

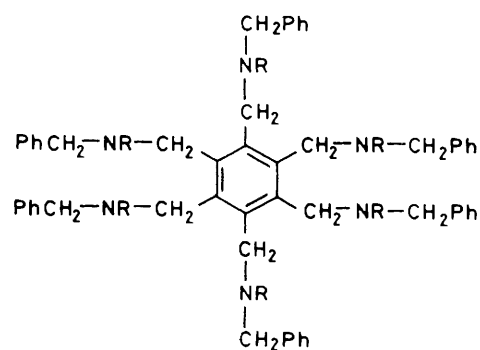
## Novel Host Molecules derived from Hexakis(benzylaminomethyl)benzene: X-Ray Analysis of a Dimethylformamide Adduct of Hexakis-(*N*-benzyltrifluoroacetamidomethyl)benzene and the 3 KSCN·H<sub>2</sub>O Complex of Hexakis-[*N*-benzyl-(2-methoxyethoxy)acetamidomethyl]-benzene

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Treatment of hexakis(benzylaminomethyl)benzene (**1**) with appropriate acid anhydrides yields the first examples of nitrogen-based hexahost molecules; X-ray analyses of the title hosts (**3**) and (**7**) with neutral molecular and ionic guest species are described.

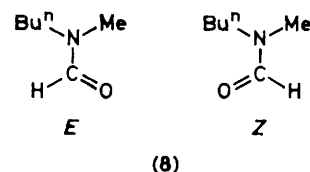
Primary amines are potentially versatile reagents for the synthesis of novel hexahost molecules,<sup>1</sup> since the nitrogen atoms introduced can be further substituted. In an extension of our earlier work,<sup>2,3</sup> we now report that reaction of a stirred suspension of finely ground hexakis(bromomethyl)benzene, (C<sub>6</sub>H<sub>2</sub>Br)<sub>6</sub> in hexane with excess of benzylamine under argon for 2 days at ambient temperature, gives after work-up, a 70% yield (not optimised) of the hexa-amine (**1**), m.p. 181–183 °C, which is a useful precursor for the preparation of new host molecules. Structure (**1**) was assigned on the basis of spectroscopic evidence.† The hexa-amides (**2**)–(**7**) were readily prepared in excellent yields by refluxing (**1**) for 2 h with an excess of the appropriate acid anhydride,<sup>4</sup> either neat or with ethyl acetate as solvent. The formulated structures were confirmed spectroscopically, and also by X-ray methods for (**3**) and (**7**). The unsolvated‡ fluorine-containing compound (**3**) forms adducts on recrystallisation from nitromethane,



- (1) R = H  
 (2) R = COCH<sub>3</sub>  
 (3) R = COCF<sub>3</sub>  
 (4) R = COCF<sub>2</sub>CF<sub>3</sub>  
 (5) R = COCF<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub>  
 (6) R = COCH<sub>2</sub>OCH<sub>3</sub>  
 (7) R = COCH<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>OCH<sub>3</sub>

† For (**1**), i.r. (KBr disc), 3295 cm<sup>-1</sup> [ν(N–H)]; <sup>1</sup>H n.m.r. τ (CDCl<sub>3</sub>) ca. 8 (6H, br. s), 6.36 (24H, s), and 2.79 (30H, narrow m); <sup>13</sup>C n.m.r. δ (CDCl<sub>3</sub>) 47.8 (t), 54.4 (t), 126.6 (d), 128.1 (superimposed d), 138.1 (s), and 140.4 p.p.m. (s).

‡ Unsolvated (**3**), m.p. 175–176 °C (evacuated sealed capillary), was obtained by recrystallisation from methanol. The higher fluorinated homologues (**4**) and (**5**), currently under study, have unsolvated forms with m.p.s 222–223 and 137–138 °C (sealed tubes), respectively.



