Journal of Inclusion Phenomena **3**, 355–377. 0167–7861/85.15.

The Supramolecular Structures and Reactivities of Some Complexes of Chiral Crown Ethers with Borane Ammonia*

HOOSHANG SHAHRIARI-ZAVAREH, J. FRASER STODDART and M. KEVIN WILLIAMS
Department of Chemistry, The University, Sheffield S3 7HF, Great Britain

BILLY L. ALLWOOD and DAVID J. WILLIAMS
Department of Chemistry, Imperial College, London SW7 2AY, Great Britain

(Received: 15 October 1984)

Abstract. Whereas 1 : 1 crystalline complexes have been isolated between borane ammonia and methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-galactopyranosido[2,3-*b*]-1,4,7,10,13,16-hexaoxacyclo-octadecane (**1**), methyl 4,6-*O*-benzylidene-2,3-dideoxy-α-D-mannopyranosido[2,3-*b*] (methyl 4′,6′-*O*-benzylidene-2′,3′-dideoxy-α-D-mannopyranosido[2′,3′-*k*]-1,4,7,10,13,16-hexaoxacyclo-octadecane (**3**), and (1*R*,2*R*,7*R*,24*R*)-3,5,8,11,14,17,20,23,26,28-decaoxatricyclo-[21.4.0.0^{2,7}]octacosane (**4**), the hosts, methyl, 4,6-*O*-benzylidene-2,3-dideoxy-α-D-mannopyranosido[2,3-*b*] 1,4,7,10,13,16-hexaoxacyclo-octadecane (**2**) and 1,4 : 1′,4′ : 3,6 : 3′,6′-tetra-anhydro-2,2′ : 5,5′-bis-*O*-oxydiethylenedi-D-mannitol (**5**) have yielded 2 : 1 (guest : host) crystalline complexes with borane ammonia as guest. X-ray analyses of the supramolecular structures of $BH_3NH_3 \cdot \mathbf{1}$, $(BH_3NH_3)_2 \cdot \mathbf{2}$, $BH_3NH_3 \cdot \mathbf{3}$, $BH_3NH_3 \cdot \mathbf{4}$, and $(BH_3NH_3)_2 \cdot \mathbf{5}$ have been carried out and $BH_3NH_3 \cdot \mathbf{1}$, $BH_3NH_3 \cdot \mathbf{2}$, and $(BH_3NH_3)_2 \cdot \mathbf{5}$ have been shown to reduce acetophenone with enantiomeric excesses of 5, 13, and 10%, respectively.

Key words: Chiral crown ethers, glycopyranosides, mannitol derivatives, borane ammonia complexes, crystal structures, enantioselective reductions.

Supplementary Data relating to this article (atomic coordinates of the hydrogen atoms and thermal parameters) are deposited with the British Library as Supplementary Publication No. SUP 82017 (74 pages).

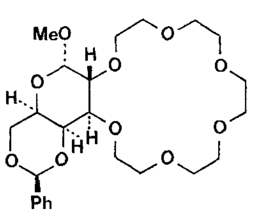
1. Introduction

Our recent observations [1,2] that borane ammonia (BH_3NH_3) forms crystalline 1 : 1 and 2 : 1 complexes with 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) and with an octamethyl-18-crown-6 derivative (2,2,3,3,11,11,12,12-octamethyl-1,4,7,10,13,16-hexaoxacyclooctadecane) has prompted us to examine the ability of chiral crown ethers derived from carbohydrate precursors [3] to form crystalline complexes with BH_3NH_3. Indeed, we have found that many of our carbohydrate-based crown ethers, including the α-D-galactosido-18-crown-6 and α-D-mannosido-18-crown-6 derivatives [4,5] (**1**) and (**2**), the αα-DD-bismannosido-18-crown-6 derivative [6] (**3**), the D-mannitolo-20-crown-6 derivative [7] (**4**), and the bisdianhydro-D-mannitolo-30-crown-10 derivative [8] (**5**), form crystalline complexes very readily with BH_3NH_3. Here, we report on the X-ray analyses of the supramolecular structures of $BH_3NH_3 \cdot \mathbf{1}$, $(BH_3NH_3)_2 \cdot \mathbf{2}$, $BH_3NH_3 \cdot \mathbf{3}$, $BH_3NH_3 \cdot \mathbf{4}$, and $(BH_3NH_3)_2 \cdot \mathbf{5}$ and compare

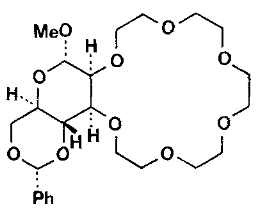
---

* Dedicated to Professor H. M. Powell.

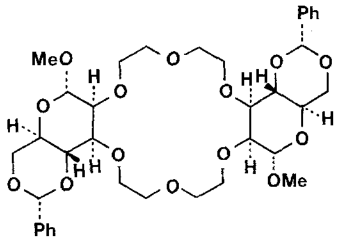
our preliminary results for the enantioselective reduction of acetophenone with those obtained [9] using BH_3NH_3 complexes of (2*R*,3*R*,11*R*,12*R*)- and (2*S*,3*S*,11*S*,12*S*)-tetraphenyl-1,4,7,10,13,16-hexaoxacyclooctadecane.



