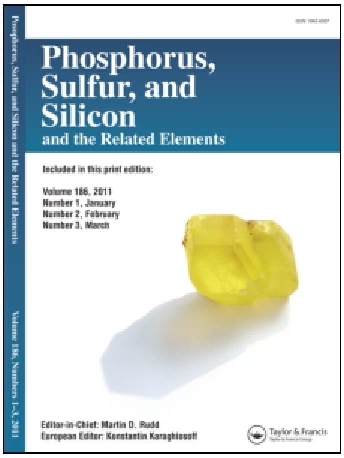

Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

The Structure of Trithiapentalenes and Related Compounds

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To cite this Article Pedersen, Carl Th.(1991) 'The Structure of Trithiapentalenes and Related Compounds', Phosphorus, Sulfur, and Silicon and the Related Elements, 58: 1, 17 — 38

To link to this Article: DOI: 10.1080/10426509108040624

URL: http://dx.doi.org/10.1080/10426509108040624

Phosphorus, Sulfur, and Silicon, 1991, Vol. 58, pp. 17–38
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THE STRUCTURE OF TRITHIAPENTALENES AND RELATED COMPOUNDS.

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Abstract Trithiapentalene is a representative of a large group of compounds where the three sulfur atoms can be substituted by sulfur, selenium, tellurium or oxygen, and the carbon atoms can be substituted by nitrogen.

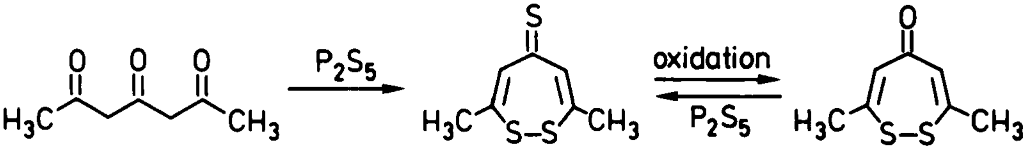
The first representative of these compounds was prepared in 1925 and the structure has since been under debate.

A bicyclic naphthalene-like structure was proposed in the fifties, but the question was raised whether the observed properties were best explained by assuming this bicyclic structure or by assuming a tautomeric equilibrium between two shortlived monocyclic tautomers. During the last 15 years modern physicochemical methods have provided answers to most structural questions. Methods such as x-ray crystallography, ESCA spectroscopy, 1-H and 13-C NMR spectroscopy in anisotropic phases, mass spectroscopy, microwave spectroscopy and electron diffraction have been used in the structure elucidation.

Analogue compounds with more than 3 sulfur atoms raise corresponding structural problems.

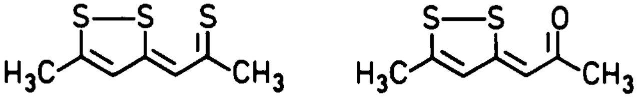
INTRODUCTION

The history of trithiapentalenes started in 1925 in Istanbul at the time when Arndt was a professor of chemistry. He reacted heptane-2,4,6-trione with phosphorus pentasulfide (1)



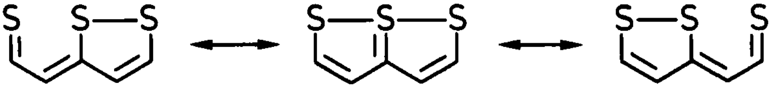
SCHEME 1

and assigned the structure shown in SCHEME 1 to the reaction product based on the observation that one sulfur atoms was different from the other two, and that it could be removed by oxidation and introduced again by means of phosphorus pentasulfide. The reaction did not attract further interest until the late fifties when structures for Arndt's two compounds were proposed by an Italien (2) based on x-ray studies and a French group (3) based on IR-studies respectively, SCHEME 2.



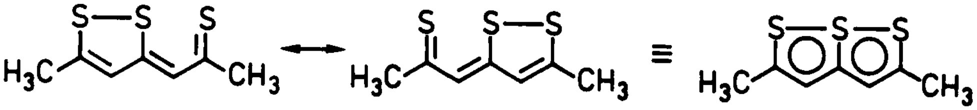
SCHEME 2

The problem, however, was that the x-ray structure determinations showed that the two sulfur-sulfur distances were equal, and proton NMR studies of the 2,5-dimethyl substituted compound showed equivalent methyl groups and methine protons (4), neither of which is in accordance with this structure. The problem was finally solved by Lozac'h who introduced the concept of no-bond-single-bond-resonance (5), SCHEME 3.



