

The structure of higher homologues of 1,6,6aλ⁴-trithiapentalenes the question of no-bond-single-bond-resonance in five sulfuratom homologues

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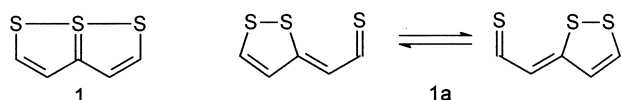
Abstract—X-Ray diffraction studies of 1,3-bis(4-methyl-5-phenyl-1,2-dithiol-3-ylidene)propane-2-thione indicates that this compound is not a fully delocalized π-electron system like 1,6,6aλ⁴-trithiapentalene although the S–S distances indicate some degree of delocalization. © 2003 Elsevier Ltd. All rights reserved.

1. Introduction

The structure of 1,6,6aλ⁴-trithiapentalenes **1** has been the subject of numerous papers during the past 50 years.^{1–8} The question discussed has been, whether **1** should be considered a 10π-electron naphthalene-like system or it should be considered a fast interconverting mixture of two valence tautomers each with one short and one long S–S distance **1a**. It can today be concluded without reasonable doubt, that we have to deal with a 10π-electron system displaying no-bond-single-bond-resonance.⁹ The bonding in trithiapentalenes can be described as an ‘electron-rich three-centre’ bond.

Higher homologues with 4 and 5 sulfur atoms such as **2** and **3** are known (Scheme 2). The structure of these compounds have been discussed but to a much lesser extent. No-bond-single-bond-resonance is not evident in these compounds.

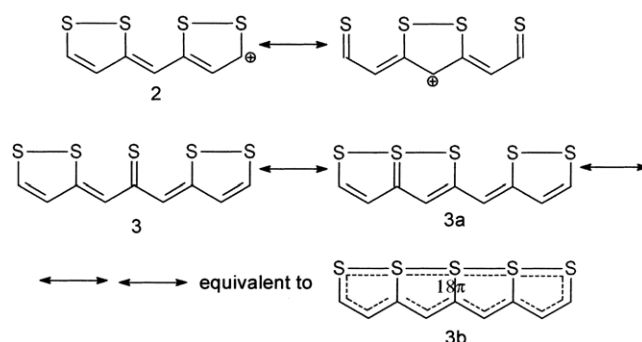
As is the case in trithiapentalenes, full delocalisation should give rise to 4 equiv. S–S distances in **3b**. If we consider the series from the 1,2-dithiolylium cation to **3b** (Scheme 5(1))



Scheme 1.

Keywords: trithiapentalenes; homologues; X-ray crystal structure; aromaticity.

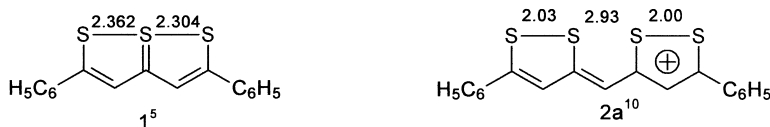
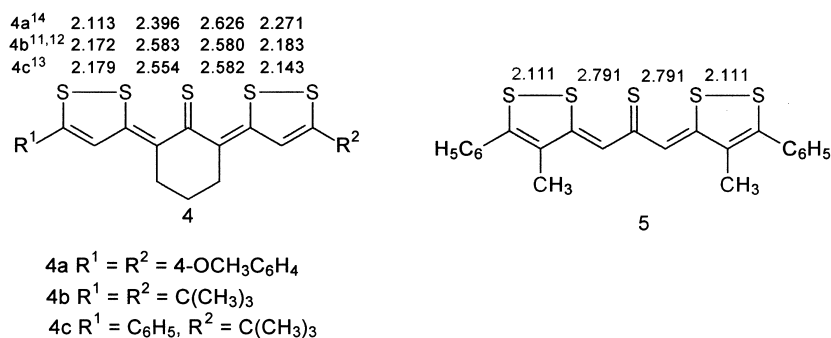
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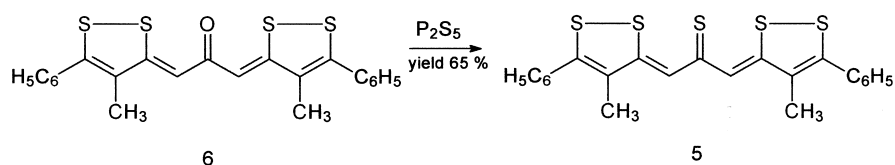
Scheme 2.