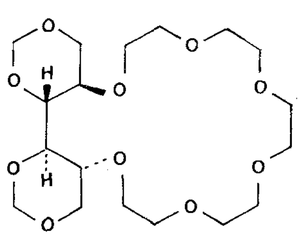
(1)



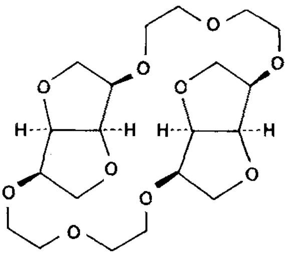
(2)



(3)



(4)



(5)

2. Experimental

The synthesis of the hosts **1–5** have been described elsewhere [4–8]. In all cases, 1 : 1 complexes with BH_3NH_3 and the hosts were prepared initially by dissolving stoichiometric amounts in methanol and then evaporating off the solvent under vacuum. Single crystals, suitable for X-ray crystallography, were then isolated from these solids by a variety of procedures [10] which are outlined below.

2.1. ISOLATION OF $BH_3NH_3 \cdot$ **1**

The 1 : 1 complex crystallised from warm methanol, mp 162–164 °C. (Found: C, 56.2; H, 8.1; N, 2.6%. Calc. for $C_{24}H_{42}BNO_{10}$: C, 55.9; H, 8.2; N, 2.7%.)

2.2. ISOLATION OF $(BH_3NH_3)_2 \cdot \mathbf{2}$

The 2 : 1 complex crystallised from chloroform on layering with light petroleum (bp 60–80 °C), mp 143–145 °C. (Found: C, 55.6; H, 8.4; N, 5.3%. Calc. for $C_{24}H_{48}B_2N_2O_{10}$: C, 52.8; H, 8.3; N, 5.1%.)

2.3. ISOLATION OF $BH_3NH_3 \cdot \mathbf{3}$

The 1 : 1 complex crystallised from warm ethanol, mp 155–170 °C. Insufficient material was obtained for an elemental analysis.

2.4. ISOLATION OF $BH_3NH_3 \cdot \mathbf{4}$

The 1 : 1 complex crystallised from dichloromethane on layering with *n*-pentane, mp 200–201 °C. Insufficient material was obtained for an elemental analysis.

2.5. ISOLATION OF $(BH_3NH_3)_2 \cdot \mathbf{5}$

The 2 : 1 complex crystallised from dichloromethane on layering with *n*-pentane, mp 210–215 °C with decomposition. (Found: C, 48.2; H, 9.0; N, 5.8%. Calc. for $C_{20}H_{44}B_2N_2O_{10}$: C, 48.4; H, 8.9; N, 5.6%.)

2.6. X-RAY DATA COLLECTION, STRUCTURE SOLUTION, AND REFINEMENT FOR $BH_3NH_3 \cdot \mathbf{1}$, $(BH_3NH_3)_2 \cdot \mathbf{2}$, $BH_3NH_3 \cdot \mathbf{3}$, $BH_3NH_3 \cdot \mathbf{4}$, AND $(BH_3NH_3)_2 \cdot \mathbf{5}$

For each single crystal, refined unit cell parameters were obtained by centering a minimum of 18 reflections on a Nicolet R3m diffractometer. Data were measured with monochromated Cu$K\alpha$ radiation (graphite monochromator) using the ω-scan routine. A summary of the crystal data and of the data collection and refinement parameters is presented in Table I. In each case, the net count of two reflections measured as references every 50 reflections did not alter significantly during any of the data collections indicating that in no case had any deterioration of the crystals occurred. In each case, the data were brought to an uniform arbitrary scale by use of these reflections and Lorentz and polarisation corrections were applied.

The supramolecular structures of $BH_3NH_3 \cdot \mathbf{1}$, $(BH_3NH_3)_2 \cdot \mathbf{2}$, $BH_3NH_3 \cdot \mathbf{4}$, and $(BH_3NH_3)_2 \cdot \mathbf{5}$ were solved straightforwardly by direct methods. The solution of the supramolecular structure of $BH_3NH_3 \cdot \mathbf{3}$, however, proved to be somewhat more difficult, resisting several attempts at semi-automatic phase solution. Finally, a starting set comprising two high probability Σ_1 phase indications together with the five principal contributors to the list of negative quartets, and a further 14 automatically selected terms, was used. The subsequent phase expansion involving a total of 38 328 permutations resulted in several phase solutions that had promising figures of merit.

Three cycles of ΔE-map recycling for one of these solutions revealed 49 potential atomic positions with a $R_E = 0.284$ for the 916 E's > 1.2 used in the calculation. The remaining nonhydrogen atomic positions were obtained from conventional ΔF maps.