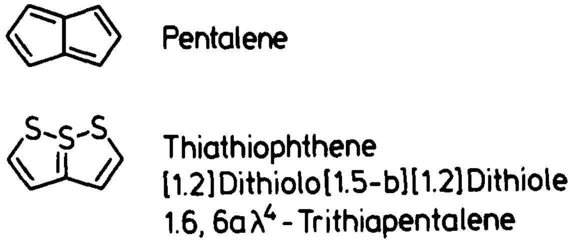
SCHEME 3

This description is consistent with the observation that the NMR spectrum of the dimethyl compound shows two equivalent methyl groups (4), SCHEME 4.



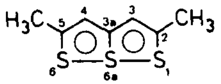
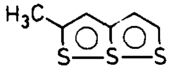
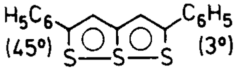
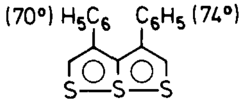
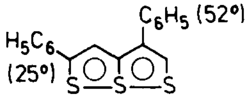
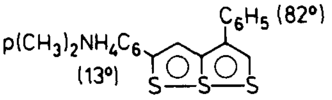
SCHEME 4

According to this concept, the compounds were called 1,6,6a-trithiapentalenes in analogy with the carbocyclic system pentalene, SCHEME 5.



SCHEME 5

Allthough the sulfur-sulfur distances were found to be equal in 2,5-dimethyl-trithiapentalene, this is not always the case for symmetrical substituted trithiapentalenes, SCHEME 6. In fact, unsymmetrical substituted ones may even have equal sulfur-sulfur distances.

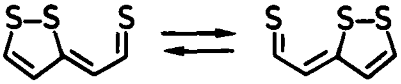
	S-S bond length [Å]	
	left	right
	2.358	2.358
	2.431	2.308
	2.362	2.304
	2.232	2.434
	2.504	2.222
	2.348	2.350

SCHEME 6

The variation of the sulfur-sulfur distance arises from the fact, that the compounds in the crystalline phase are not really symmetrical; the structure is distorted due to sterical and crystalline forces as shown for the tetraphenyl substituted compound, SCHEME 7.

SCHEME 7

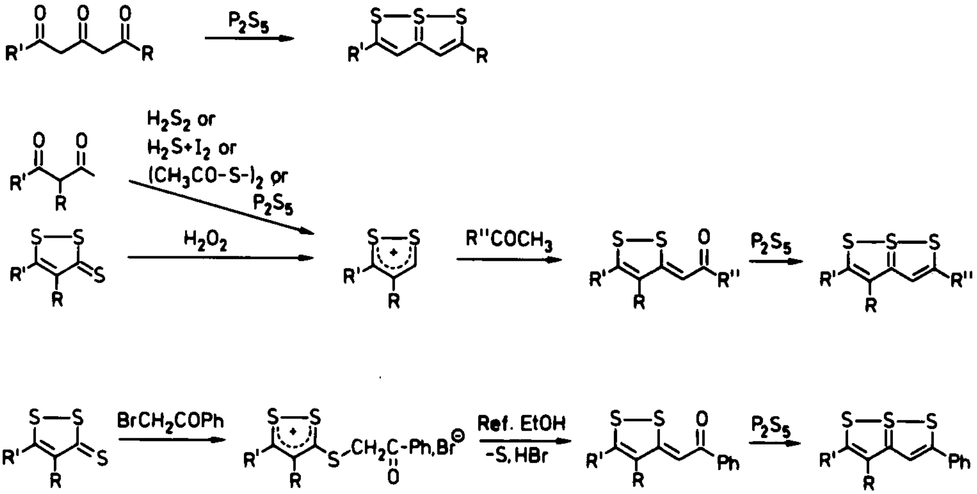
These observations raise the question: are these compounds really symmetrical 10-pi electron system such as naphthalene or have they to be described as a mixture of fast interconverting valence tautomers with a short and a long sulfur-sulfur distance which gives rise to an average equal sulfur-sulfur distance, SCHEME 8. Such a situation is known to be the case in bulvalene.



SCHEME 8

To put it in another way, has the system real C_{2v} symmetry or not? This was the situation when we started our studies of the structure of trithiapentalenes.

