SYNTHESIS AND STRUCTURE OF HEXAKIS(p-HYDROXYPHENYLOXY)BENZENE: A
VERSATILE ANALOGUE OF THE HYDROGEN-BONDED HEXAMERIC UNIT OF β-HYDRO-
QUINONE

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ABSTRACT.   The title hexaphenol (1), a direct analogue of the β-hydro-
quinone hexameric unit, has been prepared by six-fold demethylation of
hexakis(p-methoxyphenyloxy)benzene (2) with BBr₃.   Host 1 forms a
trigonal adduct, space group R3̄, a = 22.088(3), c = 12.232(3) Å, con-
taining 6 molecules of pyridine per host molecule: a detailed X-ray
study of this inclusion compound reveals a true clathrate structure,
the closed cages of which accommodate a small, non-stoichiometric amount
of water.

1.   INTRODUCTION

The hexa-host analogy, the fundamental relationship between a hexa-
substituted benzene and the pre-existing hydrogen-bonded hexameric unit
of a number of important phenolic hosts, has led to the discovery of
many new clathrate hosts.[1]   The key hydrogen-bonded hexameric unit
consolidating the host structure in the β-hydroquinone clathrates was
first defined[2] during the pioneering X-ray studies of Powell and co-
workers in the 1940s.   The present work is concerned with the synthesis

(1)

OMe

MeO

OMe

MeO

OMe

OMe

(2)
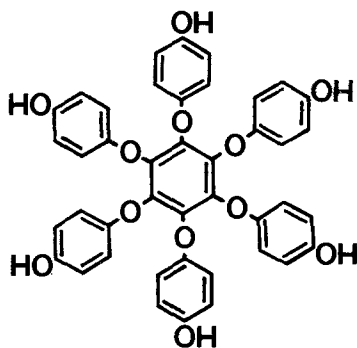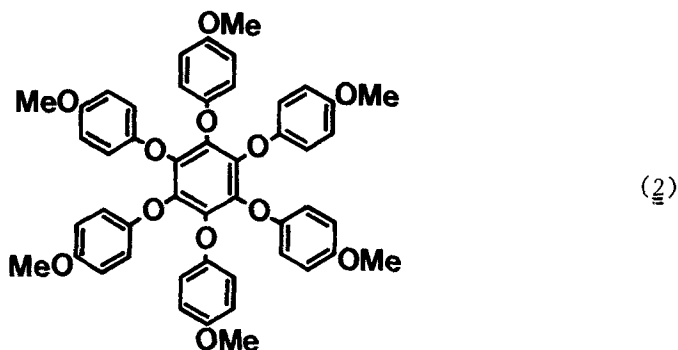
and inclusion properties of hexakis(p-hydroxyphenyloxy)benzene (1) which corresponds directly to the hexameric unit of the β-hydroquinone clathrates. The hexaphenol 1, which has six hydroxyl groups round the molecular periphery, has a functional array suggesting the possibility of formation of a "hybrid" clathrate, partaking of hexahost character, in which exactly half of the [OH]$_6$ rings of the β-hydroquinone structure are replaced by permanent, hexa-oxygen-substituted benzene units. We describe the first synthesis of hexa-phenol 1 and give detailed structural information concerning one of its inclusion compounds.

2. EXPERIMENTAL

2.1 Synthesis of hexakis(p-hydroxyphenyloxy)benzene (1)

Hexaphenol 1 was prepared from the known[3] hexaether 2 by overnight exposure of the latter to excess BBr$_3$ (ca. 36 mol equiv.) in freshly distilled CH$_2$Cl$_2$, affording after work-up, 1 (>80%) as a fine white powder. Compound 1 has: ^{1}H n.m.r. resonances (δ in d^6-DMSO) at 9.02 (s) (6H), and 6.55 (s) (24H); and m/e [M$^+$] 726.1713 amu, C$_{42}$H$_{30}$O$_{12}$ requires m/e 726.1737 amu.
     The compound is soluble in pyridine, and sparingly so in acetone. Recrystallisation from either DMSO or pyridine gives an inclusion compound with six solvent-guest components per host, the former being rapidly lost on standing in air. A second type of adduct containing about one mole of solvent (methanol and water) per host is obtained on recrystallisation from hot methanol in a sealed tube. Whilst dry hexakis(p-hydroxyphenyloxy)benzene quickly chars on heating, crystals of its pyridine inclusion compound darken in a sealed tube at 270 °C, and those of the methanol adduct can be taken to 320 °C on a hotplate with no apparent change.

2.2 Crystal data
C$_{42}$H$_{30}$O$_{12}$(1).6C$_5$H$_5$N.xH$_2$O, Formula weight = 1219.32 for x taken as 1, trigonal, R3, a = 22.088(3), c = 12.232(3) Å, V = 5168(2) Å^3, Z = 3, D$_c$ = 1.18 g cm^{-3}, μ = 0.74 cm^{-1} for Mo-K$_\alpha$ radiation, λ = 0.7107 Å.