There was evidence from ΔF maps for disorder in parts of the 18-crown-6 ring system of compounds $BH_3NH_3 \cdot \mathbf{1}$ and $BH_3NH_3 \cdot \mathbf{3}$. In $BH_3NH_3 \cdot \mathbf{1}$, atoms C(3) and O(4) were refined in two orientations with site occupancies of 0.6 and 0.4, respectively, and in $BH_3NH_3 \cdot \mathbf{3}$, C(2) was refined in two positions of equal site occupancy.

Table I. Crystal data and summary of intensity data refinement and structure refinement

Compound	$BH_3NH_3 \cdot$ **1**	$(BH_3NH_3)_2 \cdot$ **2**	$BH_3NH_3 \cdot$ **3**	$BH_3NH_3 \cdot$ **4**	$(BH_3NH_3)_2 \cdot$ **5**
Mol wt	515.4	546.2	767.6	468.1[a]	494.2
Space group	$P2_1$	$P2_1$	$P2_12_12_1$	$I4$	$P2_1$
Cell constants					
a, Å	12.834(2)	10.947(2)	14.071(5)	20.574(4)	8.414(3)
b, Å	8.628(1)	7.696(1)	15.411(4)	–	9.353(3)
c, Å	13.017(3)	18.234(4)	18.446(8)	11.849(3)	17.332(5)
β, deg	103.60(1)	97.10(2)	–	–	100.27(3)
Cell volume, Å^3	1400	1524	4000	5016	1342
Molecules/unit cell	2	2	4	8	2
ρ (calc), g cm^{-3}	1.23	1.19	1.28	1.24[a]	1.23
μ (calc), cm^{-1}	7.40	7.07	7.37	7.99	7.53
Radiation	Cu$K\alpha$	Cu$K\alpha$	Cu$K\alpha$	Cu$K\alpha$	Cu$K\alpha$
Crystal dimensions, mm	0.3 × 0.2 × 0.2	0.3 × 0.2 × 0.3	0.1 × 0.1 × 0.5	0.3 × 0.3 × 0.4	0.4 × 0.4 × 0.18
Standard reflections	$(3\ \bar{1}\ 1)$ $(3\ 0\ \bar{2})$	$(\bar{1}\ \bar{2}\ 2)$ $(1\ \bar{2}\ \bar{2})$	$(0\ 2\ 2)$ $(0\ 2\ \bar{2})$	$(1\ 4\ 1)$ $(\bar{4}\ 2\ 0)$	$(0\ 2\ \bar{5})$ $(\bar{2}\ 0\ 4)$
Reflections measured	2031	2239	3039	1789	2083
2θ range, deg	116	116	116	116	116
Reflections considered observed $\lvert F_0\rvert > 3\sigma(\lvert F_0\rvert)$	1947	2108	2166	1628	1943
Weight (G)[b]	0.0015	0.0007	0.0014	0.0014	0.0009
No. of poarameters varied	362	376	490	295	314
R	0.035	0.034	0.068	0.069	0.040
R_w	0.042	0.039	0.072	0.084	0.047
Maximum residual electron density in final ΔF map, eÅ^{-3}	0.22	0.14	0.28	0.35	0.35

[a] Contains contributions from unidentified solvent fragments.

[b] $w^{-1} = \sigma^2(F) + GF^2$.

For all structures, the non-hydrogen atoms were refined anisotropically. The carbon hydrogens, with the exception of those of the methyl groups, which were refined as rigid bodies, were placed at calculation positions (C—H = 0.96 Å), assigned isotropic thermal parameters, $U(\mathrm{H}) = 1.2\ U_{eq}(\mathrm{C})$, and allowed to ride on their parent carbon atoms. The hydrogens of the NH_3 and BH_3 groups were clearly resolved in ΔF maps and the groups refined as rigid bodies.★ Refinement was by block-cascade full-matrix least-squares to $R = 0.035$, 0.034, 0.068, 0.069, and 0.040 for structures $BH_3NH_3 \cdot$ **1**, $(BH_3NH_3)_2 \cdot$ **2**, $BH_3NH_3 \cdot$ **3**, $BH_3NH_3 \cdot$ **4**, and $(BH_3NH_3)_2 \cdot$ **5**, respectively.