this series is analogous to the series of linear acenes in Scheme 5(2). Such a delocalization seems, however, not to be present for the representative of **2**¹⁰ as well as **4**^{11–14} where unequal S–S distances are observed. Representatives of **3** could originally only be synthesized if a central cyclohexano or cyclopentano ring was annelated.^{15,16} The presence of the central ring could be the reason why these compounds showed two different sulfur distances (Scheme 3). We have, however, succeeded in preparing such compounds without this central ring (Scheme 4).¹⁷

Compound **5**, unfortunately, crystallized in tiny microcrystals and we were not able to grow larger crystals suitable for X-ray diffraction at that time. We concluded, however, based on spectroscopic evidences, that the sulfur atoms were on a straight line but could not give any evidences for the equivalence of the S–S distances. We have now succeeded in obtaining a structure from the original microcrystals by X-ray diffraction.



Scheme 3.



Scheme 4.

2. Results and discussion

2.1. Chemistry

We have prepared compound **5** in 65% yield by sulfuration of **6** with phosphorus pentasulfide (Scheme 4).¹⁷

2.2. Theoretical calculations

The aromaticity and stability of the acenes have been studied theoretically^{18,19} and it has been shown that the resonance energy per π -electron is nearly constant from 5.98 kcal/mol for naphthalene (corresponding to trithiapentalene) to tetracene 5.82 kcal/mol¹⁹ corresponding to **3b**. It is concluded that the stability and the reactivity of the acenes increases with the number of rings in the acene series. One could therefore expect that the same was the case in the dithiolenes. Von Schleyer et al.¹⁹ have calculated the NICS (nuclear independent chemical shift) for acenes with 1–7 rings i.e. benzene to heptacene. They find in all cases that the NICS for the outer rings are higher than for the central rings and NICS for the inner rings are lower than for benzene, which means that they are more aromatic.

Geometry optimisation of **3** at the B3LYP/6-31G(d) level gives a qualitatively correct structure compared to **4/5** with S–S distances of 2.21 and 2.75 Å. The energy difference between the fully optimized structure and that optimized subject to the constraint of equal S–S distances at 2.45 Å is 8.7 kcal/mol.

To probe the aromaticity of the 1,2-dithiolenes in Scheme 1, we have calculated NICS values at the B3LYP/

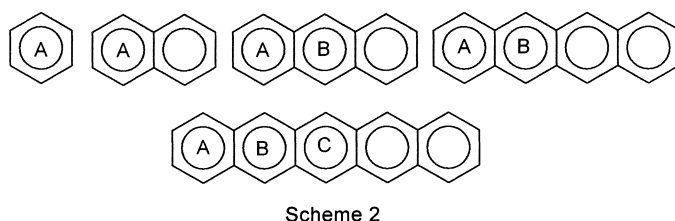
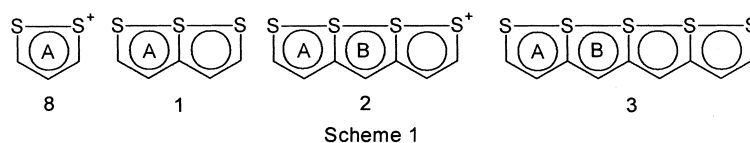
cc-pVTZ level for idealized geometries with C–C=1.40 Å, C–S=1.70 Å and S–S=2.45 Å. The results shown in Table 1 indicate that the outer ring A is more aromatic than benzene, but the central ring B is less aromatic than the A ring. These results are consistent with the nonequivalent S–S distances observed in the X-ray structures for compounds **2a** and **4/5** (Scheme 5).

