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SYNTHESIS OF 1,2,11,12-TETRATHIA[2.2](2,7)NAPHTHALENOPHANE

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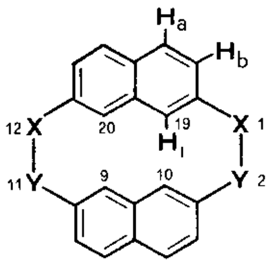
Abstract - Mild oxidation of 2,7-dimercapto-naphthalene under highly dilute conditions has afforded the title compound (4), which has been found to exist in a stepped *anti* conformation.

Considerable crystallographic and ^{1}H nmr evidence in [2.2]metacyclophanes has established the stepped nature of the ring system.[1] [2.2](2,7)Naphthalenophanes are closely related to [2.2]metacyclophanes with respect to the relative stereochemistry of the constituent aromatic ring. Rigid, stepped, *anti* conformations were in fact found in [2.2](2,7)naphthalenophane (1)[2] and 1,12-dithia[2.2](2,7)naphthalenophane (2),[3] the unusually high field strength of the absorptions due to the intra-annular hydrogen atoms being taken as diagnostic for such a conformation.
Recently the synthesis and some properties of [2.2](2,7)naphthalenophane-1,11-diene (3) have been also reported.[4]
We wish to report here the synthesis of 1,2,11,12-tetrathia[2.2](2,7)naphthalenophane (4), a metacyclophane based on the naphthalene nucleus and incorporating disulphide groups. We felt that the study of polysulphur bridged metacyclophanes, a



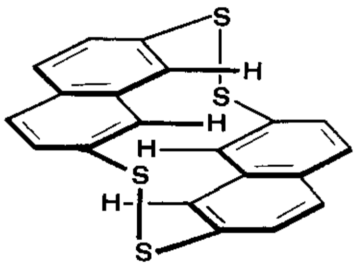
(1) X = Y = CH_2
(2) X = S; Y = CH_2
(3) X = Y = CH
(4) X = Y = S

recent class of organic compounds,[5,7] could be of particular interest, in view of a comparison of their structures and properties with those of corresponding metacyclophanes having hydrocarbon bridges.

Compound (4) was synthesized in 30-40% yield by mild oxidation of 2,7-dimercapto-naphthalene with iodine in benzene, under highly dilute conditions. The product was obtained as light yellow prisms, m.p. 238-240° (from chloroform), hardly soluble in organic solvents.

The mass spectrum (70 eV) of the bis-disulphide (4) shows the molecular ion at m/e 380 (base peak) and fragmentation ions at m/e 314 (5%) and 282 (5%), resulting from the molecular ion by subsequent loss of H_2S_2 (metastable peak at about m/e 259) and S, respectively. Symmetrical splitting of the molecule leads to the fragment at m/e 190 (16%), which loses subsequently two CS molecules to generate the fragments at m/e 146 (21%) (metastable peak at about m/e 112) and 102 (14%) (metastable peak at about m/e 71).

The 90 Mz ^1H nmr spectrum ($C_6D_5NO_2$) of the bis-disulphide (4) at 100° shows resonance peaks at δ 5.46 (4H, apparent s, H_i), 7.78 (4H, 2d, J 8.8 and 1.6 Hz, H_b), and 8.00 (4H, d, J 8.8 Hz, H_a). Inspection of molecular models reveals that 1,2,11,12-tetrathia[2.2](2,7)naphthalenophane (4) should exist in a stepped conformation (4a), in which the two halves of the molecule are arranged in two parallel planes. The upfield signal of intra-annular hydrogen atoms, H_i δ 5.46, suggest that these protons experience the ring current shielding effect of the opposing naphthalene nucleus, and provides a strong evidence in favour of the stepped *anti* conformation (4a). This high field absorption of intra-annular hydrogen atoms well agrees with those found for the corresponding intra-annular hydrogen atoms of compounds (1) (H_i δ 5.12) and (2)[δ 5.00 (9-H and 10-H) and 5.52 (19-H and 20-H)]. Therefore, it appears that the introduction of disulphide units in a [2.2](2,7)naphthalenophane structure should not change markedly the stereochemistry of the resulting cyclophane, although smaller steric interactions between the opposing naphthalene moieties can be foreseen because of the larger value of the S-S bond length with respect to C-C and C-S bonds.



(4a)

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REFERENCES

1. F. Vogtle and P. Neumann, Angew. Chem. Internat. Edn., 1972, 11, 73, and references therein.
2. W. Baker, F. Glockling, and J. F. W. McOmie, J. Chem. Soc., 1951, 1118; R. W. Griffin Jr. and N. Orr, Tetrahedron Letters, 1969, 4567.
3. F. Vögtle, R. Schäfer, L. Schunder, and P. Neumann, Liebig Ann. Chem., 1970, 734, 102.
4. J. R. Davy and J. A. Reiss, Chem. Comm., 1973, 806; Aust. J. Chem., 1976, 29, 163.
5. J. S. Bradshaw and J. Y. K. Hui, J. Heterocyclic Chem., 1974, 11, 649.
6. F. Fehér, K. Glinka, and F. Malcharek, Angew. Chem. Internat. Edn., 1971, 10, 413.
7. F. Bottino, S. Foti, S. Pappalardo, P. Finocchiaro, and M. Ferrugia, J. Chem. Soc. Perkin I, 1979, 198; F. Bottino, S. Foti, S. Pappalardo, and N. Bresciani Pahor, Tetrahedron Letters, 1979, 1171.

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