Table II. Atom coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$) for $BH_3NH_3 \cdot$ **1**

Atom	*x*	*y*	*z*	*U*
O(1)	7409(2)	6221(2)	2761(1)	65(1)[a]
C(2)	7658(3)	4633(4)	2646(2)	69(1)[a]
C(3)	8543(6)	4437(8)	2081(5)	81(2)[a]
C(3′)	7840(6)	4439(10)	1546(5)	69(3)[a]
O(4)	8236(4)	4970(5)	1058(4)	86(2)[a]
O(4′)	8840(5)	5290(9)	1624(5)	78(2)[a]
C(5)	9150(5)	4798(7)	596(4)	138(3)[a]
C(6)	8757(5)	5320(7)	-444(4)	132(2)[a]
O(7)	8533(2)	6933(4)	-477(2)	105(1)[a]
C(8)	8192(3)	7506(7)	-1508(3)	104(2)[a]
C(9)	7704(3)	9063(6)	-1490(3)	93(2)[a]
O(10)	6721(2)	8915(3)	-1201(2)	82(1)[a]
C(11)	6191(3)	10344(5)	-1206(3)	86(1)[a]
C(12)	5253(3)	10122(5)	-752(2)	82(1)[a]
O(13)	5613(2)	9919(3)	358(1)	78(1)[a]
C(14)	4777(2)	9876(5)	900(2)	73(1)[a]
C(15)	5267(3)	9781(4)	2053(2)	70(1)[a]
O(16)	5716(1)	8289(2)	2307(1)	58(1)[a]
C(17)	6373(2)	8150(3)	3343(2)	51(1)[a]
C(18)	6790(2)	6514(3)	3503(2)	54(1)[a]
C(19)	7441(2)	6297(3)	4637(2)	56(1)[a]
O(20)	6801(1)	6631(2)	5365(1)	56(1)[a]
C(21)	6414(2)	8195(3)	5293(2)	53(1)[a]
C(22)	5716(2)	8372(4)	6074(2)	60(1)[a]
O(23)	4711(1)	7616(3)	5731(1)	60(1)[a]
C(24)	4193(2)	8169(3)	4727(2)	54(1)[a]
O(25)	4771(1)	7729(2)	3971(1)	51(1)[a]
C(26)	5768(2)	8571(3)	4188(2)	51(1)[a]
O(27)	8344(1)	7263(3)	4797(2)	69(1)[a]
C(28)	9079(3)	7036(7)	5776(3)	102(2)[a]
C(29)	3069(2)	7561(4)	4412(2)	60(1)[a]
C(30)	2583(2)	6891(4)	5155(3)	69(1)[a]
C(31)	1528(3)	6472(5)	4886(4)	94(2)[a]
C(32)	939(3)	6720(7)	3900(4)	114(2)[a]
C(33)	1386(3)	7392(7)	3147(4)	115(2)[a]
C(34)	2472(2)	7786(5)	3402(3)	84(1)[a]
N	7831(2)	8654(3)	1292(2)	66(1)[a]
B	8543(4)	10089(6)	1752(4)	97(2)[a]

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalised U_{ij} tensor.

★ In $(BH_3NH_3)_2 \cdot$ **5**, the BH_3 group hydrogen positions were fixed and only the NH_3 group was refined as a rigid body.

Computations were carried out on an Eclipse S140 Computer using the SHELXTL program system [11].

Tables II–VI record the fractional atomic coordinates for the nonhydrogen atoms for $BH_3NH_3 \cdot$ **1**, $(BH_3NH_3)_2 \cdot$ **2**, $BH_3NH_3 \cdot$ **3**, $BH_3NH_3 \cdot$ **4**, and $(BH_3NH_3)_2 \cdot$ **5**, respectively (with esd's in parentheses).

2.7. ENANTIOSELECTIVE REDUCTIONS OF ACETOPHENONE

To a stirred solution of the 1 : 1 or 2 : 1 complex (0.45 mmol) in dry toluene (10 ml) under nitrogen at − 78 °C were added acetophenone (0.50 mmol) and boron trifluoride etherate

Table III. Atom coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$) for $(BH_3NH_3)_2 \cdot$ **2**

Atom	*x*	*y*	*z*	*U*
O(1)	5649(1)	360(3)	1151(1)	56(1)[a]
C(2)	4708(2)	760(5)	558(1)	65(1)[a]
C(3)	3562(2)	− 143(5)	685(2)	69(1)[a]
O(4)	3059(2)	626(3)	1282(1)	67(1)[a]
C(5)	1935(3)	− 160(6)	1413(2)	85(1)[a]
C(6)	1411(2)	811(6)	2002(2)	85(1)[a]
O(7)	2195(2)	675(3)	2664(1)	73(1)[a]
C(8)	1700(3)	1437(6)	3265(2)	87(1)[a]
C(9)	2615(3)	1315(6)	3927(2)	83(1)[a]
O(10)	3665(2)	2293(3)	3798(1)	68(1)[a]
C(11)	4569(3)	2317(5)	4423(1)	74(1)[a]
C(12)	5651(3)	3310(4)	4250(1)	64(1)[a]
O(13)	6236(2)	2372(3)	3717(1)	58(1)[a]
C(14)	7202(3)	3326(4)	3468(1)	59(1)[a]
C(15)	7872(2)	2207(4)	2987(1)	57(1)[a]
O(16)	7069(1)	1766(3)	2333(1)	51(1)[a]
C(17)	7642(2)	872(4)	1784(1)	51(1)[a]
C(18)	6816(2)	1043(4)	1050(1)	57(1)[a]
C(19)	7375(3)	52(5)	448(2)	70(1)[a]
O(20)	7543(2)	− 1729(3)	626(1)	69(1)[a]
C(21)	8328(2)	− 1964(4)	1302(1)	59(1)[a]
C(22)	8439(3)	− 3855(4)	1495(2)	71(1)[a]
O(23)	9263(2)	− 4047(3)	2160(1)	70(1)[a]
C(24)	8875(2)	− 3076(4)	2746(1)	57(1)[a]
O(25)	8766(1)	− 1286(2)	2571(1)	50(1)[a]
C(26)	7854(2)	− 1025(4)	1941(1)	50(1)[a]
O(27)	8478(2)	897(4)	352(1)	86(1)[a]
C(28)	8984(4)	338(8)	− 286(2)	113(2)[a]
C(29)	9790(2)	− 3282(4)	3425(2)	58(1)[a]
C(30)	9422(3)	− 3125(6)	4106(2)	87(1)[a]
C(31)	10240(4)	− 3341(8)	4735(2)	109(2)[a]
C(32)	11434(3)	− 3715(5)	4688(2)	90(1)[a]
C(33)	11834(3)	− 3828(5)	4022(2)	90(1)[a]
C(34)	11018(3)	− 3618(5)	3379(2)	78(1)[a]
N(1)	4461(2)	3555(4)	2161(1)	71(1)[a]
B(1)	4468(7)	5214(7)	1627(3)	124(2)[a]
N(2)	4868(2)	− 680(4)	2849(1)	64(1)[a]
B(2)	5235(5)	− 2185(6)	3437(3)	100(2)[a]

