A New Synthesis of Bridged Aromatics: 10,15-Dihydro-5*H*-tribenzo[*a,d,g*]cyclononene and its Analogues

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Summary Cycloalkylation of benzene using compounds (I), *e.g.* 2,2′-bis(hydroxymethyl)diphenylmethane, in sulphuric acid produces the bridged aromatic compounds (II) with a novel nine-membered ring system, to which a rigid crown conformation and a flexible form have been suggested for the parent hydrocarbon (IIa) and sulphur analogue (IId), and for the ketone (IIb) and the oxygen analogue (IIc), respectively.

The chemistry of medium and large-sized bridged aromatics with one or two aromatic rings has been extensively studied.[1] Only a few examples of compounds containing three or more aromatic rings have been reported[2] and these are mostly oligomers formed as by-products during the synthesis of the lowest members.[3] We have developed a simple, efficient method for the preparation of the title compounds which are difficult to prepare by other methods.

A key step is the cycloalkylation of benzene with diol (I) using sulphuric acid.[4] For example, a dilute benzene solution (*ca.* 1×10^{-2}M) of (Ia), m.p. 157·5—158·5°,† was added to a mixture of benzene and conc. H_2SO_4 (each 20 ml) over a period of up to 48 h using a modified Hershberg funnel at room temperature. By chromatographic separation 10,15-dihydro-5*H*-tribenzo[*a,d,g*]cyclononene (IIa) was obtained in 74·5% yield as colourless needles, m.p. 274—276°. It showed a parent ion peak at *m/e* 270 and was correctly analysed for $C_{21}H_{18}$.

Similarly (Ic), m.p. 96—98°, prepared from 2,2′-dimethyldiphenyl ether, gave the oxygen analogue (IIc), m.p. 194—195°, as colourless needles in 40·5% yield: ν_{C-O}

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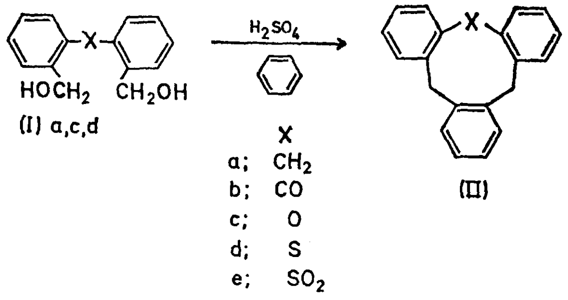
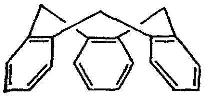
† Prepared from 2,2′-di-iododiphenylmethane by a sequence of reactions including the conversion, I → CN → CO_2H → CO_2Me → CH_2OH.

1220 cm^{-1}; *m/e* 272. The sulphur analogue (IId) was obtained from (Id) in 83·3% yield as colourless needles, m.p. 218—219°; *m/e* 288. Oxidation of (IId) gave the sulphone (IIe), m.p. 208·5—210°; ν_{SO_2} 1315, 1298, and 1150 cm^{-1}; *m/e* 320.

Conclusive evidence for the suggested structures was obtained from ^{1}H and natural abundance ^{13}C n.m.r. spectra. The proton-decoupled spectrum of (IIc), for example, showed one methylene carbon resonance at 35·0 p.p.m. (downfield from Me_4Si) and nine aromatic carbon resonances at 121·3, 124·4, 126·4, 127·3, 129·9, 130·3, 134·4, 138·5, and 156·3 p.p.m., all of equal intensity as was expected from the structure. The last three resonances have no proton induced splitting, and thus can be assigned to quaternary carbons. The lowest field signal can be assigned to carbon atoms connected to oxygen. The sulphur analogue (IId) had similar spectral features.





(III)

The hydrocarbon (IIa) is the parent compound of cyclotriveratrylene[5] and has the rigid crown conformation found for the latter,[6] as shown by ^{1}H n.m.r. measurements. It had benzyl methylene proton resonances as an AB quartet at δ 3·74 (quasi-equatorial) and 4·90 (quasi-axial). The band position, J 13 Hz, and $\Delta\nu$, 1·16 p.p.m., are comparable with values found for cyclotriveratrylene; δ 3·45 and 4·70, J 14 Hz, and $\Delta\nu$ 1·25 p.p.m.[6] The AB quartet remained unchanged up to 150° ($CDBr_3$) suggesting the rigidity of the crown conformation (III).

(IId) showed an AB quartet at δ 3·78 and 5·67 (J 13 Hz) which remained unchanged up to 150°. For the sulphone (IIe) $\Delta\nu_{AB}$ was larger and reached 2·10 p.p.m. (δ 3·85 and 5·95).

The downfield shift of the quasi-axial proton signals can be explained by steric compression effect caused by the overcrowding at the crown top.

The oxygen analogue (IIc) showed a singlet for methylene protons at δ 4·29. It remained as a singlet in a wide variety of solvents and at temperatures down to $< -70°$, suggesting a flexible conformation,‡ as had been postulated by Cookson *et al.*[6b]

The monoketone (IIb) obtained by oxidation of (IIa) is also a flexible molecule since the methylene resonance at δ 3·85 remains a singlet even at $-65°$.‡

Compared with acyclic models such as 2,2′-dimethyldiphenylmethane or *o*-dibenzylbenzene, (IIa) showed general bathochromic shifts in ^1L_b bands of 4—5 nm, indicating π–π interaction in the rigid crown conformation. This was reflected in the higher π-basicity of (IIa) compared with *o*-dibenzylbenzene as revealed by comparison of the λ_{max} (CH_2Cl_2) for the charge-transfer bands between tetracyanoethylene which occurred at 430—440 and 410—420 nm, respectively.

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‡ Using a 60 MHz spectrometer, the oxygen analogue (IIc) in CD_2Cl_2 showed two broad absorptions at δ 3·75 and 4·85 at $-81°$, whereas the singlet for (IIb) remained unsplit even at $-90°$ only with an increase in half-band width (*ca.* 5 times).

[1] *E.g.*, D. J. Cram and J. M. Cram, *Accounts Chem. Res.*, 1971, **4**, 204.

[2] *E.g.*, M. Haenel and H. A. Staab, *Tetrahedron Letters*, 1970, 3585.

[3] W. Baker, J. F. W. McOmie, and J. M. Norton, *J. Chem. Soc.*, 1951, 1114; K. Burri and W. Jenny, *Helv. Chim. Acta*, 1967, **50**, 1978; R. Flammang, H. P. Figeys, and R. H. Martin, *Tetrahedron*, 1968, **24**, 1171.

[4] For synthesis of [2,1,1]metacyclophane see T. Sato, M. Wakabayashi, and K. Hata, *Bull. Chem. Soc. Japan*, 1970, **43**, 3632.

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[6] (a) B. Miller and B. D. Gesner, *Tetrahedron Letters*, 1965, 3351; (b) R. C. Cookson, B. Halton, and I. D. R. Stevens, *J. Chem. Soc.* (*B*), 1968, 767.