Novel Multi-bridged Macrocyclic Systems[1]

By FRITZ VÖGTLE,* GERD HOHNER, and EDWIN WEBER
(Institut für Organische Chemie der Universität, D87 *Würzburg, Landwehr, Germany)*

Summary New macrocyclic compounds, in which a large cavity is enclosed by three or four aliphatic bridges between two parallel aromatic systems, have been synthesized by making use of the dilution principle.

RING systems containing aromatic systems arranged face to face[2] are interesting, because of their spherical form, as a host lattice for inclusion compounds, and for the study of transanular interactions. Whilst a three-fold bridge connection has been achieved only for the benzene ring,[3] the four-fold bridging of an aromatic system has not so far been reported.

Although the hydrocarbon (I) has not yet been obtained by Wurtz-type dimerization, the compound (IIa)†‡, *m/e* 786 (M^+), m.p. >450°, which is important as an intermediate in the production of (I), was isolated in a yield of up to 31% from the reaction of 1,3,5-tris-[(*p*-bromomethyl)-phenyl]benzene, m.p. 194—196° with 1,3,5-tris-[(*p*-mercaptomethyl)phenyl]benzene, m.p. 163—165°, using a dilution-principle apparatus (3C-DP-reaction).[4] The almost insoluble trisulphone (IIb), *m/e* 882 (M^+), m.p. >450°, is formed by H_2O_2 oxidation.

The compounds (III)‡ were obtained by analogous dilution-principle reactions of 1,3,5-tris-[(*p*-bromomethyl)-phenyl]benzene with the corresponding 1,ω-dimercapto-alkanes. Compound (IIIb) could also be obtained from the complementary reaction of 1,3,5-tris-[(*p*-mercaptomethyl)phenyl]benzene with 1,3-dibromopropane, but this method was found in general to give a lower yield.

In the mass spectra (which show that no bromine atoms are present in the colourless crystalline compounds) the molecular peaks (M^+) were either entirely absent (IIIb—d) or only weak (IIIa). Osmometric determination of the molecular weight is not possible because of the low solubility. However, in the ^1H n.m.r. spectra (in $CDCl_3$) all the compounds (III) showed, as expected, only one singlet for all the benzylic CH_2 protons between δ 3·67 and 3·90 [(IIa) 3·90]. For the ethano-protons in (IIIa) a singlet was also

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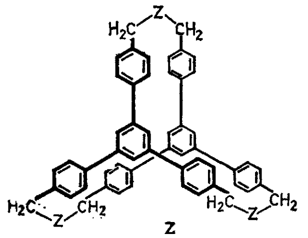
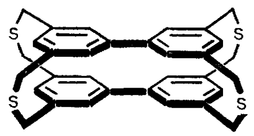
† Phane name: 2,23,50-trithia[3,3,3] (4′,4″, 4‴)-*sym*-triphenylbenzeno<8>phane.[1]

‡ Satisfactory elemental analyses were obtained for all compounds described.

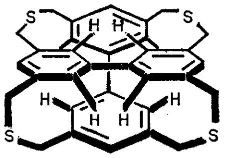
observed, whilst the corresponding bridge protons in the compounds (IIIb—d) formed multiplets. The singlet of the total of six hydrogen atoms of the two central benzene rings at δ 7·60—7·42 could be clearly recognized in all cases.



Z
(I) Single bond
(IIa) S
(IIb) SO$_2$



(IV)

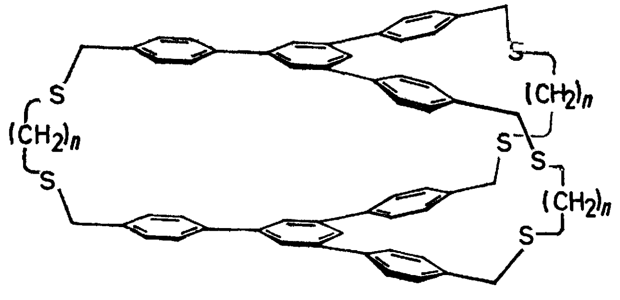


(V)

The successful preparation of doubly bridged biphenylophanes by Haenel and Staab[5] encouraged us to attempt the four-fold bridging of the biphenyl system. From the reaction of 3,3′,5,5′-tetrakis(bromomethyl)biphenyl, m.p. 208—210°, with 3,3′,5,5′-tetrakis(mercaptomethyl)biphenyl, m.p. 104—105°, according to the dilution principle a compound was obtained in 8% yield which crystallized in platelets and decomposed with dark colouration at 290°.

The elemental analysis and the mass spectrum§ of this compound is consistent with the structure (IV), in which the biphenyl systems are arranged parallel to one another, or the structure (V) with crossed biphenyl units.

Whilst the AB system from the benzyl protons (δ_A 3·78, δ_B 4·00, J_{AB} 15 Hz) found in the ^{1}H n.m.r. spectrum is in agreement with both isomers, the structures (IV) and (V) can be distinguished by the resonance of the aromatic protons. It can be seen from molecular models that in (V), but not in (IV), all the biphenyl 2,2′,6,6′-protons lie just above or below the plane of one of the opposite benzene rings. In the case of (V) a strong upfield shift for 8 aromatic protons is therefore to be expected on account of the anisotropy effect. This is not observed, however. Absorption lines are found only at δ 6·84 (rel. int. 8) and δ 7·12 (rel. int. 4). The slight upfield shift observed for the 8 2,2′,6,6′-protons is in agreement with the face to face arrangement of the aromatic groups in (IV).¶



	n	Decomp. point (°)	Yield (%)
(III) a	2	280	4
b	3	280	5
c	4	280	5
d	5	270	5

Attempts are at present being made to prepare hydrocarbons corresponding to (II) and (IV) with bridges having only two members by extrusion of sulphur through sulphone pyrolysis[6] and Stevens rearrangement.[7]

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§ The elemental composition of this compound was also established by double focussing mass spectrometry.

¶ Phane name: 2,17,32,35-tetrathia[3,3,3,3](3,3′,5,5′)biphenylo<4>phane.

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