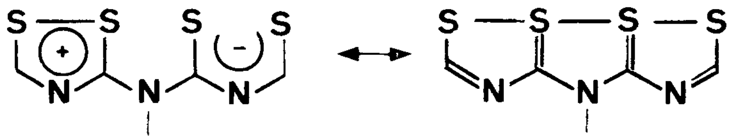
215

216 $R^1 = R^2 = R^3 = \text{Me}$

217 $R^1 = R^3 = \text{Me}, R^2 = \text{Ph}$

218 $R^1 = R^3 = \text{i-Pr}, R^2 = \text{Me}$

219 $R^1 = R^3 = \text{i-Pr}, R^2 = 4\text{-}NO_2C_6H_4$



220 221

have made X-ray determination on **216** and **217** and have reported the following S. .S distances:

	216	217
S(1)–S(2)	2.742 Å	2.784 Å
S(2)–S(3)	2.161 -	2.171 -
S(3)–S(4)	2.785 -	2.784 -

These distances fit nicely with structure **215**, but are different from those of the 4-sulfur compound **127**. The molecule is planar and in the case of **217** the benzene ring is twisted out of this plane by 93.8°.

Sletten has determined the structures of **218**,[304] and **219**[305] and has reported the following S. .S distances:

	218	219
S(1)–S(2)	2.763 Å	2.747 Å
S(2)–S(3)	2.167 -	2.194 -
S(3)–S(4)	2.763 -	2.883 -

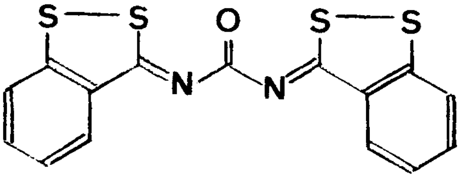
She suggests a bonding scheme with delocalized σ-bonding across all four sulfur atoms. A strong interaction between the outer sulfur atoms is probably caused by contribution of forms in which the terminal sulfur atoms are negatively charged. This is consistent with the results from CNDO/2 calculations, in which the terminal sulfur atoms are found to carry a negative charge of 0.44 electrons.[304]

Oliver[306] has on the basis of S-alkylation of **215** suggested that no-bond resonance is operative in this system.

The phenyl group in **219** is oriented almost perpendicular to the main molecular plane. The asymmetry in the sulfur sequence is reflected in different crystallographic environments for S(1) and S(4). Three crystallographically independent molecules with minor differences in their geometry were found.[305]

2. *1,3-Bis(1,2-benzodithiol-3-ylidene)ureas.*

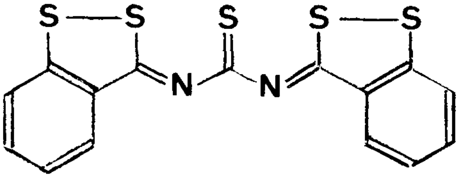
The compound **223** has been described by Klingsberg.[307] who gives its UV–VIS spectrum.



223

3. *1,3-Bis(1,2-benzodithiol-3-ylidene)2-thioureas*

Compound **224** was prepared by Klingsberg. The UV–VIS spectrum was much like the spectrum of a trithiapentalene.[307]



224

VIII. CONCLUSIONS

1,2-Dithiolylium ions:

From the physico-chemical data available until now the 1,2-dithiolylium ion system may be considered as an aromatic system. This is reflected in the length of the S–S bond which for most dithiolylium salts is in the order 2.0 Å. This should be compared to the normal single S–S bond in a *cis*-planar disulfide group with a bond length of 2.10 Å.[308] This shortening of the S–S bond may be taken as evidence for π-orbital delocalization.