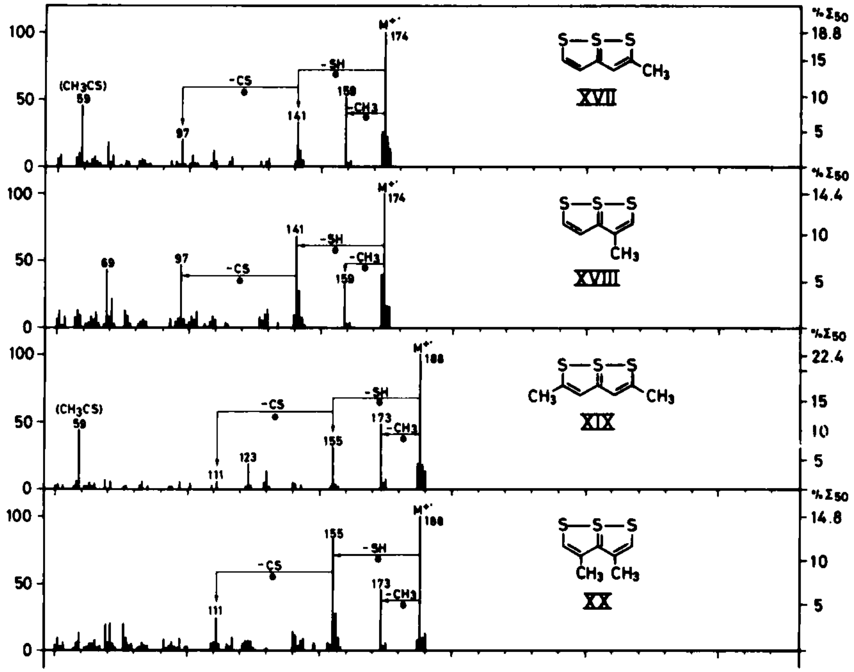
Only a few general methods exist for the synthesis of trithiapentalenes, SCHEME 9. The yields are very dependent on the substituents. Highest yields are obtained when aryl substituents are present.



SCHEME 9

MASS SPECTROMETRY

If one looks at the mass spectra of trithiapentalenes (6), SCHEME 10, one sees that they look very much like the mass spectra of aromatic naphthalene-like systems with intense peaks corresponding to molecu-

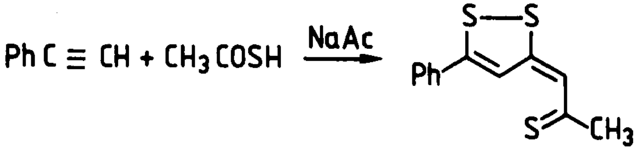


SCHEME 10

lar ions. However, the mass spectra cannot give us much information concerning our structural problems.

As the peculiarity of trithiapentalenes is without doubt related to the interaction between all 3 sulfur atoms, it could therefore be of interest to study a compound with the same structural elements but without the interaction between the 3 sulfur atoms.

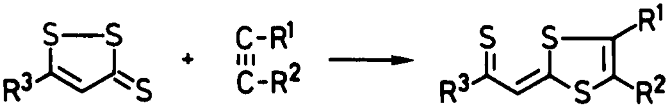
In the literature the reaction in SCHEME 11 is described (7).



SCHEME 11

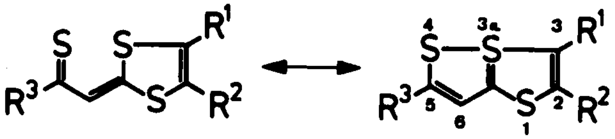
As indicated it is expected that it should give rise to what we can call a trans-trithiapentalene.

Another class of compounds, isomeric with trithiapentalenes, is known. These compounds are called iso-trithiapertalenes. They are formed from 1,2-dithiol-3-thiones and alkynes (8), SCHEME 12.



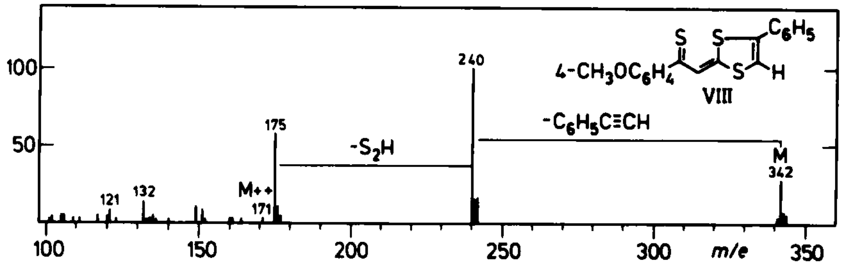
SCHEME 12

In these compounds no-bond-single-bond-ressonance is also possible, SCHEME 13.



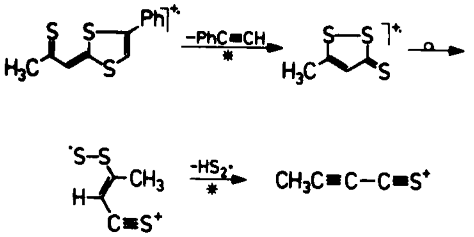
SCHEME 13

The mass spectrum of such an iso-trithiapentalene is shown in SCHEME 14.



