

Crystal and Molecular Structure of Cyclo{quater[(5-t-butyl-2-hydroxy-1,3-phenylene)methylene]} Toluene (1:1) Clathrate

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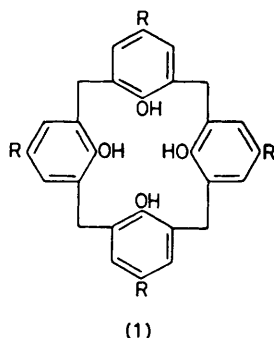
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Summary Single-crystal X-ray analysis has shown the tetrameric structure of the low melting point product obtained from the base catalysed condensation of

formaldehyde and *para*-t-butylphenol and its ability to form a stable cage-type clathrate with toluene.

PHENOLIC [1,1,1,1]metacyclophanes (**1**),^{1,2} cyclic tetranuclear oligomers obtained from the base-catalysed condensation of *para*-substituted phenols and formaldehyde, have received renewed attention recently.²⁻⁴ However



the structures of these compounds, mainly based on chemical,^{5,6} spectroscopic,² and unit cell crystal⁶ data, have not been well established. Recently⁴ Gutsche *et al.* questioned the long-established tetrameric structure of these compounds. By comparing their results with those of Kammerer,⁷ who used the Hayes and Hunter³ 'step-wise' procedure for the synthesis of (**1**), they concluded that products obtained from the 'direct'⁵ condensation of *para*-substituted phenols and formaldehyde are 'mixtures of two or more components which appear to be cyclic oligomers with five or more aromatic nuclei in the cyclic array.' Our interest in this field arose from the possibility of using these systems as potential clathrating agents for organic molecules and as 'building blocks' for crown-ether type guest molecules.

We now report the crystal and molecular structure of the compound (**1**, R = Bu^t) derived from the direct 'one flask' condensation of *para*-*t*-butylphenol and formaldehyde which corresponds to the low melting material (m.p.

320–322 °C) isolated by Cornforth⁶ and which was obtained following essentially his procedure. Recrystallization from toluene yields air-stable, colourless, tetragonal plates of (**1**, R = Bu^t), (m.p. 328–329 °C): space group $P4/n$, $a = b = 12.756(2)$, $c = 13.793(3)$ Å, $Z = 2$. Least-squares anisotropic refinement using 1251 reflections (merged from measurements of $2571 \pm h, k, l$ reflections) gave $R = 0.092$, $R_w = 0.086$ and indicated the structure depicted in Figure 1.†

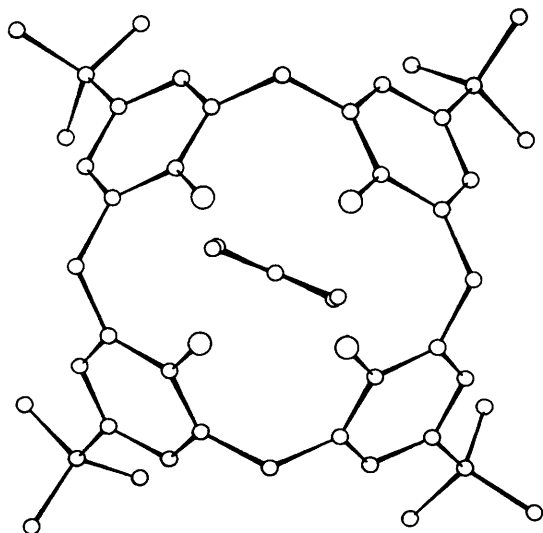


FIGURE 1. View along the fourfold axis of the cage-type clathrate formed between (**1**, R=Bu^t) and toluene.

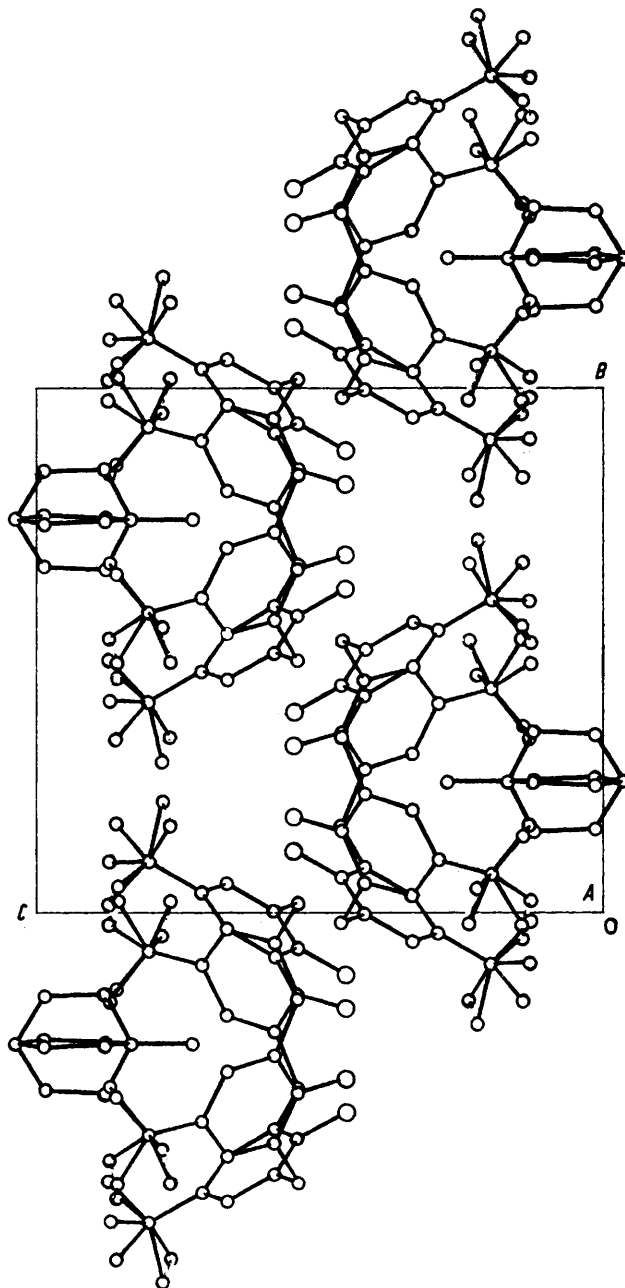


FIGURE 2. Molecular packing of the clathrate of (**1**, R=Bu^t) and toluene.

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

Both the toluene molecule and the t-butyl groups show disorder. The toluene molecule lies on a fourfold axis passing through the C-CH₃ bond, and thus can have two equivalent orientations in the cavity of (1). The t-butyl groups are disordered in two orientations by rotation of 29° and with occupancy 0.77 and 0.23. In Figure 1 only the t-butyl groups with the highest occupancy and one of the two orientations of the toluene molecule are shown.

The crystal packing is shown in Figure 2. The conformation of the tetramer, which has a fourfold symmetry, is calix shaped and is mainly determined by the four

intramolecular hydrogen bonds [O...O = 2.670(9) Å]. The dihedral angle formed by the phenyl rings with the molecular fourfold axis is 123°. Bond lengths and angles are as expected. The interactions between the host molecule and the cavity are mainly due to the t-butyl groups.

Further structural work is in progress on the same class of clathrates and on the other oligomer (m.p. 380 °C) obtained by Cornforth.

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