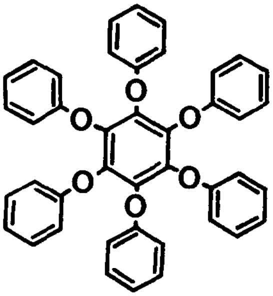
Tetrahedron Letters,Vol.24,No.31,pp 3269-3272,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain

SYNTHESIS OF HEXAKIS(ARYLOXY)BENZENES: X-RAY ANALYSIS OF HEXAKIS(PHENYLOXY)BENZENE AND OF THE ACETONITRILE CLATHRATE OF HEXAKIS(3,5-DIMETHYLPHENYLOXY)BENZENE

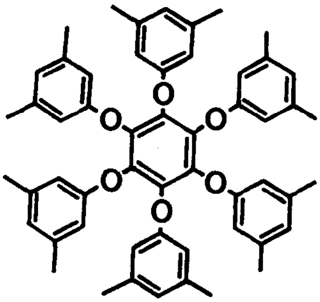
Christopher J. Gilmore, David D. MacNicol*, Anthony Murphy, and Marie A. Russell
Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, Scotland

Summary Hexakis(aryloxy)benzenes (I)-(IV), representatives of a new class of molecule, have been prepared by reaction of hexafluorobenzene with the sodium salt of the appropriate phenol in 1,3-dimethyl-2-imidazolidinone (DMEU) as solvent. X-ray analyses of parent (I) and of the acetonitrile clathrate of (II) are described, a novel edge-on interaction between host and guest being found in the latter.

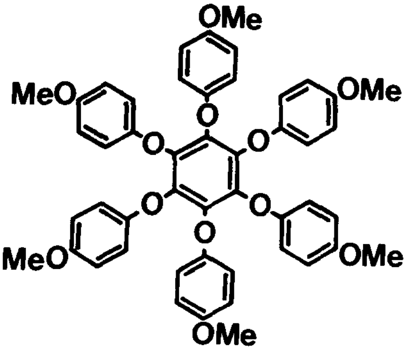
Hexakis(aryloxy)benzenes, comprising a new class of molecule, are of particular interest in the design of new inclusion compounds owing to their close structural correspondence to the hydrogen-bonded hexameric unit present in many phenolic clathrates.[1] Recently we have described[2] the synthesis of the first member of this series, hexakis(phenyloxy)benzene (I). Compound (I), although a direct



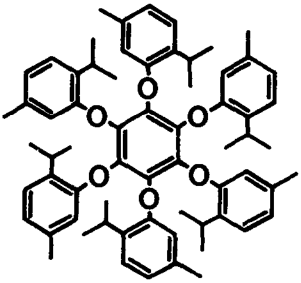
(I)



(II)



(III)



(IV)

analogue of the sextet unit present in the clathrates of phenol itself,[3] has however shown no ability to form clathrates, reflecting a different mode of crystal packing (see below). We now report that hexakis(3,5-dimethylphenyloxy)-benzene (II), unlike (I), readily forms adducts with, for example, acetonitrile (1:1), nitromethane (1:1), toluene (1:1), and acetone (2:1), the host-guest ratio[4] being indicated in parentheses in each case. An X-ray analysis of the acetonitrile inclusion compound of (II), the first hexakis(aryloxy)benzene to exhibit inclusion properties, was undertaken to elucidate the void geometry, the nature of host-guest interactions, and the conformation of host (II). Compound (II) and related molecules hexakis(*p*-methoxyphenyloxy)benzene (III) and hexakis-(2-isopropyl-5-methylphenyloxy)benzene (IV) were prepared in a similar way to (I),[5] the polar aprotic solvent DMEU being employed to promote complete aromatic halogen displacement in reactions of hexafluorobenzene with the sodium salt of the appropriate phenol. These new compounds (II)-(IV) had spectroscopic properties (^{1}H and ^{13}C n.m.r., i.r., and m.s.) and microanalytical data in full accord with their formulated structures.[6]