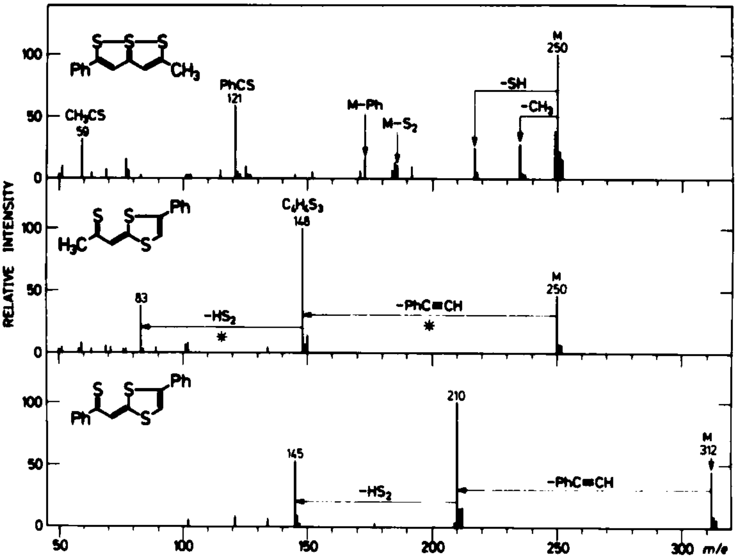
SCHEME 14

The characteristic difference between the mass spectra of these compounds and those of trithiapentalenes is that in the iso-compounds the molecular ion is not the base peak. The base peak is a peak corresponding to the loss of HS_2 from the molecular ion (9), SCHEME 15. This fragmentation indicates a lower stability of the molecular ion in the case of the iso-trithiapentalenes than the trithiapentalenes.



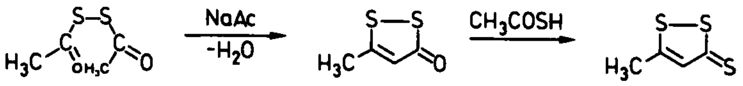
SCHEME 15

If one looks at the mass spectrum of a trans trithiapentalene, it is obvious that it has a strong resemblance to that of an iso-trithiapentalene (10), and, in fact the compound is an iso-trithiapentalene, SCHEME 16.



SCHEME 16

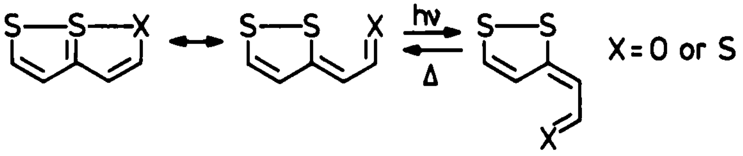
The formation of this compound can be explained as depicted in SCHEME 17.



SCHEME 17

The compound can in fact be synthesised starting from diacetyldisulfide.

We were happy finding that the trans-trithiapentalenes were not stable isolatable compopunds, as we had observed during a photochemical study of trithiapentalenes that upon irradiation trithiapentalenes were transformed into compounds which reversible revert, by a dark process, to the starting trithiapentalenes (11), SCHEME 18.



SCHEME 18

A trans structure has been ascribed to the photoproduct. Our observations are inconsistent with the fact that it should be possible to isolate the stable trans compounds.

NMR-STUDIES

Until now it has never been possible to detect different NMR signals from equivalent substituents in symmetrical substituted trithiapentalenes neither by proton nor by C-13 NMR studies (12). A priori it seems relevant to use S-33 NMR for the study of these compounds. However, the problem is that we need a method with high sensivity. Due to the quadropole moment of S-33, SCHEME 19.

^{33}S
Spin 3/2
Quadropole moment -6.4×10^{-2}
Natural abundance 0.76 %
Relative sensivity (H=1) 2.26×10^{-3}

SCHEME 19

S-33 spectra have very broad lines in the range 500-1000 Hertz with very little fine structure. We have, nevertheless, tried to record the S-33 spectrum of a saturated solution of trithiapentalene but we did not obtain any signals even after 24 hours. This is probably due to the long relaxation time of S-33, which means that the dispersion signal has fallen to zero before we are able to start recording after the pulse.

We have much structural information on the trithiapentalenes from the crystalline phase, but as their structure is strongly dependent on crystal forces, it would be of intrest to have structural data from other phases as well.

By use of NMR spectroscopy in a non-isotropic, liquid crystal phase, we have been able to obtain such information for the liquid phase. Three principal liquid crystalline phases exists, SCHEME 20.

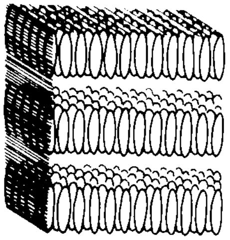


Fig.1. **Smectic** phase (4,4'-ethoxycarbonyl-azoxy-benzene).

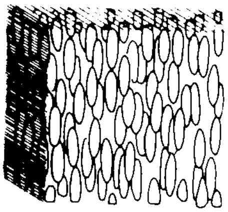


Fig. 2. **Nematic** phase (4,4'-dimethoxy-azoxybenzene).