Table 1. B3LYP/cc-pVTZ calculated NICS values for the systems 1,2,3 and 7 with an idealized geometry

Compound	A-ring	B-ring
Benzene	–8.2	
8	–16.3	
1	–10.2	
2	–10.9	–6.0
3	–10.3	–8.9

2.3. X-Ray diffraction structure of **5**

Compound **5** (Fig. 1) possesses crystallographically imposed two-fold symmetry with the central thione residing on the two-fold axis. A slight twist is observed in the otherwise essentially planar molecule with the two outer dithiolenes forming an angle of 21.4(4)°. The phenyl group forms an angle of 50.8(3)° to the dithiolenes. There are no intermolecular S...S interactions, but H(21c) of the methyl group is only 2.818 Å from S(3). This gives rise to layers along the *b*-axis perpendicular to the [101] direction. These are extended in that plane by 3.6 Å π ... π stacking of the phenyl groups. The stacking of layers along [101] has a H(16)...S(5) distance of 2.969 Å as the closest contact, but more interesting is probably the co-planarity of the C(1)–C(2)–C(3)–C(4)–C(5)–C(4') ($i=1-x, y, -z-1/2$)



Scheme 5.

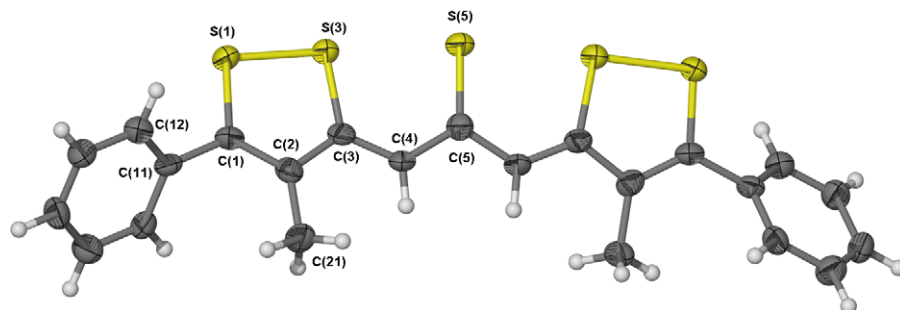


Figure 1.

fragment with its own glide-plane image ($x, 1-y, 1/2+z$) in a distance of 3.6 Å.

It is evident that the compound displays two different S–S distances (Table 2), a long one corresponding to the A ring and a short one corresponding to the B ring (Scheme 5(1)).

Table 2. Bond lengths (Å) and angles (°) for **5**

C(1)–C(2)	1.398(11)
C(1)–C(11)	1.492(12)
C(1)–S(1)	1.738(8)
C(2)–C(3)	1.429(12)
C(2)–C(21)	1.483(11)
C(3)–C(4)	1.369(11)
C(3)–S(3)	1.760(8)
C(4)–C(5)	1.436(10)
C(5)–S(5)	1.694(12)
S(1)–S(3)	2.111(3)
S(3)–S(5)	2.791(2)
C(2)–C(1)–C(11)	127.0(7)
C(2)–C(1)–S(1)	116.2(6)
C(11)–C(1)–S(1)	116.7(6)
C(1)–C(2)–C(3)	117.2(7)
C(1)–C(2)–C(21)	122.6(8)
C(3)–C(2)–C(21)	120.1(8)
C(4)–C(3)–C(2)	121.7(8)
C(4)–C(3)–S(3)	121.9(6)
C(2)–C(3)–S(3)	116.4(6)
C(3)–C(4)–C(5)	126.0(7)
C(4)–C(5)–C(4) ^a	117.3(10)
C(4)–C(5)–S(5)	121.3(5)
C(1)–S(1)–S(3)	96.0(3)
C(3)–S(3)–S(1)	93.8(3)
S(1)–S(3)–S(5)	173.75(15)

^a Symmetry transformations used to generate equivalent atoms: $-x+1, y, -z-1/2$.

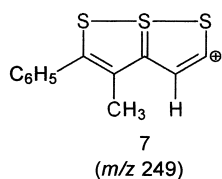
The difference in S–S distances are not much different from what is the case in the cyclohexano-annulated compounds. This shows that the different S–S distances are not caused by the presence of the cyclohexane ring.

From our observations we can conclude that we do not have a fully delocalised system corresponding to **3b** which in terms corresponding to the trithiapentalene case should involve an electron-rich-five-centre bond. However, the fact that the central sulfur distances of 2.791 Å is well below the van der Waals distance (3.7 Å)²⁰ indicates that the contribution of other canonical structures than **3** are important. However, from the structure obtained by X-ray diffraction it would be most correct to describe **5** as 1,3-bis(4-methyl-5-phenyl-1,2-dithiol-3-ylidene)propane-2-thione in the solid state.