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalised U_{ij} tensor.

Table IV. Atom coordinates (× 10^4) and temperature factors (Å^2 × 10^3) for $BH_3NH_3 \cdot 3$

Atom	x	y	z	U
O(1)	2645(4)	8589(3)	2555(4)	114(1)[a]
C(2′)	2960(13)	7790(11)	2672(12)	130(2)[a]
C(2)	2930(11)	8057(10)	3290(9)	100(2)[a]
C(3)	3705(7)	7622(7)	3153(7)	153(2)[a]
O(4)	4535(4)	8040(4)	2945(5)	136(1)[a]
C(5)	5345(6)	7741(6)	3259(5)	109(2)[a]
C(6)	6193(6)	8207(6)	2983(7)	140(2)[a]
O(7)	6182(3)	9035(3)	3022(3)	75(1)[a]
C(8)	7049(5)	9458(5)	2946(3)	64(1)[a]
C(9)	6999(5)	10270(5)	3411(4)	82(1)[a]
O(10)	6183(3)	10749(4)	3247(3)	88(1)[a]
C(11)	5650(6)	10969(7)	3852(5)	124(2)[a]
C(12)	4896(5)	11568(6)	3705(5)	98(2)[a]
O(13)	4172(4)	11236(4)	3277(3)	113(1)[a]
C(14)	3286(6)	11415(6)	3492(6)	131(2)[a]
C(15)	2539(7)	11076(7)	3063(8)	190(2)[a]
O(16)	2590(3)	10298(3))	2807(3)	73(1)[a]
C(17)	1760(4)	9904(4)	2519(3)	58(1)[a]
C(18)	1772(5)	8941(5)	2745(4)	75(1)[a]
C(19)	971(5)	8445(4)	2402(4)	67(1)[a]
O(20)	882(3)	8573(3)	1646(2)	68(1)[a]
C(21)	815(5)	9462(4)	1457(3)	57(1)[a]
C(22)	721(5)	9567(4)	664(3)	75(1)[a]
O(23)	696(4)	10463(3)	482(3)	82(1)[a]
C(24)	1513(6)	10891(5)	720(4)	77(2)[a]
O(25)	1595(3)	10847(3)	1487(2)	64(1)[a]
C(26)	1690(4)	9971(4)	1713(3)	57(1)[a]
C(27)	7259(4)	9713(4)	2194(3)	60(1)[a]
O(28)	7405(3)	8970(3)	1732(2)	54(1)[a]
C(29)	7560(5)	9244(4)	1013(3)	56(1)[a]
O(30)	8371(3)	9760(3)	943(2)	63(1)[a]
C(31)	8308(5)	10534(4)	1372(4)	77(2)[a]
C(32)	8148(5)	10256(4)	2147(4)	64(1)[a]
O(33)	8062(4)	11033(3)	2578(3)	81(1)[a]
C(34)	7872(5)	10836(6)	3310(4)	90(2)[a]
O(35)	132(3)	8653(3)	2765(3)	77(1)[a]
C(36)	−609(5)	8015(5)	2722(4)	93(2)[a]
C(37)	1502(7)	11820(5)	506(4)	94(2)[a]
C(38)	2337(8)	12278(6)	449(5)	128(2)[a]
C(39)	2311(10)	13163(7)	261(7)	170(2)[a]
C(40)	1491(9)	13547(7)	150(5)	164(2)[a]
C(41)	664(10)	13146(7)	221(6)	162(2)[a]
C(42)	643(9)	12252(6))	383(5)	131(2)[a]
C(43)	7702(5)	8449(4)	557(3)	56(1)[a]
C(44)	7007(5)	8176(4)	88(4)	68(1)[a]
C(45)	7148(7)	7452(5)	−342(4)	93(2)[a]
C(46)	7979(7)	6987(5)	−289(4)	89(2)[a]
C(47)	8670(6)	7248(4)	178(4)	78(2)[a]
C(48)	8532(5)	7961(4)	604(4)	64(1)[a]
O(49)	8629(4)	10387(4)	3637(3)	103(1)[a]
C(50)	9500(5)	10854(7)	3623(5)	141(2)[a]
N	4499(4)	9782(4)	2126(3)	72(1)[a]
B	4648(7)	9945(7)	1301(5)	90(2)[a]