Number of independent reflections: 2503 from hexagonal needle, 0.6x0.2 mm. T = 293K.   Final $\underline{R}$ for 537 reflections with $\underline{F}^2 > 2\sigma(\underline{F}^2)$: 0.094, $\underline{R}'$ 0.109.
    X-ray intensity measurements for all possible reflections with sin $\theta/\lambda < 0.64$ Å^{-1} were made by $\theta-\omega$ scan on a Nonius CAD4 diffractometer. The small proportion of significant reflections, not caused by the use of an insufficiently large crystal, limits the precision of this analysis. The structure was solved by the MITHRIL computer program[4] and refined using the GX package.[5]   During the anisotropic least-squares refinement, all aromatic hydrogen atoms of the host and pyridine guest molecules were placed in theoretical positions and allowed to ride on their attached carbon atoms.   The hydroxyl hydrogen atom was not located.   Two independent electron density peaks observed on and near the three-fold axis were ascribed to two types of statistically-disordered water molecule, the former oxygen site being of lower occupancy.

3. DISCUSSION

Figure 1(a) illustrates the individual hexakis(p-hydroxyphenyloxy)-benzene (1) host molecule in its pyridine adduct.   Comparison [Figure 1(b)] with the hydrogen-bonded hexameric unit of β-hydroquinone (empty cage form) reveals a close parallel.   Both units are located on a point of crystallographic $\bar{3}$ symmetry, with corresponding alternation of hydroxyl-containing moieties above and below the central core.   A significant change is, however, found between the two units in that the torsion angle τ [denoted by the dotted line in Figure 1(b)], -58°, is significantly smaller in magnitude compared to the corresponding torsion angle O(1*)-O(1)-C(2)-C(7), -105°, for 1.   In contrast to the situation for β-hydroquinone where each hydroxyl group is involved in forming hydrogen-bonded hexamers, for 1, as shown in Figure 2, six pyridine molecules are hydrogen-bonded to each host molecule.
    Units comprising one host molecule and six pyridine molecules are stacked along the c-axis, parts of two neighbouring infinite columns being shown in the stereoview at right angles to the c-axis in Figure 3. Hydrogen bonds, length 2.71(2) Å, linking oxygen and nitrogen atoms are denoted by broken lines.   The molecular packing is further illustrated in the view down the c-axis, Figure 4.
    The central benzene ring of 1 does not deviate significantly from planarity; the attached oxygen atoms, however, are disposed alternately 0.15(1) Å above and below this plane.   The ether oxygen O(1) is displaced slightly from the plane of the outer benzene ring, by 0.06(1) Å.
    An interesting feature of the molecular packing described above is that large centrosymmetric voids possessing 3-fold symmetry are formed between adjacent host molecules stacked along c.   The top and bottom of each such void are formed by the hexa-substituted benzene rings of 1, while the walls consist of p-hydroxyphenyl moieties, each hydrogen-bonded to a pyridine molecule.   Figure 5 shows illustrative cavity contours drawn at right angles to the c axis at indicated fractions of the c-spacing, showing the shape and indicating the closed nature of the clathrate cage.   Residual electron density, corresponding to atoms
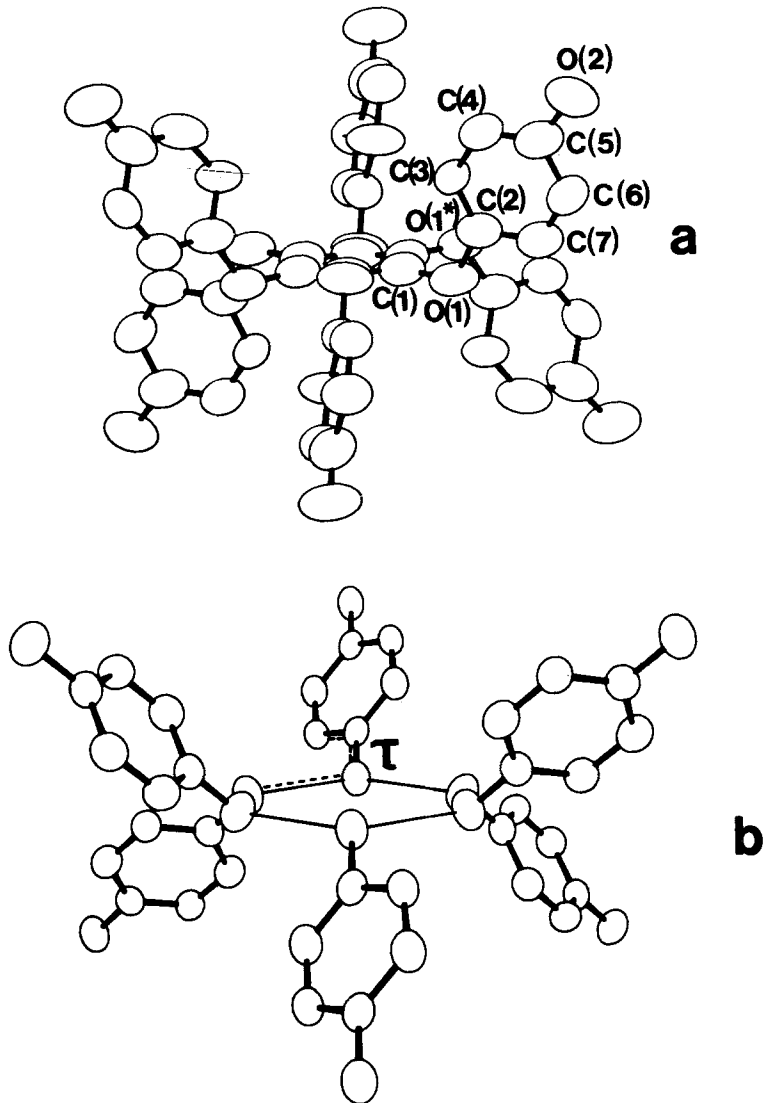
Figure 1.   A comparison of (a) the molecule of hexakis(p-
hydroxylphenyloxy)benzene (1) in its pyridine adduct with
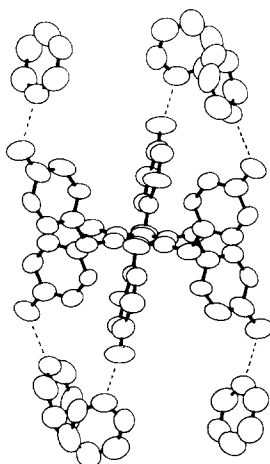(b) the hydrogen-bonded hexameric unit of β-hydroquinone.