Crystal structures of compounds (I) and (II). Crystal data: hexakis-(phenyloxy)benzene (I), $C_{42}H_{30}O_6$, *M* = 630.7, triclinic, space group $P\bar{1}$, *a* = 9.585(2), *b* = 9.610(1), *c* = 19.171(3) Å, α = 99.65(1), β = 91.95(2), γ = 114.67(2)°, *U* = 1571.3 Å^3, *F*(000) = 660, *Z* = 2, D_c = 1.33 g cm^{-3}, μ(Mo-K_α = 1.0 cm^{-1}; hexakis(3,5-dimethylphenyloxy)benzene (II), 1:1 acetonitrile adduct, $C_{54}H_{54}O_6 \cdot C_2H_3N$, *M* = 840.1, triclinic, space group $P\bar{1}$, *a* = 14.505(3), *b* = 14.663(3), c = 14.869(4) Å, α = 117.46(2), β = 109.43(2), γ = 62.95(2)°, *U* = 2468.7 Å^3, *F*(000) = 896, *Z* = 2, D_c = 1.13 g cm^{-3}, μ(Mo-K_α) = 0.8 cm^{-1}.

Diffraction intensities for both crystals were measured on an Enraf-Nonius CAD-4 diffractometer. 2162 [$I \geqslant 2.5\sigma(I)$] and 3412 [$I \geqslant 2.0\sigma(I)$] independent reflections were recorded[7,8] for (I) and (II) respectively.* The structures were solved by direct methods.[9] During the course of the analysis all the hydrogen atoms were located, except those of the CH_3CN guest in (II), and subsequent refinement (with isotropic temperature factors for hydrogen atoms) converged at final *R*-factors of 0.037 (R_w = 0.049) and 0.058 (R_w = 0.065) for (I) and (II) respectively.

The molecule of parent (I) occupies a general position in the unit cell and both enantiomers are present. The molecular conformation of (I) (Fig. 1) displays an alternation of phenyl groups above and below the plane of the central benzene ring. Significantly, the molecular packing in (I) differs from the 'open' rhombohedral packing (space group $R\bar{3}$) of the phenol clathrates,[3] the C_1 symmetry of (I) contrasting with the exact C_3 symmetry of the hydrogen-bonded

---

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

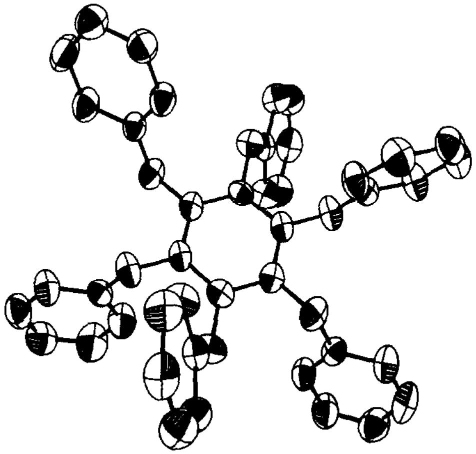


Figure 1

A general view of hexakis(phenyloxy)benzene (I) in the molecular crystal.

hexameric unit present in the clathrates of phenol.[3]

In the acetonitrile adduct of (II) there are two centrosymmetric crystallographically non-equivalent host molecules, located at centres of symmetry at (0, 0, 0) and (½, ½, ½). The host-guest packing is illustrated in the stereoview shown in Figure 2. The acetonitrile guest molecules are accommodated in effectively closed cages and hence the structure is of the true clathrate type. As can be seen from Figure 3, the acetonitrile guest molecule interacts *edge-on* with a neighbouring host molecule with methyl····O distances[10] of 3.252(2) Å and 3.366(3) Å. The CH_3CN molecule is almost co-planar with the molecule of (II) with which it interacts, the (methyl) C, C, and N atoms being displaced by 0.037 Å, 0.016 Å, -0.052 Å respectively from the mean plane defined by the central ring of (II).

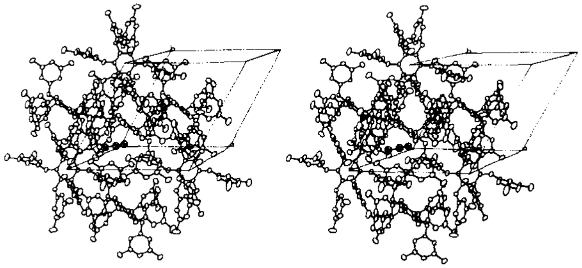


Figure 2

A stereoview illustrating the structure of the (1:1) inclusion compound of hexakis(3,5-dimethylphenyloxy)benzene (II) with acetonitrile as guest. Crystallographically non-equivalent host molecules are located at (0, 0, 0) and (½, ½, ½) and there are two $CH_3C{\equiv}N$ guest molecules in each unit cell, one of which is shown.