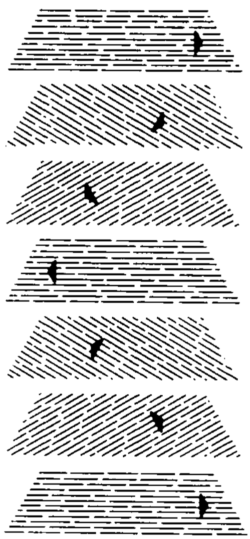
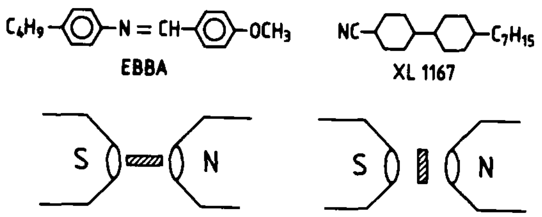


Fig. 3. Cholesteric phase (Cholesteryl propionate).

SCHEME 20

For our studies (13,14) we used the nematic phase, which have ordering only in one direction.

For earlier studies the phase EBBA was used, SCHEME 21. However this phase has the disadvantage of being oriented parallel to the magnetic field, which means that the probe cannot be spinned, as it will change the orientation of the molecules in the magnetic field. Without spinning, however, one gets broad signals in the spectra (13). In later studies we have therefore used a phase called XL 1167 which orients perpendicular to the field. The probe can then be spinned producing narrow lines which enables observation of the C-13 satellites in natural abundance (14).



SCHEME 21

From these spectra one can find the C-13 coupling constants. Normal spin-spin coupling constants are not directly related to the distances between the nucleus as these are electronic transitions. However, the dipole-dipole coupling constants, which can be obtained directly from the spectra in the anisotropic phase, are directly related to the distances, SCHEME 22.

$$D_{ij} = -(\hbar\gamma_i\gamma_j)2\pi\left\langle\frac{1}{r_{ij}^3}\right\rangle S_{ij}$$

SCHEME 22

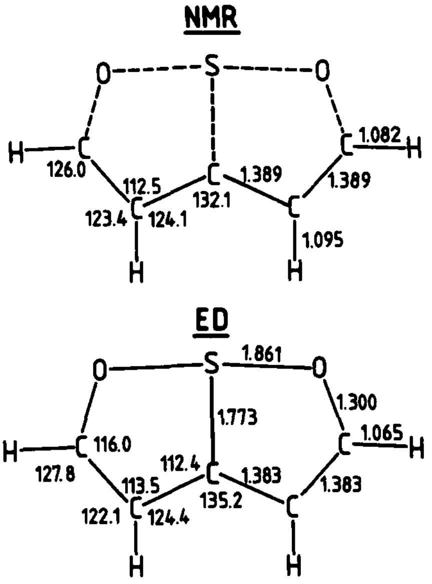
If a molecule has lower symmetry than C_{2v} two ordering parameters are needed to calculate the distances between the nuclei.

We have found for trithiapentalene and 1,6-dioxa-6a-thiapentalene, SCHEME 23, that only two ordering parameters are needed to calculate the distances. This observation gives a strong indication for a structure with a rigid C_{2v} symmetry.

SCHEME 23

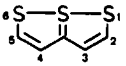
If a tautomeric equilibrium were present, and we assume that the rate of interconversion is slower than the rate of reorientation of the molecules in the nematic phase, we need 3 ordering parameters to relate the values of the dipole-dipole coupling constants to the geometry (14). Our observation that only 2 parameters are needed implies that if a tautomeric equilibrium is present the rate of interconversion between two possible tautomers of the molecule is very high. This implies the lifetime of a possible tautomer has to be shorter than 10^{-10} sec. This is equivalent to the statement that the molecule has not internal motions other than the normal vibrational displacements. Since we have included the C-13 couplings in our calculations, our system consists of a highly overdetermined set of dipole-dipole couplings. It therefore seems rather resonable to assume that the iterative fit of the dipole-dipole couplings would not have succeded unless the molecule had a rigid C_{2v} symmetry.

We have calculated the geometry of 1,6-dioxa-6a-thiapentalene from the dipole-dipole couplings, this calculation is in accordance with electron diffraction studies. Unfortunately it has not been possible to carry out an x-ray study of the parent compound, but the structure found is in agreement with the x-ray structure obtained for the dimethyl substituted compound, SCHEME 24.



SCHEME 24

The structure of trithiapentalene has been studied by means of several different methods, SCHEME 25. The methods used give slightly different results, which is not unexpected as the different methods determine different functions of the atomic coordinates.



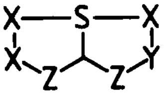
	R(C2-H2)	R(C2-C3)	C3A-C3-H3	C3A-C3-C2
NMR (ZLI 1132)	1.084 Å	1.387 Å	119.4	120.7
NMR (ZLI 1167)	1.082 -	1.394 -	119.4	120.2
ED	1.114 -	1.365 -	118.3	119.2
X-RAY		1.354 -	116	120.3

SCHEME 25

I feel that from what we know today, we can conclude that trithiapentalene is a naphthalene like 10-pi electron system with a rigid C_{2v} symmetry.