The 1,2-dithiolylium ion is a highly reactive species. Like other cationic systems such as the tropylium ion system, the 1,2-dithiolylium ion is stabilized towards electrophilic reagents. No electrophilic substitution on the dithiolylium ion is reported. Attempts to nitrate the 4-phenyl-1,2-dithiolylium ion resulted in nitration of the 4-position of the phenyl group.[309]

However, as an electron deficient reagent the 1,2-dithiolylium ion is extremely reactive and unselective towards nucleophilic reagents, which often by secondary reactions destroy the dithiole ring system. This reactivity, however, does not invalidate the assumption of the 1,2-dithiolylium system as an aromatic system. The 1,2-dithiolylium cation is a highly stable system, which only decomposes at high temperature. A hypothetical 1,2-dithiolylium ion not stabilized by aromatic resonance would probably be so reactive as to make its isolation impossible. In this respect it falls into the same category of aromatic systems as the pyrylium cation, the tropylium cation and the cyclopentadienyl anion.

1,6,6aλ^4-Trithiapentalenes:

The trithiapentalene system is the 1,2-dithiole system, which has been most intensively studied. Numerous studies dealing with physico-chemical aspects and syntheses and reactions have appeared since the trithiapentalene structure was established in 1958.

From all these physico-chemical studies we will conclude, based on the time scale of the methods used that there is no doubt that the trithiapentalene system possesses C_{2v} symmetry, but whether this is a real C_{2v} symmetry or only time-averaged C_{2v} symmetry is still a question under debate. The two cases which are to be considered are as follows:

case 1 : resonance $\quad$ $S(6) : S(6a)\cdot \cdot S(1) \leftrightarrow S(6)\cdot \cdot S(6a) : S(1)$

case 2 : valence tautomerism $\quad$ $S(6) : S(6a)\cdot \cdot S(1) \rightleftarrows S(6)\cdot \cdot S(6a) : S(1)$

Case 1 corresponds to a single minimum of the potential surface whereas case 2 corresponds to a double minimum. The problem of proving which of these alternatives is the correct one can be described in the following way:

While proper evidence for case 2 can be taken as proof for a double minimum, its absence cannot be taken as evidence for a single minimum. It may be that we have to deal with a double minimum, where the energy barrier is too low to be observed by the methods used.

From the point we have reached today, it is probably more a question of philosophy than chemistry, whether we consider trithiapentalenes to have real C_{2v} symmetry or not.

This conclusion leaves the question of the nature of the bonding in these compounds. Here no definite answer can be given at the present time. Several problems have to be solved, the contribution of d orbitals, problems of parameterization and variation of geometrical parameters in the calculations.

The physico-chemical parameters obtained in different studies indicate an electron delocalization which can be described as aromatic character in the sense we use in this connectio

The aromatic character proposed on the basis of physico-chemical properties is to some extent reflected in the reactions of trithiapentalenes. It has been found that trithiapentalenes are able to undergo electrophilic substitution in the 3-and 5-positions. Reports have occurred of such types of electrophilic reactions as bromination,[147] Vilsmeier formylation,[310] nitrosation,[311] and substitution with arenediazonium fluoroborates.[281] Although the last two types of reactions give rise to rearranged products with loss of sulfur, it has been shown that the primary process is an electrophilic substitution.

Nucleophilic substitution can occur in position 2 and 4.[151,312] This is analogous to other heteroaromatic systems which undergo both electrophilic and nucleophilic substitution reactions.

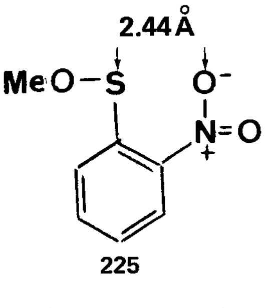
The reaction of a methyl group in position 2 with aldehydes[152] finds its parallel in the reaction of the methyl group of 2-methylpyridine.

1,2-Dithiol-3-ylidene ketones and aldehydes.

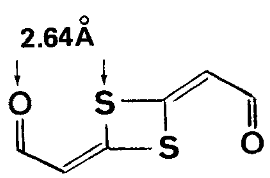
The physico-chemical properties of this group of compounds have been studied less than those of the corresponding trithiapentalenes. Many papers dealing with syntheses and reactions have been published as the dithiolylidene ketones are the key starting materials for the synthesis of trithiapentalenes.