Although no inclusion compounds have yet been found for the hexamethoxy compound (III), compound (IV), derived from thymol, exhibits host properties and its highly crystalline 1:1 adduct with CCl_4 is currently under X-ray investigation.

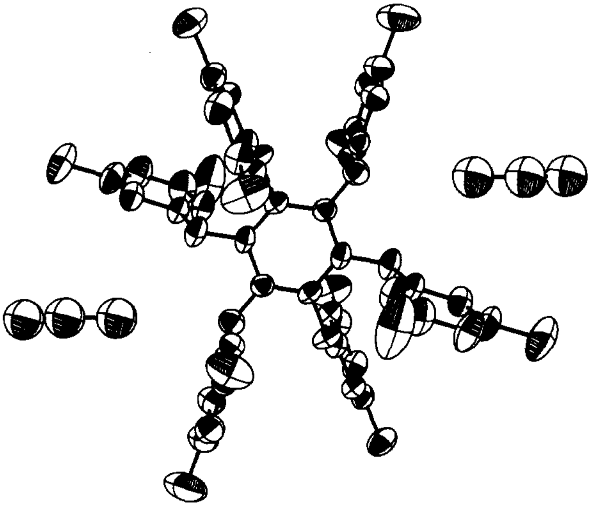


Figure 3

An illustration of an edge-on host-guest interaction in the acetonitrile clathrate of hexakis(3,5-dimethylphenyloxy)benzene (II).

References and Notes

1. See, for example, D.D. MacNicol, J.J. McKendrick, and D.R. Wilson, Chem. Soc. Rev., 1978, 7, 65; H.M. Powell, in 'Non-stoichiometric Compounds', ed. L. Mandelcorn, Academic Press, New York, 1964, ch. 7; D.D. MacNicol, in 'Inclusion Compounds', ed. J. Atwood, J.E.D. Davies, and D.D. MacNicol, Academic Press, in press.
2. D.D. MacNicol, P.R. Mallinson, A. Murphy, and G.J. Sym, Tetrahedron Letters, 1982, 23, 4131.
3. M.V. Stackelberg, A. Hoverath, and Ch. Scheringer, Z. Elektrochem., 1958, 62, 123; B.A. Nikitin, Compt. rend. U.S.S.R., 1940, 29, 571.
4. Host-guest ratios were determined by multiple ^{1}H n.m.r. integration.
5. Compounds (II)-(IV) were prepared by reaction of hexafluorobenzene with 18 molar equivalents of the sodium salt of the appropriate phenol for several weeks at 120°C in DMEU, 0.85 molar equivalent of [2.2.1] cryptand being added in each case. It has not yet been determined whether extended reaction time and added cryptand (cf. ref. 2) are strictly necessary for the successful preparation of compounds (II)-(IV).
6. Representative data, for hexakis(3,5-dimethylphenyloxy)benzene (II), m.p. 172-173°C (unsolvated), are: m/e 798 (M^+); i.r. ν_{max} (KBr, unsolvated material) 3012, 2915, 1616, 1591, 1453, 1309, 1288, 1275, 1137, 1046, 829, 677 cm^{-1}; ^{1}H n.m.r., δ (CCl_4) 2.15 (36H, s), 6.26 (12H, s), 6.46 (6H, s); ^{13}C n.m.r., δ_C ($CDCl_3$) 21.3 (q), 113.8 (d), 124.0 (d), 138.5 (s), 140.5 (s), 157.7 (s); found: C, 81.07; H, 6.81%; $C_{54}H_{54}O_6$ requires C, 81.20; H, 6.77%; yield 75%, after two recrystallisations from MeOH/toluene.
7. The crystal of the adduct of (II) was enclosed in a thin-walled glass capillary tube.
8. Initial Laue photographs in (I) exhibited some diffuse reflections, the origin of which is currently unknown.
9. C.J. Gilmore, MITHRIL - a direct methods program. In preparation.
10. These distances may be compared with methyl····O contacts of 3.24(7) Å, 3.26(9) Å, and 3.38(12) Å found recently between (co-ordinated) acetonitrile and 18-crown-6 (18-C-6) in the complex $\{trans\text{-}Ir(CO)(CH_3CN)(PPh_3)_2]_2^{+}18\text{-}C\text{-}6\}[PF_6]_2^{-}\cdot 2CH_2Cl_2$; see H.M. Colquhoun, J.F. Stoddart, and D.J. Williams, J. Am. Chem. Soc., 1982, 104, 1426.

(Received in UK 16 May 1983)