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UNSYMMETRICAL POLYSULPHUR METACYCLOPHANES FROM THE REACTION OF MESITYLENE-2,4-DITHIOL WITH SULPHUR CHLORIDES

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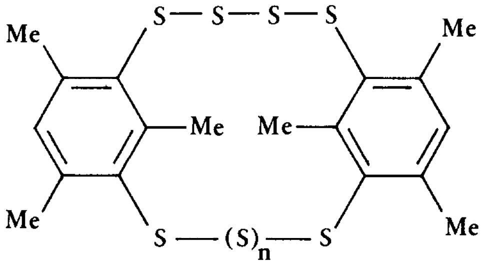
We report novel macrocyclic polysulphur compounds, i.e. 6,8,10,14,16,18-hexamethyl-1,2,3,4,11,12-hexathia[4.2]metacyclophane 1, and 6,8,10,15,17,19-hexamethyl-1,2,3,4,11,12,13-heptathia[4.3]metacyclophane 2, isolated in an attempted synthesis in the hexathia[3.3]metacyclophane series.

Dithioresorcinol and a number of 4,6-disubstituted derivatives react with sulphur dichloride (SCl_2) in 1:1 molecular ratio in diethyl ether under highly dilute conditions to give hexathia[3.3]metacyclophanes 3 in 10-15% yield.[1,2] Surprisingly, when mesitylene-2,4-dithiol is treated with SCl_2 under identical conditions, compounds 1, m.p. 211-213°, and 2, m.p. 179-181°, are obtained after chromatography on neutral alumina(benzene as an eluent) and recrystallization, in a 55% overall yield (ratio 1 to 2 ca. 10:1 by ^{1}H-n.m.r. analysis).



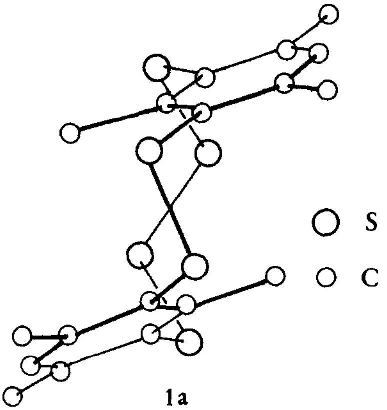
1: n=0
2: n=1

Compounds 1 and 2 are formed in identical yield also using sulphur monochloride instead of SCl_2. Other cyclic products were not detected in either reaction.

Satisfactory elemental analyses and mass spectra were obtained for these compounds.

The crystal structure of 1 was solved by MULTAN and refined to R = 0.033 for 3849 independent reflexions recorded on a SIEMENS AED diffractometer with MoKα radiation. The cell parameters are: $\underline{a}$ = 14.895(7), $\underline{b}$ = 17.156(7), $\underline{c}$ = 15.622(7) Å, $\underline{V}$ = 3991.6 Å^3, $\underline{D}_m$ = 1.44 g.cm^{-3}, $\underline{Z}$ = 8, $\underline{D}_c$ = 1.43, space group $Pca2_1$ (from Patterson analysis and structure refinement).

The structure analysis shows that the geometry of the two crystallographically independent molecules corresponds to the [4.2] isomer in the *anti* conformation 1a.

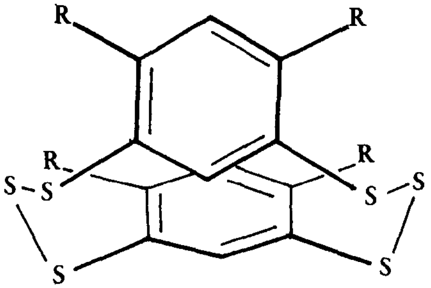


1a

The ^{1}H-n.m.r. spectrum ($CDCl_3$) of compound 1 shows resonance peaks at δ 7.21 (2H,s,ArH), 2.71 (6H,s,Me), 2.53 (6H,s,Me), and 1.78 (6H,s,Me) p.p.m. A pattern of three signals for methyl groups is consistent with the unsymmetrical structure 1a. Considering that the deshielding effect of the neighbouring sulphur atoms is additive,[2-4] the lowfield signal (δ 2.71) can be assigned to the methyl groups adjacent the tetrasulphide bridge, and the intermediate signal (δ 2.53) to the methyl groups adjacent the disulphide bridge. In spite of the deshielding effect of the surrounding sulphur atoms, the intra-annular methyl groups resonate at a higher field (δ 1.78). This suggests that these protons experience the ring current shielding effect of the opposite aromatic ring,[5] thus indicating that the stepped conformation is also retained in solution. Moreover, a variable temperature study of the n.m.r. of 1 showed no change in the spectral pattern between -88° and +186°C.

The ^{1}H-n.m.r. spectrum ($CDCl_3$) of compound 2 shows resonance peaks at δ 7.10 (2H,s,ArH), 2.78 (6H,s,Me), 2.63 (6H,s,Me) and 2.08 (6H,s,Me) p.p.m. The introduction of an additional sulphur atom in the bridging chain shifts the signals of the external methyl groups to slightly lower fields than those of compouns 1. A more relevant difference (Δδ 0.3 p.p.m.) is found in the absorption of the intra-annular methyl groups which, because of the ring expansion, experience a less effective ring current shielding effect of the opposite aromatic ring. An X-ray investigation of compound 2 is underway.

A reasonable explanation of the unexpected formation of compounds 1 and 2, instead of the generally observed formation of compounds of type 3, in the reaction of mesitylene-2,4-dithiol with sulphur chlorides can be given, considering the conformational preferences of hexathia[3.3]metacyclophanes 3. Between the two possible syn and anti onformations, the latter appears to be unlikely, since the molecular models show that in this case the values of the C-S-S-S dihedral angles are close to 0°, which should result in a strong repulsion of the unshared pπ electron pairs of the adjacent sulphur atoms. In fact, a literature survey[6] indicates that the dihedral angles for polythionic compounds range from 74° to 110°. On the other hand, the syn conformation appears to be more stable, since it involves dihedral angles of about 90°. In agreement with these considerations, preliminary results of structural analysis of one of these compounds (R = OCH_3)[2] show that the molecule exists in the syn conformation 3a, with dihedral angles close to 90°. Although it is certainly



3a

not valid to extrapolate directly from the crystalline state to solution, it is usually the case that the conformation assumed in the crystalline state at least predominates in solution.

In view of these findings, while excluding the existence of stable *anti* conformers, we believe that the *syn* hexathia[3.3]metacyclophane ring closure with internal groups as large as methyl is prevented, owing to mutual sterical repulsions. Therefore, sterically more favoured compounds such as *1* and *2* are formed when mesitylene-2,4-dithiol is treated with sulphur chlorides.

These results also point out the stereochemical differences of hexathia [3.3]metacyclophanes compared with 2,11-dithia[3.3]metacyclophanes.[5,7]

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