The most striking featureof the dithiolylidene ketones and aldehydes is the short O–S bond. Considering the van der Waals radii of oxygen and sulfur (*cf.* ref. 9) a contact distance of 3.10-3.25 Å would be reasonable. The distance reported for dithiolylidene ketones is in the range 2.184-2.443 Å[114] much less than the van der Waals separation.

Reports of such short sulfur distances are also given for compounds which are not directly related to the 1,2-dithiole system e.g. **225**[313] and **226**.[314]



225



226

At a very early stage in trithiapentalene chemistry[79] the absence of a normal carbonyl vibration was observed for dithiolylidene ketones. This was later confirmed by numerous studies. This rules out the true ketonic form **85** and indicates some sort of interaction or partial bonding between oxygen and sulfur. Thus it is in accordance with the zwitterionic form **86** or the oxadithiapentalene structure **87**.

On the basis of our present knowledge we cannot draw any definite conclusion as to whether these compounds are monocyclic or bicyclic. ESCA studies,[52] ^{13}C and ^{1}H NMR studies[74,199] seem to favor a dipolar structure. Theoretical studies do not permit us to decide whether a covalent bond is present between oxygen and sulfur or not, as some calculations indicate such a covalent bond,[208,209] whereas others are not in favor of it.[207]

More studies are needed to solve this problem. It may be that some relevant information could be obtained from X-ray studies at different temperatures and neutron-diffraction measurements, which could give some information concerning the electron density between oxygen and sulfur.

A bicyclic structure should probably be aromatic in the same sense as the trithiapentalenes, but no reports of electrophilic substitution reactions, or other reactions characteristic for aromatic systems have occurred.

Extended structures.

Very little physico-chemical data are available for the discussion of the structure and aromaticity of extended structures. ^{1}H NMR spectra of symmetrically substituted derivatives indicate a symmetrical structure, but no detailed investigations have been carried out. The only physical parameter which has been studied in detail is the bond lengths in these compounds.

It has been found that the sulfur-sulfur sequence is normally nearly linear. The S—S bond lengths seem to indicate that there is no electron delocalization over the total sulfur row, as the sulfur distances are normally not equal in such a way that the outer S—S distances are shorter than the inner distances, but are symmetrically displayed round the center of the molecule. It seems that compounds of this type have a tendency "to split up" in small units with dithiolylium or trithiapentalene structure. This is in accordance with theoretical calculations.[230]

In the series of five-sulfur compounds all X-ray structure determinations have been carried out on compounds which have a cyclohexane ring condensed in the center of the molecule. This may have some influence on the sulfur-sulfur distances, if the potential curve has a broad flat minimum as that found in the case of trithiapentalenes. However, this cyclohexane ring has hitherto been a prerequisite for the synthesis of these types of compounds to avoid rearrangement.[221,315,316] It is therefore of great interest to have a structure determination of a compound of type **154** without the cyclohexane ring.

Mass spectra indicate a strong stabilization in the molecular ions, which may be ascribed to an aromatic character, but no definite conclusions can be drawn.

No parent compounds are known in this series.

Trithiapentalene analogues.

For most of the trithiapentalene analogues the situation is the same as for the extended structures: That very few physico-chemical data are available for the discussion of structure and aromaticity.

^{1}H NMR data are given for some systems and it has been shown in some cases by temperature variation experiments that symmetrically substituted compounds possess C_{2v} symmetry.

X-ray structure determination is the physical method used most in the study of these compounds, but often only a single representative for a ring system has been investigated.

The only system which has been studied by several methods is the 1,6-dioxa-6aλ^4-thiapentalene system. This system seems to be much like the trithiapentalene system and has been shown to undergo electrophilic substitution in the 3- and 4-postions.[317] Reactions such as bromination, iodination, tritylation and acetoxymercuration have been reported to take place, whereas attempts to formylate, acetylate, or nitrate the system were unsuccessful.

As to the other systems more studies have to be carried out before anything can be said concerning the electronic structure. In the case of many systems syntheses and reactions have also received little treatment.

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