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

Table V. Atom coordinates (× 10^4) and temperature factors ($Å^2$ × 10^3) for $BH_3NH_3 \cdot$ **4**

Atom	*x*	*y*	*z*	*U*
O(1)	6851(2)	9265(2)	4046(4)	76(1)[a]
C(2)	7124(4)	9132(4)	3029(7)	108(3)[a]
C(3)	7483(4)	9659(5)	2580(7)	111(4)[a]
O(4)	7947(2)	9922(2)	3279(4)	88(2)[a]
C(5)	8212(5)	10496(4)	2919(7)	103(3)[a]
C(6)	8721(7)	10740(7)	3596(9)	180(7)[a]
O(7)	8637(2)	10791(2)	4710(5)	93(2)[a]
C(8)	9075(5)	11078(6)	5358(10)	136(5)[a]
C(9)	8958(6)	11193(5)	6467(10)	135(5)[a]
O(10)	8630(2)	10741(2)	7099(5)	91(2)[a]
C(11)	8409(7)	10851(5)	8106(9)	174(7)[a]
C(12)	8110(4)	10420(4)	8796(8)	101(3)[a]
O(13)	7705(3)	9967(2)	8290(4)	92(2)[a]
C(14)	7341(4)	9581(4)	8960(7)	94(3)[a]
C(15)	6942(4)	9108(4)	8461(8)	97(3)[a]
O(16)	7186(2)	8778(3)	7563(5)	99(2)[a]
C(17)	6851(3)	8226(3)	7170(7)	76(2)[a]
C(18)	7255(4)	7613(4)	7396(7)	94(3)[a]
O(19)	7011(2)	7073(2)	6837(5)	97(2)[a]
C(20)	7011(4)	7196(3)	5687(9)	96(3)[a]
O(21)	6573(2)	7700(2)	5406(5)	79(2)[a]
C(22)	6759(3)	8303(3)	5905(6)	65(2)[a]
C(23)	6283(3)	8811(3)	5575(6)	67(2)[a]
O(24)	5656(2)	8616(2)	5970(5)	77(2)[a]
C(25)	5193(3)	9101(3)	5705(8)	94(3)[a]
O(26)	5110(2)	9179(2)	4550(6)	93(2)[a]
C(27)	5689(3)	9409(3)	4077(8)	87(3)[a]
C(28)	6257(3)	8952(3)	4334(6)	65(2)[a]
N	7385(2)	10287(2)	5777(5)	63(2)[a]
B	6848(4)	10842(4)	5871(11)	99(4)[a]
X(1)[b]	5870(4)	5511(4)	5796(7)	84(3)[a]
X(2)	10000	10000	7873(54)	236(21)
X(3)	5000	5000	5160(60)	249(23)
X(4)	4728(10)	5453(8)	5951(20)	192(7)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalised U_{ij} tensor.
[b] X represents unidentified solvent fragments.

(0.45 mmol). The reaction mixture was stirred for 75 min, water (10 ml) was added, and the organic products were isolated and chromatographed (dichloromethane-light petroleum, 7 : 3 followed by dichloromethane-methanol, 9 : 1) on silica gel. The alcohol (PhCHOHMe) was converted into the menthoxyacetate ester in the standard manner. The diasteroisomeric ratios were determined (integration) by ^1H NMR spectroscopy after addition of the chiral shift reagent, $Eu(hfbc)_3$.

The results obtained on reduction of acetophenone with $BH_3NH_3 \cdot$ **1**, $BH_3NH_3 \cdot$ **2**, and $(BH_3NH_3)_2 \cdot$ **5** are summarised in Table VII.

