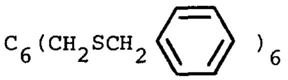
Tetrahedron Letters No. 38, pp 3579 - 3582.
0040-4039/78/0915-3579$02.00/0

HEXAKIS(BENZYLTHIOMETHYL)BENZENE: STRUCTURE OF THE 1,4-DIOXAN CLATHRATE AND PROPERTIES OF RELATED HOSTS

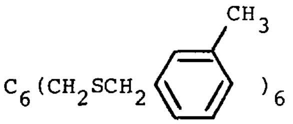
Andrew D.U. Hardy, David D. MacNicol*, Stephen Swanson, and Derek R. Wilson,
Department of Chemistry, University of Glasgow, Glasgow, G12 8QQ

The use of analogy[1-3] has led to the discovery of a series of inclusion hosts[4] based on a hexa-substituted benzene skeleton. We now report the results of an X-ray study of the 1,4-dioxan clathrate of hexakis(benzylthiomethyl)-benzene[1] (I) which has a three atom CH_2SCH_2 linkage between each side-chain aromatic ring and the central core of the molecule. Also briefly described are the varying inclusion properties of the related molecules (II), (III), and (IV), which were prepared[5] by reaction of hexakis(bromomethyl)benzene, $C_6(CH_2Br)_6$, with the appropriate aralkyl mercaptan in NaOEt/EtOH.

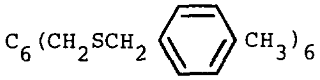
(I)



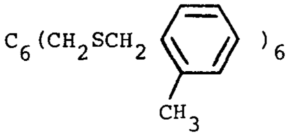
(III)



(II)



(IV)



The dioxan adduct of (I) crystallises in the monoclinic space group $P2_1/c$ with two host and two guest molecules in the unit cell (Table). The structure was solved by direct methods employing 2495 independent diffractometer data (using a Lindemann capillary to inhibit solvent loss), and refined to a final R value of 0.045. All the hydrogen atoms have been located and allowed for; full details of the structural analysis will be published elsewhere.

Figure 1 shows a view looking directly onto the central benzene ring of the host molecule. The molecule is located on a crystallographic centre of inversion and is thus constrained to be centrosymmetric. Although (I) lacks the exact three-fold symmetry found for a clathrate[3] of hexaphenylthiobenzene, $C_6(SPh)_6$, the 'legs' of this molecule still point alternately above and below the plane of the central benzene ring. Figure 2 illustrates the host to guest packing in the crystal, the host and guest molecules above and below those shown being directly superposed in this view. All the host and guest molecules are situated at crystallographic centres of symmetry on the *b c* plane. The chair-shaped dioxan guest molecule is accommodated in a closed cage and no short host-guest contacts have been found.

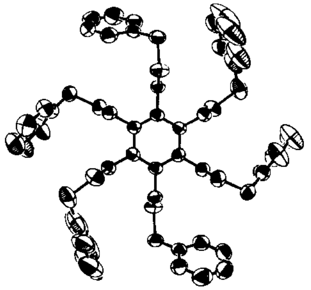


Figure 1. An ORTEP drawing showing a view normal to the plane of the central benzene ring of host molecule hexakis-(benzylthiomethyl)benzene (I) in its dioxan clathrate. The hydrogen atoms have been omitted for clarity.

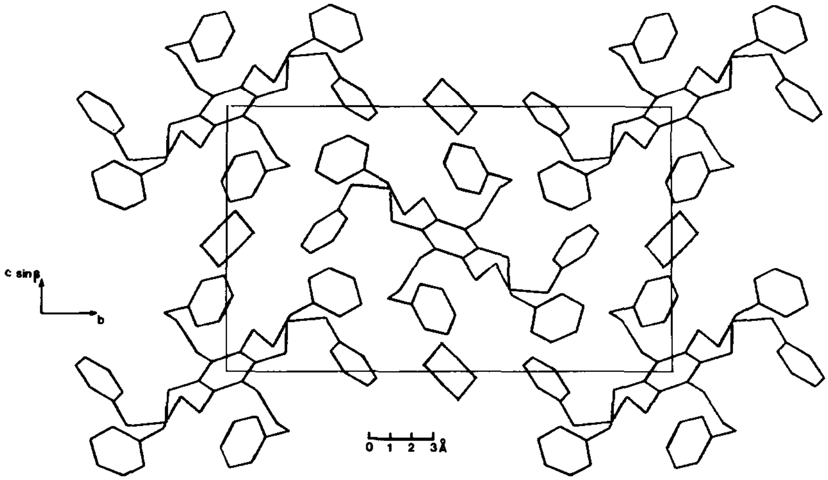


Figure 2. Host to guest packing in the dioxan clathrate of (I), as viewed along the *a*-axis.

Among the compounds related to (I) which have been studied are the methyl derivatives (II), (III), and (IV). The *para*-derivative (II) forms orthorhombic crystals of an adduct with 1,4-dioxan (see Table). In contrast to the *ortho*-derivative (IV), for which inclusion behaviour has not been observed, the *meta* compound (III) behaves similarly to the parent (I) including a wide range of guest molecules. For example (III) forms inclusion compounds with cyclohexane (1:1), acetone (1:2), benzene (1:1), furan (1:2), 1,4-dioxan (1:1), ethyl acetate (1:1), anisole (1:1), ethyl benzene (1:1), and *p*-xylene (1:1), the host to guest ratio being indicated in each case. Interestingly, when (III) is recrystallised from an equimolar mixture of *para* and *ortho*-xylene a marked preference for the *para*-isomer is found;[6] the relative isomer percentages included by (III), 85%:15%, may be compared with the corresponding values of 75%:25% found[2] for the parent (I). Work on related hosts is underway.

We thank the S.R.C. for support.

Table   Some Selected Crystal Data for Hexakis(benzylthiomethyl)-benzene (I) and Related Molecules

Host	Guest (host:guest ratio†)	Space Group	Lattice Parameters
(I)	1,4-dioxan (1:1)	$P2_1/c$ monoclinic	a = 10.542, b = 20.863, c = 12.496Å, β = 95.48°, Z = 2(host).
(II)	1,4-dioxan (1:1)	$Pcab$ orthorhombic	a = 18.67, b = 14.18, c = 23.22Å, Z = 4(host).
(III)	p/o-xylene§ (1:1)	$P2_1/c$ monoclinic	a = 9.62, b = 15.45, c = 22.72Å, β = 111.0°, Z = 2(host).

† Ratio determined by ^1H n.m.r. employing $CDCl_3$ as solvent.

§ Crystals prepared by recrystallisation from an equimolar mixture of ortho and para-xylene; a marked selectivity for the para-isomer is found (see text).

References

1. D.D. MacNicol and D.R. Wilson, J.C.S. Chem. Comm., 1976, 494.

2. D.D. MacNicol and D.R. Wilson, Chem. and Ind., 1977, 84.

3. D.D. MacNicol, A.D.U. Hardy, and D.R. Wilson, Nature, 1977, 266, 611.

4. For a recent review of clathrates and molecular inclusion phenomena see, for example, D.D. MacNicol, J.J. McKendrick, and D.R. Wilson, Chem. Soc. Revs., 1978, 65.

5. All new compounds gave a satisfactory microanalysis and had spectral properties in keeping with their formulated structure.

6. For other recent work on the selective inclusion of para-xylene from mixtures see D.H. Brown, R.J. Cross, and D.D. MacNicol, Chem. and Ind., 1977, 766.

(Received in UK 9 June 1978; accepted for publication 20 July 1978)