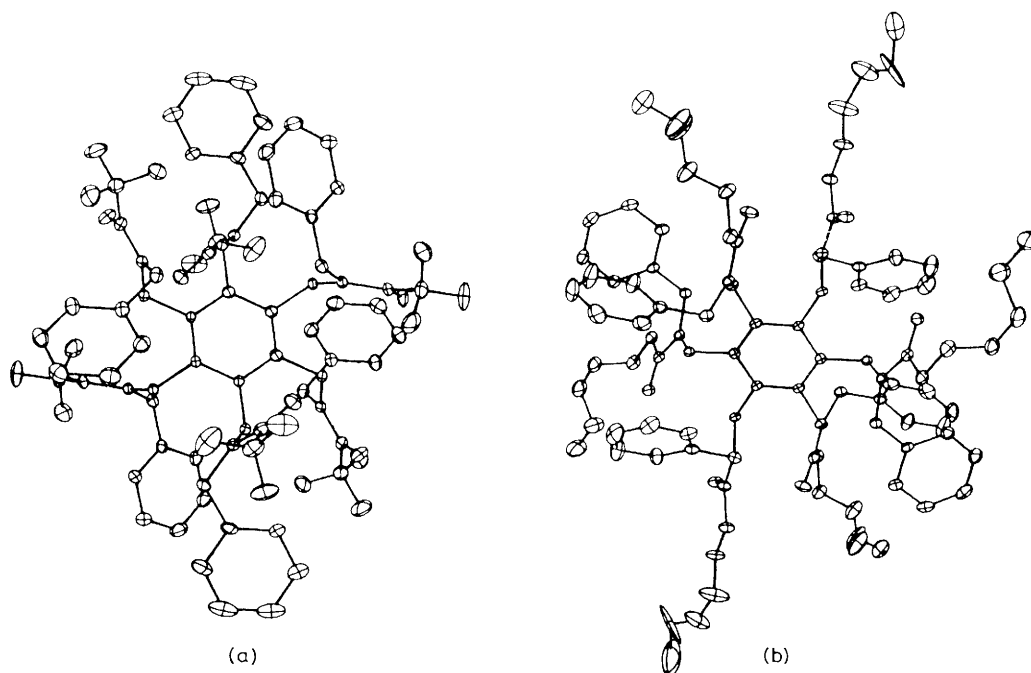


Figure 1. ORTEP drawings showing general views of (a) host molecule (3) in its DMF adduct and (b) host molecule (7) in its 3 KSCN·H<sub>2</sub>O complex.

tetramethylurea, *N,N*-dimethylformamide (DMF), *N,N*-dimethylacetamide, and *N*-*n*-butyl-*N*-methylformamide (8), the host to guest ratio, measured by <sup>1</sup>H n.m.r. spectroscopy, being 1:2 in each case. In contrast, the structurally related hexa-amide (2) has shown no evidence of guest inclusion to date. The inclusion of (8) by the host (3) is of particular interest since this occurs with effectively complete *configurational selection*<sup>5</sup> of the thermodynamically less stable<sup>6</sup> *Z*-form. This was established by dissolving a specimen of the adduct (previously washed with cold ether) in CDCl<sub>3</sub> at -40 °C, and <sup>1</sup>H n.m.r. monitoring at -20 °C. The absence of a methyl resonance from the *E*-form, known to occur at  $\tau$  7.13 at -20 °C, allows one to estimate a *minimum* purity of ca. 97% for the *Z*-form, the configuration of (8) disfavoured in the normal solution equilibrium.