MICROWAVE SPECTRA AND ELECTRON DIFFRACTION

We are not in possesion of much information concerning the structure of familiar compounds, SCHEME 26.



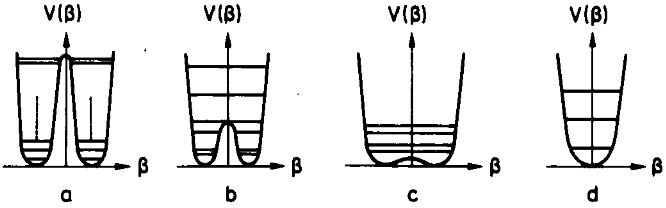
X=S, Se, Te, O or NR
Y, Z = C or N

SCHEME 26

But many of them probably have C_{2v} symmetry as well. We have studied the 1,6-dioxa-6a-thiapentalene and 1,6-dioxa-2,5-diaza-6a-thiapentalene, SCHEME 27, by microwave spectroscopy (15,16),

SCHEME 27

and by electron diffraction (17) in order to have information from the gas phase too. I shall not go into details with these studies. If we take a look at the potential curves for such compounds, SCHEME 28, a corresponds to valence tautomerism. It is possible to find different heights of the barrier until we come to d where we find only a single minimum corresponding to one single compound.

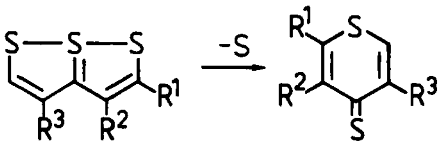


SCHEME 28

Calculations based on these observations in situation d are in agreement with both the microwave spectrum and the electron diffraction study.

We also tried to obtain a microwave spectrum from trithiapentalene. However, the vapour pressure of trithiapentalene is too low to allow us to record the microwave spectrum at room temperature. In a hot cell, however, only the spectrum from thiapyrane-4-thione was obtained.

During our studies of the mass spectra of the trithiapentalenes (18), we have observed that they lose sulfur in the mass spectrometer and form thiapyrane-4-thiones, SCHEME 29. This is probably a thermal reaction catalyzed by metal in the spectrometer. This reaction probably occurs in the microwave spectrometer too.

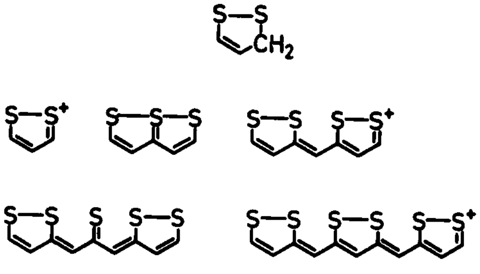


SCHEME 29

However, when we pump out the content of the cell we find that the main product was still the trithiapentalene. Trithiapentalene has a dipole moment (3.01 D), which is necessesary for the observation of a microwave spectrum. Thus the only explanation for the absent spectrum is that we have a broad minimum potential with many close lying energy levels, each signal is then too small to be detected.

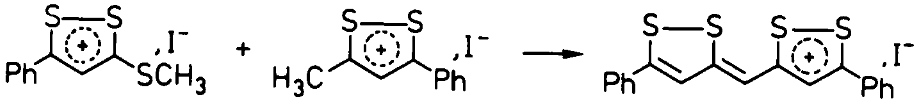
TRITHIAPENTALENE HOMOLOGUES

Trithiapentalene is just one member of a great family of compounds, SCHEME 30.



SCHEME 30

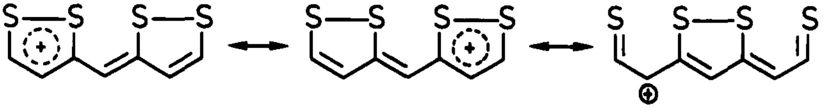
All compounds with an even number of sulfur atoms are cations whereas those with an uneven number are neutral compounds such as trithiapentalene. So far only compounds of this type with 2 to 5 sulfur atoms in a row are known. The first compound with 4 sulfur atoms was synthesized by Klingsberg in 1966 (19), SCHEME 31.



SCHEME 31

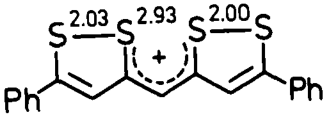
The compounds formed is a crystalline purple compound. It is characteristic for this type of compounds, that the introduction of more sulfur atoms intensifies the colour and shifts it towards the blue end of the spectrum. Dithiolylium salts are yellow, trithiapentalenes orange to red, the compounds with 4 sulfur atoms purple and those with 5 sulfur atoms deep blue-violet.