3. Results and Discussion

All five hosts **1–5** are chiral. Hosts **1** and **2** have C_1 molecular symmetry; hosts **3** and **4** have potential C_2 molecular symmetry and host **5** has potential D_2 molecular symmetry. In addition,

Table VI. Atom coordinates ($\times 10^4$) and temperature factors ($Å^2 \times 10^3$) for $(BH_3NH_3)_2 \cdot$ **5**

Atom	x	y	z	U
O(1)	8235(2)	4612(3)	3755(1)	57(1)[a]
C(2)	7633(4)	5847(4)	3334(2)	67(1)[a]
C(3)	5842(4)	5931(4)	3318(2)	61(1)[a]
O(4)	5006(2)	4667(3)	3032(1)	55(1)[a]
C(5)	4779(5)	4509(4)	2210(2)	67(1)[a]
C(6)	4066(4)	3085(4)	1994(2)	67(1)[a]
O(7)	5261(2)	2016(3)	2196(1)	57(1)[a]
C(8)	4688(4)	620(4)	1993(2)	65(1)[a]
C(9)	5996(5)	−466(4)	2296(2)	72(1)[a]
O(10)	5562(4)	−1693(3)	1815(2)	82(1)[a]
C(11)	4883(5)	−1217(4)	1053(2)	73(1)[a]
C(12)	4300(4)	319(4)	1119(2)	65(1)[a]
O(13)	5252(3)	1190(3)	709(1)	67(1)[a]
C(14)	5628(5)	323(5)	84(2)	77(1)[a]
C(15)	6104(4)	−1103(4)	474(2)	70(1)[a]
O(16)	7722(3)	−972(3)	863(1)	71(1)[a]
C(17)	8601(5)	−2276(5)	953(3)	88(2)[a]
C(18)	10354(5)	−1905(6)	1153(2)	90(2)[a]
O(19)	10816(3)	−1068(3)	1838(1)	72(1)[a]
C(20)	11012(5)	−1870(4)	2538(2)	72(1)[a]
C(21)	11335(4)	−933(4)	3221(2)	64(1)[a]
O(22)	9959(2)	−106(3)	3282(1)	54(1)[a]
C(23)	10166(3)	770(4)	3952(2)	48(1)[a]
C(24)	8573(3)	1356(3)	4096(2)	50(1)[a]
O(25)	9024(2)	2449(2)	4655(1)	51(1)[a]
C(26)	10394(3)	3180(4)	4439(2)	48(1)[a]
C(27)	11100(3)	2151(3)	3907(2)	49(1)[a]
O(28)	10725(2)	2732(3)	3135(1)	55(1)[a]
C(29)	10754(4)	4256(4)	3233(2)	60(1)[a]
C(30)	9937(3)	4527(4)	3939(2)	52(1)[a]
N(1)	5601(3)	3264(3)	4585(1)	51(1)[a]
B(1)	4827(4)	4376(5)	5126(2)	56(1)[a]
N(2)	8692(4)	2069(4)	1573(2)	68(1)[a]
B(2)	9064(7)	3398(8)	1048(3)	101(2)[a]

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

it should be noted that in hosts **1–3**, the macrocyclic rings have diastereotopic faces★ whereas hosts **4** and **5** have homotopic faces. There appears to be no correlation between either molecular symmetry or topicity and guest : host stoichiometry. In fact, hosts **1**, **3**, and **4** form 1 : 1 complexes with BH_3NH_3 and hosts **2** and **5** form 2 : 1 complexes.

In the 1 : 1 complex of the α-D-galactosido-18-crown-6 derivative (**1**), the X-ray analysis revealed disorder in the macrocyclic component of the host. The supramolecular structures A and B and the relevant atomic numbering schemes are shown in Figure 1. Tables VIII and IX give the bond lengths and angles, respectively. Complexation occurs at the α-face of the macrocycle with three-point binding of the BH_3NH_3 guest in the perching mode [12]. Clearly, the fusion of a galactopyranosidic ring to the macrocycle has not influenced the local pseudo

---

★ It is convenient [3] to refer to the two diastereotopic faces as the α- and β-faces respectively depending on their *syn*-relationship with the α- and β-positions at the anomeric centres of the glycopyranosidic residues.

Table VII. Reductions of acetophenone with $BH_3NH_3 \cdot \mathbf{1}$, $BH_3NH_3 \cdot \mathbf{2}$, and $(BH_3NH_3)_2 \cdot \mathbf{5}$ in toluene at −78 °C for 75 mins.

Crown ether (CE)	BH_3NH_3 : CE	Yield[a] (%)	e.e.[b] (%)	Absolute configuration
1	1 : 1	45	5	(*S*)
2	1 : 1[c]	56	13	(*R*)
5	2 : 1	62	10	(*R*)

[a] All yields quoted refer to isolated yields.

[b] These were deduced from the diasteroisomeric excesses for the menthoxyacetate ester (see Experimental).

[c] Although the crystalline complex was $(BH_3NH_3)_2 \cdot \mathbf{2}$ the reduction was performed with the 1 : 1 complex.

D_{3d} symmetry adopted by the major occupancy conformation (A) of the ring. However, a consequence of this conformation is a short nonbonded intramolecular H···H contact (2.13 Å) between one (H_a) of the methylene hydrogen atoms on C(2) and the anomeric hydrogen atom on C(19). In the minor occupancy conformation (B), this situation is relieved by a change to a bisecting relationship between the anomeric hydrogen atom and the two methylene hydrogen atoms, such that the intramolecular H···H contacts are 2.5 and 2.8 Å. It is noteworthy that a similar interaction (2.3 Å) encountered between H(26) and one (H_a) of the methylene hydrogen atoms on C(15) is not sufficient to induce disorder in the C(11) to O(16) regions of the macrocycle.