*Crystal data for the DMF adduct of (3):* C<sub>66</sub>H<sub>54</sub>F<sub>18</sub>N<sub>6</sub>O<sub>6</sub>·2(C<sub>3</sub>H<sub>7</sub>NO), *M* = 1515.4, triclinic, space group *P*1̄, *a* = 12.511(3), *b* = 12.781(3), *c* = 13.224(3) Å,  $\alpha$  = 70.94(1),  $\beta$  = 66.04(2),  $\gamma$  = 75.27(2)°, *U* = 1808.2 Å<sup>3</sup>, *F*(000) = 782, *Z* = 1, *D*<sub>c</sub> = 1.39 g cm<sup>-3</sup>;  $\mu$ (Mo-*K*<sub>α</sub>) = 1.34 cm<sup>-1</sup>. *Crystal data for an ionic complex of (7):* C<sub>84</sub>H<sub>108</sub>N<sub>6</sub>O<sub>18</sub>·(3KSCN·H<sub>2</sub>O), *M* = 1799.4, monoclinic, space group *P*2<sub>1</sub>/*c*, *a* = 15.249(2), *b* = 10.087(2), *c* = 30.328(6) Å,  $\beta$  = 95.10(2)°, *U* = 4646.4 Å<sup>3</sup>, *F*(000) = 1904, *Z* = 2, *D*<sub>c</sub> = 1.29 g cm<sup>-3</sup>;  $\mu$ (Cu-*K*<sub>α</sub>) = 24.7 cm<sup>-1</sup>. Both data sets were collected on an Enraf-Nonius CAD-4 diffractometer which yielded 3142 and 3886 independent reflections [*I* > 3σ(*I*)] for (3), with Mo-*K*<sub>α</sub> radiation, and (7) with Cu-*K*<sub>α</sub> radiation, respectively.†

§ This complex (m.p. 210–212 °C) was prepared by recrystallisation of (7) from a methanolic solution containing an excess of KSCN. Compound (6) also forms a KSCN adduct (m.p. 233–235 °C).

† 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.

Structure elucidation of (3) was achieved by direct methods using 203 negative quartets in a modified version of MULTAN<sup>7</sup> which revealed the positions of all the host atoms. Subsequent least-squares refinement and Fourier syntheses found the DMF guest, further refinement leading to a current *R* factor of 0.083. For (7) routine MULTAN techniques located one potassium atom and 45 atoms of the host molecule, whereupon several cycles of least-squares, followed by difference Fourier syntheses, yielded the remainder of the structure. The penultimate Fourier map showed the position of the oxygen atom of the water molecule which was included in further refinement procedures to give a current *R* value of 0.084. In both cases hydrogen atom co-ordinates were calculated and included in the refinement procedure.

The structures of the host molecules (3) and (7) are illustrated in Figure 1, a marked deviation from 3-fold symmetry being apparent for each of the centrosymmetric molecules. A common feature of both structures is the alternation of near-planar nitrogen atoms above and below the plane of the central benzene ring. In (3), each of the three independent CF<sub>3</sub> groups has a C–F bond almost eclipsing the adjacent C–O bond. Interestingly, each carbonyl oxygen atom in (3) and (7) is *trans* to the corresponding benzyl group.

The DMF molecule occupies a general position in (3) and undergoes considerable thermal motion; no evidence has been found to suggest the guest deviates greatly from planarity.

Two independent sites have been found for the potassium ions in (7), one corresponding to a general position in the unit cell, the other located on a two-fold rotation axis. The potassium ion in the first site is co-ordinated to 4 ether oxygens [K<sup>+</sup> ···· O; 2.70(1), 2.81(1), 2.96(1), 3.08(1) Å] and 2 carbonyl oxygens [2.76(1), 2.84(1) Å] belonging to non-equivalent 'legs' of adjacent host molecules, a K<sup>+</sup> ···· N contact of 3.03(1) Å to a thiocyanate ion in a general position also being found. The K<sup>+</sup> ion on the two-fold rotation axis (co-ordinated to a water molecule) is situated between two equivalent host molecules, though here severe disorder of the two equivalent 2-methoxyethoxy units involved in co-ordination

reduces the accuracy with which contact distances can be measured. The corresponding thiocyanate ion, not coordinated to  $K^+$ , has its nitrogen atom on a two-fold rotation axis. It is interesting to note that the theoretically possible mode of binding of  $K^+$  by three legs of a single host molecule is not employed at either site in (7).

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