Delocalisation of electrons, as it is described for the trithiapentalenes by no-bond-single-bond-resonance, could give the 4 sulfur compounds a symmetrical structure, SCHEME 32.



SCHEME 32

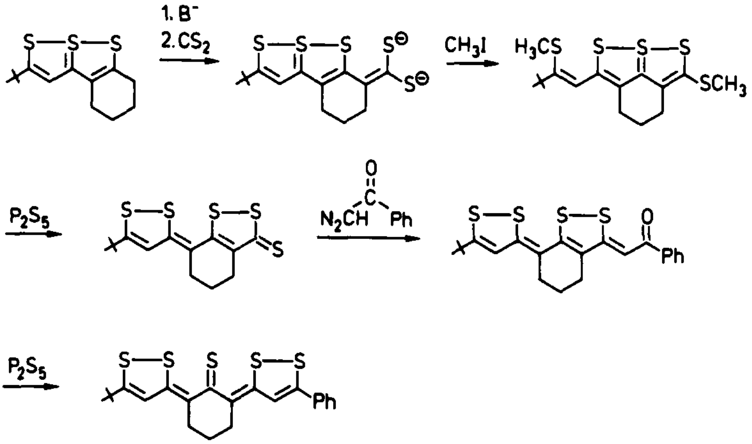
In any case, x-ray data indicates that the central sulfur bond is



SCHEME 33

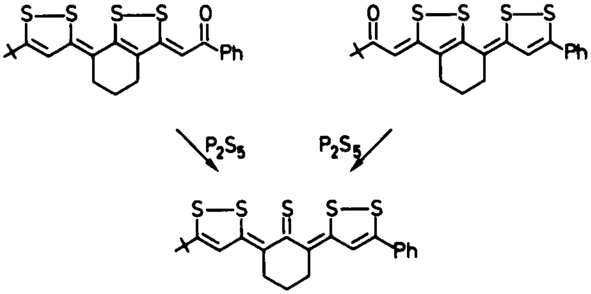
longer than the external ones (20), SCHEME 33. This means that there can only be a weak interaction between the two central sulfur atoms in these compounds.

The first compound with 5 sulfur atoms in a row was prepared by Stavaux and Lozac'h in 1967 (21), SCHEME 34.



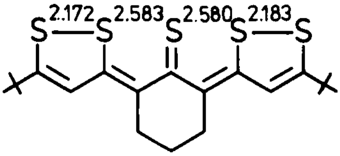
SCHEME 34

Stavaux gave a synthetic proof of the presence of no-bond-single-bond-resonance in these compounds, SCHEME 35. Without a reorganisation of the electrons, the two different ketones should give rise to two different compounds in the reaction with phosphorus pentasulfide. Nevertheless, Stavaux was only able to isolate a single product from the two different ketones (22).



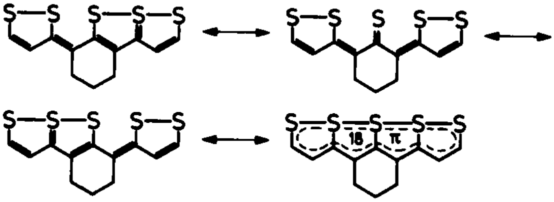
SCHEME 35

In this case too, x-ray structure determination shows that the sulfur-sulfur distances are different (23), SCHEME 36. This means delocaliza-



SCHEME 36

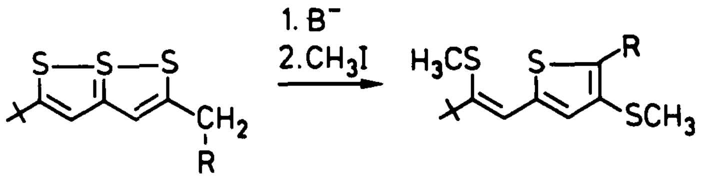
tion, SCHEME 37, as in trithiapentalene, does not exist. It is a pos-



SCHEME 37

sibility that the difference in sulfur-sulfur distances were caused by the cyclohexane ring, however this ring is an necessity for the synthesis. Without the cyclohexane ring complications occur (23).

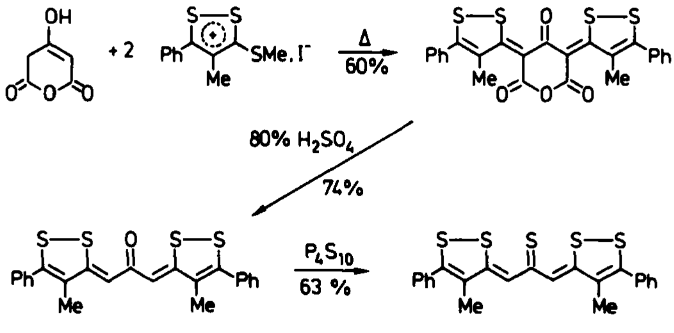
If the 2 and 3 positions of the trithiapentalene nucleus are not blocked by a cycloalkane ring, the anion will isomerize to give rise to a thiophene derivative, which can be isolated after methylation, SCHEME 38.



