X-Ray Crystal and Molecular Structure of the p-t-Butylphenol–Formaldehyde Cyclic Octamer Cyclo{octa[(5-t-butyl-2-acetoxy-1,3-phenylene)methylene]}

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Summary   Single-crystal X-ray analysis has confirmed the octameric structure of the high melting point product obtained from the base-catalysed condensation of formaldehyde and p-t-butylphenol.

Cyclic oligomers (1) derived from the condensation of phenols and formaldehyde, and recently named[1] calix[n]-arenes, are an interesting class of synthetic matrices of different sizes, interesting in their ability to form molecular complexes with neutral organic molecules and, after suitable functionalisation, to act as selective catalysts. We have undertaken a systematic study of these compounds and recently reported a preliminary account of the formation of a 1:1 complex between calix[4]arene and toluene which is included in the molecular cavity as a guest molecule,[2] and the complexing properties of podands built on these matrices towards alkali and ammonium cations.[3]
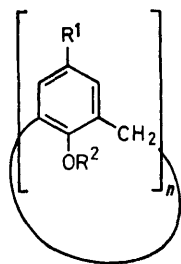
(1) R^2=H
(2) R^2=Ac

For the cyclic compound formed as a major product in the base-catalysed condensation of p-t-butylphenol and formaldehyde (Cornforth's HBC[4]), which can be obtained in yields as high as 91% with a recently reported modified procedure,[5] an octameric structure has been postulated on the bases of chemical[6] and physicochemical evidence[1] (osmometry and mass spectroscopy).

The compound, crystallised from chloroform, forms triclinic plates which lose solvent of crystallization very rapidly giving a powder, m.p. 400 °C. Acetylation (acetic anhydride–MeCO$_2$K) gives HBC octa-acetate which forms, from acetic acid, crystals, m.p. 352 °C (decomp.), suitable for an X-ray structure analysis, which was carried out with the aim to establish definitively the number of phenolic units in the cyclo-oligomer and to supply information on the conformational arrangement of the chains in the

macro-ring, which is important for complexation studies of the podands built on this matrix.

Crystal data: $C_{104}H_{128}O_{16}$, triclinic prisms, space group $P\bar{1}$, $a = 11.518(3)$, $b = 14.880(7)$, $c = 16.356(6)$ Å, $\alpha = 106.49(3)$, $\beta = 77.67(2)$, $\gamma = 100.00(1)°$, $Z = 1$. Least-squares anisotropic refinement using 7711 observed [$I \geqslant 2\sigma(I)$] reflections (out of 9877 measured) gave $R = 0.087$ and indicated the structure depicted in the Figure.†
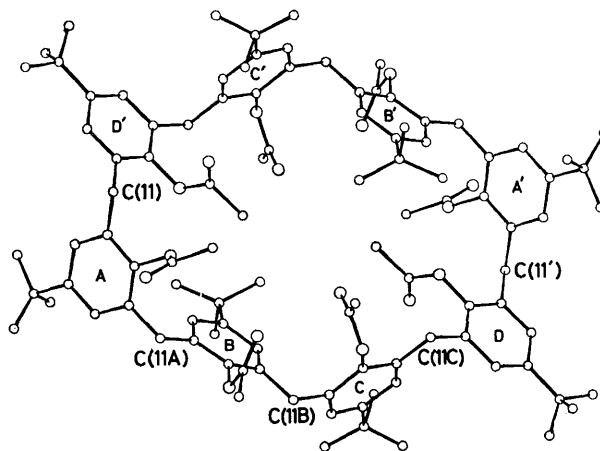
FIGURE. Structure of the cyclic octamer (2; R^1 = Bu^t, $n = 8$).

All the t-butyl groups show disorder in at least two orientations by rotation of approximately 60° and with occupancy from 0.62 to 0.53. In the Figure only the groups with the highest occupancy are shown.

The molecule lies on a centre of symmetry and possesses an ellipsoidal shape with the polar acetyl groups oriented within the cavity and the hydrophobic t-butyl groups outside. The four methylene bridging carbon atoms of the asymmetric unit roughly lie on a plane [the distances from the least-squares plane being C(11) 0.038(6), C(11A) −0.091(6), C(11B) 0.133(8), and C(11C) −0.053(7) Å] with the centre of symmetry out of the plane by 1.569(6) Å, so the molecule possesses a step along the elongation of its ellipsoid C(11) .. C(11'). The conformation of the molecule can be described by the dihedral angles between the benzene rings and the methylene mean plane [ring A 49.7(5), B 60.2(5), C 59.6(6), and D 40.0(5)°] and between the acetoxy-groups and the benzene rings attached to them [A 79.2(5), B 86.8(5), C 81.7(5), and D 77.3(6)°]. The benzene rings show an helical arrangement around the

macromolecular ring with dihedral angles A:B 84·8(5), B:C 86·4(5), C:D 85·1(5), and D:A′ 81·7(5)°. In this crystal the internal cavity is not occupied (from X-ray analysis and n.m.r. spectroscopy) and has an approximate size of 1·51 × 3·73 × 4·56 Å (ca. 107 Å³) as determined with a computer programme which approximated the cavity shape to an ellipsoid. This size should be compared with the 2·42 × 2·54 × 2·13 Å (ca. 55 Å³) in the α-cyclodextrin $(H_2O)_2$[7] inclusion complex.

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