

OCTAKIS(ARYLOXY)NAPHTHALENES: A NEW CLASS OF HOST MOLECULE.

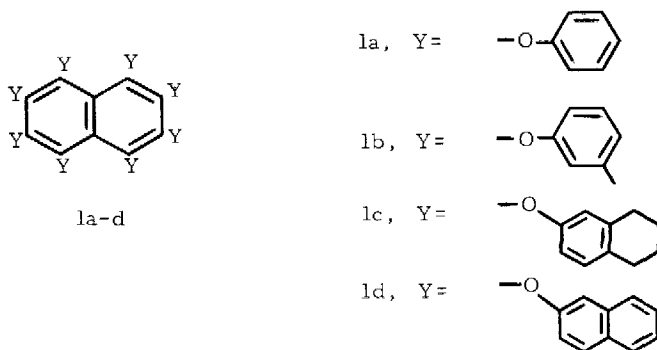
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Summary. The first octakis(aryloxy)naphthalenes, 1a-d, have been synthesised in DMEU (*N,N*-dimethylimidazolidin-2-one) from octafluoronaphthalene and the sodium salts of appropriate phenols. Compounds 1a, 1c and 1d form crystalline inclusion compounds. X-ray crystal structure analysis of the acetone clathrate of 1d, the most general host, reveals a novel host conformation, whilst the crystal packing of unsolvated 1b is found to be distinct from that of its thio-ether counterpart, octakis(*m*-tolylthio)naphthalene.

At present very few successful general strategies exist for the discovery of new classes of solid-state host materials. Recognition of the importance of incorporation of appropriate molecular symmetry, allied with favourable structural features, has been an essential element in the recent design of new clathrates. These concepts have been applied by a number of research groups¹, and the well-known Hexa-host analogy, later extended to other systems², has been recognised³ as the first rational use of this approach.

Compounds 1a-d, similarly conceived with suitable shape and conformational properties in mind, are the first members of a new class of per(aryloxy)-substituted host molecule, prospective for the formation of crystalline inclusion compounds.



Octakis(aryloxy)naphthalenes, new molecules unprecedented in having an oxygen atom attached to each available position of the aromatic binuclear skeleton, were prepared from octafluoronaphthalene by DMEU-promoted complete nucleophilic substitution, previously employed for benzene-based systems⁴. The reactions were carried out at ca. 90°C over several weeks and gave unoptimised yields in the range 55-85%. Typically the parent 1a, m.p. 209-210°C, was produced in an isolated yield of 85% using 32 molar equivalents of sodium phenoxide at 90°C for eight weeks. Host 1d was characterised by the following data: M.p. 259-260°C (unsolvated); *m/e* M^+ 1264; i.r. (KBr disc) selected bands at 1630, 1600, 1515, 1465, 1405, 1365, 1245, 1215, 1160 cm^{-1} (all s); 90 MHz ^1H n.m.r. δ (CDCl_3) 6.6-7.1 (complex, 16H) 7.1-7.8 (complex, 40H); found: C, 85.5%; H, 4.6%. $\text{C}_{90}\text{H}_{56}\text{O}_8$ requires C, 85.4%; H, 4.5%. Compounds 1a-c also had properties in accord with their assigned structure.

A novel empty-cage clathrate structure, stable even in the absence of guest, found for octakis(*m*-tolylthio)naphthalene⁵ prompted the present X-ray study^{‡§} of the unsolvated form of its oxygen analogue 1b; and a single-crystal structure analysis^{‡§} of the acetone inclusion compound (host/guest ratio 1:2) of octakis(β -naphthylthio)naphthalene 1d, was undertaken to elucidate the nature of the host-guest packing in this adduct.

Crystal Data.⁶ $\text{C}_{66}\text{H}_{56}\text{O}_8$, (1b): $M = 977.2$, monoclinic, space group $P2_1/n$, $a = 7.831(1)$, $b = 14.092(3)$, $c = 23.934(3)$ Å, $\beta = 96.97(1)^\circ$, $U = 2622(1)$ Å³, $Z = 2$, $D_c = 1.24$ g cm⁻³. $T = 293\text{K}$, $R = 0.058$, $R' = 0.070$ for 1503 independent reflections with $F_o^2 > 2\sigma(F_o^2)$.

$\text{C}_{90}\text{H}_{56}\text{O}_8(1d).2(\text{C}_3\text{H}_6\text{O})$: $M = 1381.6$, triclinic, space group $P\bar{1}$, $a = 11.064(3)$, $b = 12.377(7)$, $c = 15.975(9)$ Å, $\alpha = 117.09(4)$, $\beta = 112.27(4)$, $\gamma = 75.23(4)^\circ$, $U = 1793(1)$ Å³, $Z = 1$, $D_c = 1.28$ g cm⁻³. $T = 293\text{K}$, $R = 0.085$, $R' = 0.083$ for 3109 independent reflections with $F_o^2 > 2\sigma(F_o^2)$.

‡ The atomic coordinates for 1b and the acetone adduct of 1d 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.

§ Supplementary data available for 1b and the acetone adduct of 1d: structure factors. See Announcement to Authors, *Tetrahedron Letters*, 47, 5154 (1983).