Figure 2. A view of the host molecule 1 with its six associated pyridine molecules. All hydrogen atoms have been omitted, and hydrogen bonds between oxygen and nitrogen are denoted by broken lines.
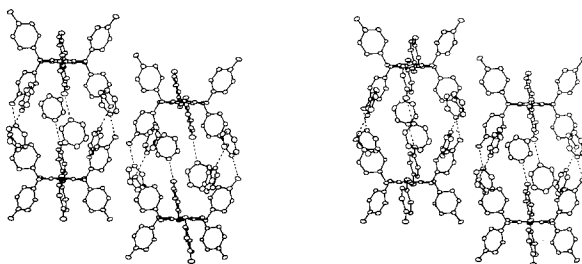

Figure 3. A stereoview normal to the c-axis illustrating the inter-column packing in the pyridine adduct of host 1 (as in Figure 4, included water is not shown).
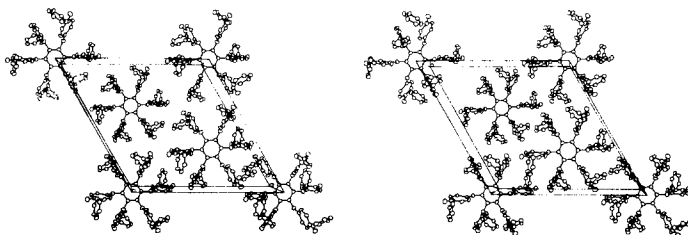

Figure 4. A stereoview looking down the c-axis showing the molecular packing in the pyridine complex of 1.
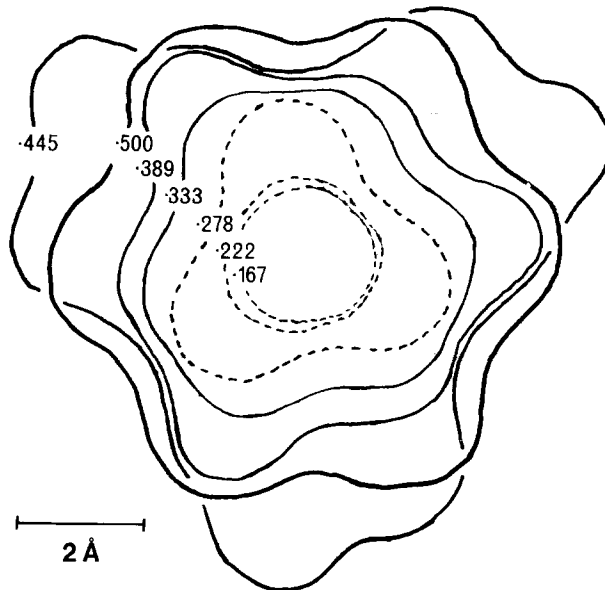
Figure 5.   Cavity contours drawn at right angles to the c-
axis at various fractional heights, indicating the free space
available in the cage after allowing for the van der Waals
volumes of the cage-wall atoms (drawn with the VDW computer
program, ref. 6).

O (W1) and O(W2), within the cage may represent partial occupancy by
water, this being consistent with small amounts of water (less than
mole H_2O per 1) detected by ^1H n.m.r. analysis.

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