2.4. Electron induced fragmentation

The mass spectra of **4** have been studied.²¹ In most cases is the molecular ion the base peak in these spectra and they display peaks corresponding to M–SH, M–S₂, M–S₃, M–S₄ and when phenyl substituents are present also m/z 121 (C₆H₅CS). The same is observed in the mass spectrum of **5** with the difference that the base peak is m/z 249 and the molecular ion only has a relative abundance of 12%. Accurate mass measurement of the m/z 249 ion gives an exact mass of 248.9866 corresponding to the composition C₁₂H₉S₃. From the structure of **5** it is assumed that the m/z 249 ion has structure **7** (Scheme 6).

This structure is substantiated by the CA (Collisional Activation) spectrum of the m/z 249 ions (collisional gas



Scheme 6.

helium), which features abundant peaks at m/z 216 (M–HS), m/z 185 (M–S₂), m/z 171 (M–C₆H₅) and m/z 121 (C₆H₅CS). This fragmentation mode is the same as observed for substituted 1,6,6aλ⁴-trithiapentalenes.^{22,23}

These fragmentations may be an indication that although the ground state of **5** corresponds to structure **3**, the structure of the excited state in the molecular ion more closely corresponds to **3a**.

3. Experimental

3.1. General

The EI mass spectra were recorded on a SSQ 710 Finnigan MAT (Germany) mass spectrometer and high resolution mass spectra were measured on a MALDI FTMS (Ionspec, Irvine CA, USA) spectrometer. The Collisional Activation (CA) spectra (He as collisional gas) were recorded on a six sector tandem mass spectrometer (Micromass Autospec 5F, Manchester).

3.1.1. Sample. 1,3-Bis(4-methyl-5-phenyl-1,2-dithiol-3-ylidene)propane-2-thione **5** was prepared as earlier described.¹⁷ EIMS m/z (%): (M⁺, 454), 11,(421), 2, (389), 2, (357), 1, (249), 100, (121)15. HRMS (MALDI) for m/z M⁺: calculated for C₂₃H₁₉S₅:455.0085. Found 455.0102. HRMS (MALDI) for m/z 249: calculated for C₁₂H₉S₃: 248.9861. Found: 248.9866.

3.1.2. X-Ray structure determination. Deep red, needle-shaped crystals of **5** were grown from cyclohexane. These were typically a maximum of 10 μm long and 1 μm thick. A single crystal of sufficient bulk (0.34×0.07×0.01 mm³) to show observable diffraction at a laboratory source was found and mounted in perfluoroether oil at 150 K on a 4-circle Nonius diffractometer equipped with a CCD detector. The highly anisotropic habit of the crystal prompted us to perform numerical absorption correction.²⁴ Nevertheless, the standard uncertainties of the measured unit cell parameters (and subsequently the bond lengths and angles) show a ten-fold increase over what must be considered standard. The structure was solved by direct methods using SIR97,²⁵ and refined (full-matrix on F^2) with SHELXL-97.²⁶ X-Seed²⁷ was used in preparing structure drawings, and WinGX²⁸ served to coordinate the programs.

Crystallographic data for **5**: C₂₃H₁₈S₅, $M=454.67$, $T=150$ K, $\lambda=0.71069$ Å, monoclinic, $C2/c$ (No. 15), $a=26.434(5)$ Å, $b=7.235(5)$ Å, $c=11.203(5)$ Å, $\beta=105.957(5)^\circ$, $V=2060.0(17)$ Å³, $Z=4$, $D_c=1.466$ mg cm⁻³, $\mu=0.57$ mm⁻¹, $F(000)=944$, 2344 unique reflections collected ($R_{int}=0.35$), 129 parameters, $R1[I>2\sigma(I)]=$

0.0937 , $wR2[\text{all data}]=0.2501$, $\Delta_{\text{final}}\rho(\text{min/max})=-0.51/0.44$ e Å⁻³.

Crystallographic data for the structure (excluding structure factors) in this paper have been deposited with the Cambridge Crystallographic data Centre (CCDC) as supplementary publication number CCDC 212786. Copies of the data can be obtained free of charge, on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: data_request@ccdc.cam.ac.uk).

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