SCHEME 38

For many years we have tried to enlarge the family of multi-sulfur compounds with members containing more than 5 sulfur atoms in a row, but without success, partly because of the low solubility of the compounds. The synthesis gives low yields and complicated mixtures of compounds, which can only be separated by chromatografic methods.

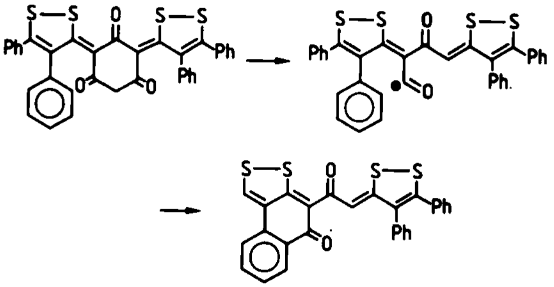
If one were able to prepare compounds with long chains of sulfur atoms in a row, these compounds could be of interest as organic conductors. Attempts to prepare such compounds has been made by Fanghänel and his group in Merseburg, but without success (24). During our studies to prepare such compounds we found a method to prepare 5-sulfur compounds without the central cycloalkane ring in the center (25,26), SCHEME 39.



SCHEME 39

It is necessary to split off the ring before reaction with phosphorus pentasulfide, as the compound with the central ring intact does not react with phosphorus pentasulfide. Unfortunately, until now we have not been able to prepare crystals suitable for x-ray studies, but NMR and UV data are in accordance with the observations by Stavaux.

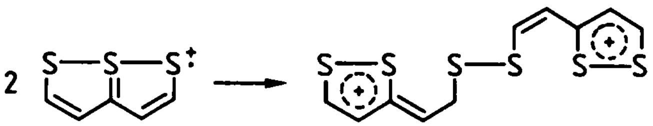
The method is suitable for different substituents. It only fails when an aryl substituent is present in position 3 of the dithiolylium salts used for the condensation, due to intramolecular cyclisation (26), SCHEME 40.



SCHEME 40

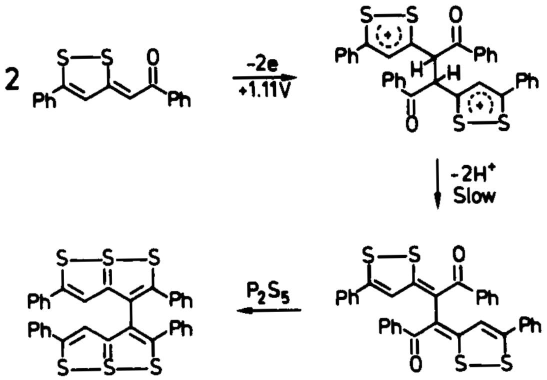
I want to mention, that compounds with more than 5 sulfur atoms are known in the 1,2-dithiole series, but they are not linear, and of rather exotic character.

If we oxidize trithiapentalene electrochemically, the following compound can be isolated (27), SCHEME 41.



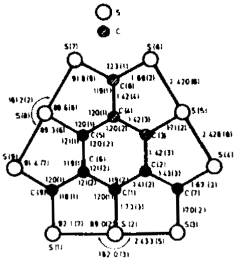
SCHEME 41

Another dimer can be obtained from electrochemical dimerization of 1,2-dithiol-3-ylidene ketones (28), SCHEME 42.



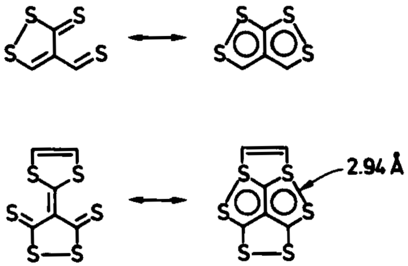
SCHEME 42

Another class of exotic compounds in a coronene analogue (29), SCHEME 43.



SCHEME 43

The last compound I will mention is the compound in SCHEME 44 (30).



SCHEME 44

You have here the possibility of a 10-pi electron system with no-bond-single-bond-resonance. However, x-ray studies of the p-tolyl compound show two different sulfur-sulfur distances.

The chemistry of 1,2-dithiole compounds shows great diversity with many intriguing problems but by the use of many different physical methods one is able to come to a final solution of these structural problems.

If I should answer the question: "Has the final structure of trithiapentalene been found?" - the answer is yes! It is my opinion that the question today is rather a philosophical question than a chemical one. The fundamental question is: How long a lifetime does a structure require in order for us to call it a compound?

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