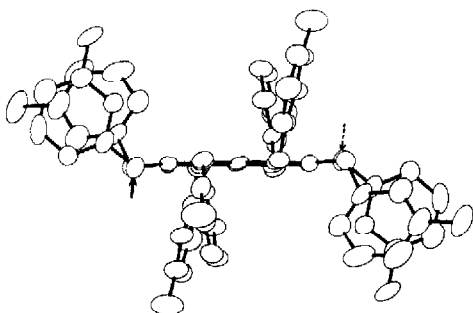


Figure 1 (a). The conformation of octakis(*m*-tolylloxy)naphthalene (1b) in the unsolvated molecular crystal. The atoms O(2) and O(6), indicated by arrows, are displaced by 0.172(5)Å from the central naphthalene plane.

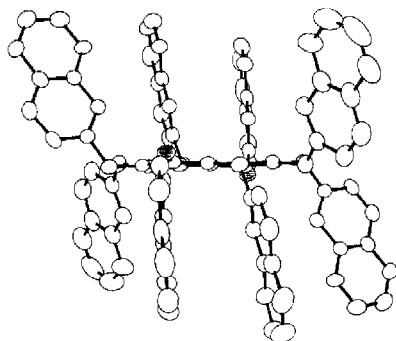


Figure 1(b). The host conformation of octakis(β -naphthylloxy)naphthalene (1d) in its 1:2 acetone inclusion compound, illustrating the unique *cis-peri* relationship of side-chain naphthyl moieties. The oxygen atoms O(1) and O(5), both shaded, have the largest displacements from the central naphthalene plane.

Figure 2. A stereoview illustrating the host-guest arrangement in the 1:2 adduct of octakis(β -naphthylloxy)naphthalene (1d) with acetone. The approximate centres of two centrosymmetrically related guest molecules are denoted by the letters G and G'.

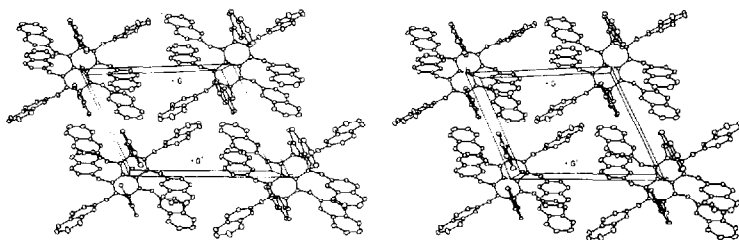


Figure 1a shows the centrosymmetric conformation of octakis(m-tolyloxy)naphthalene (1b) in the unsolvated molecular crystal. Using previous nomenclature⁵, it has the type III *abbabaab* conformation. This conformation was previously found in the 1,4-dioxane adduct of octakis(p-tolythio)naphthalene⁵. The central naphthalene ring and the four independent benzene rings do not deviate significantly from planarity. The displacements of the four independent oxygens, both from the naphthalene and benzene ring planes, are less than ca. 0.06Å with the exception of O(2) and O(6) (indicated by arrows in Figure 1a) which are displaced by 0.172(5)Å from the mean naphthalene plane.

The centrosymmetric conformation of the host molecule 1d is shown in Figure 1b. It exhibits a unique and unexpected *ababbaba* conformation, not previously categorised⁵, which has a *cis* arrangement of *peri*-related side-chain moieties. The displacements of the oxygen atoms from associated mean aromatic planes are in general larger for 1d than for 1b, the most pronounced being found for centrosymmetrically related atoms O(1) and O(5), shaded in Figure 1b. The magnitudes of the displacements from the central and outer rings are 0.326(4)Å and 0.219(4)Å respectively.

Figure 2 is a stereoview illustrating the host-guest packing in 1d. The approximate centres of two centrosymmetrically related guest molecules are denoted by the points G and G'. The guest molecules (not shown) exhibit high thermal motion and are almost certainly disordered.

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References and Notes

1. See, for example, *Inclusion Compounds*, eds. J.L. Atwood, J.E.D. Davies, and D.D. MacNicol, vol. 2, Academic Press, 1984; *Topics in Current Chemistry*, ed. E. Weber, 1987, 140; 1988, 149.
2. R.H. Barbour, A.A. Freer, and D.D. MacNicol, *J. Chem. Soc., Chem. Commun.*, 1983, 362.
3. E. Weber, *Topics in Current Chemistry*, 1987, 140, 1.
4. C.J. Gilmore, D.D. MacNicol, A. Murphy, and M. Russell, *Tetrahedron Letters*, 1983, 24, 3269.
5. D.D. MacNicol, P.R. Mallinson, and C.D. Robertson, *J. Chem. Soc., Chem. Commun.*, 1985, 1649.
6. X-Ray intensity measurements were made by $2\theta-\omega$ scan on a Nonius CAD4 diffractometer using graphite-monochromated Mo K_{α} radiation. Unit cell parameters were determined by least-squares refinement of diffractometer setting angles for 25 reflections. Hydrogen atom parameters were not included in the refinement. The principal computer programs used in structure solution and refinement are: MITHRIL, A Computer Program for the Automatic Solution of Crystal Structures from X-Ray Data, C.J. Gilmore, *J. Appl. Crystallogr.* 1984, 17, 42; the GX Crystallographic Program System, P.R. Mallinson and K.W. Muir, *J. Appl. Crystallogr.* 1985, 18, 51.

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