X-ray analysis revealed that in the 2 : 1 complex of the α-D-mannosido-18-crown-6 derivative (**2**), complexation of the two BH_3NH_3 guest molecules is to the two (α and β) diastereotopic faces of the macrocycle. The supramolecular structure and atomic numbering scheme are

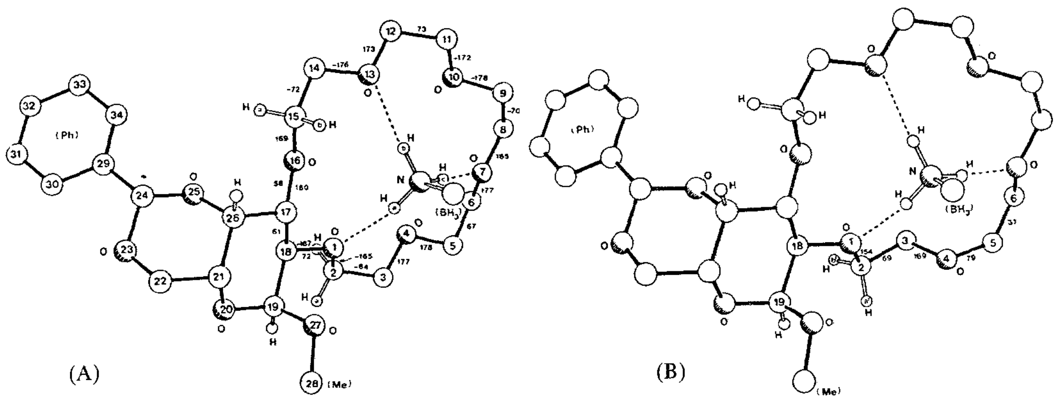


Fig. 1. The supramolecular structure of the major (A) and minor (B) occupancy conformations of $BH_3NH_3 \cdot \mathbf{1}$ showing selected hydrogen atoms involved in steric interactions between the pyranosidic and macrocyclic rings. The torsional angles (°) around the macrocyclic ring for the major occupancy conformation (A) are indicated beside the relevant C—C and C—O bonds. The sequence of torsional angles in the minor occupancy conformation (B) differs in the region O(1) to O(6) due to the alternative sites for C(3) and O(4). The magnitudes of the torsional angles in this region are shown in (B). Hydrogen bond distances *R*[N···O] (Å), *R*[H···O] (Å), angles (θ_N and θ_H °) between COC planes and (a) NO vectors and (b) HO vectors, N—H···O angles (°) at H atoms in major occupancy conformation (A): [N···O(1)] 2.97, [H_a···O] 2.04, (a) 6.7, (b) 3.0, H_a 165; [N···O(7)] 3.05, [H_b···O] 2.09, (a) 22.7, (b) 20.4, H_b 173; [N···O(13)] 3.02, [H_c···O] 2.06, (a) 16.4, (b) 17.2, H_c 177. Nonbonded [N···O] (Å) distances in the major occupancy conformation (A): 3.25, 3.23, and 3.30 to O(4), O(10), and O(16), respectively. Distance of N from mean plane of six O atoms in the macrocyclic ring of the major occupancy conformation (A), 1.30 Å. The B—N bond is inclined by 11° to the normal to this plane.

Table VIII. Bond lengths (Å) in $BH_3NH_3 \cdot \mathbf{1}$

O(1)—C(2)	1.423(4)	O(1)—C(18)	1.411(4)
C(2)—C(3)	1.501(9)	C(2)—C(3′)	1.513(8)
C(3)—O(4)	1.376(8)	C(3′)—O(4′)	1.462(11)
O(4)—C(5)	1.445(9)	O(4′)—C(5)	1.542(10)
C(5)—C(6)	1.403(7)	C(6)—O(7)	1.420(7)
O(7)—C(8)	1.401(4)	C(8)—C(9)	1.485(7)
C(9)—O(10)	1.404(5)	O(10)—C(11)	1.408(5)
C(11)—C(12)	1.473(6)	C(12)—O(13)	1.421(3)
O(13)—C(14)	1.416(4)	C(14)—C(15)	1.487(4)
C(15)—O(16)	1.418(4)	O(16)—C(17)	1.418(3)
C(17)—C(18)	1.507(4)	C(17)—C(26)	1.532(4)
C(18)—C(19)	1.526(3)	C(19)—O(20)	1.422(3)
C(19)—O(27)	1.403(3)	O(20)—C(21)	1.433(3)
C(21)—C(22)	1.513(4)	C(21)—C(26)	1.517(3)
C(22)—O(23)	1.420(3)	O(23)—C(24)	1.403(3)
C(24)—O(25)	1.415(3)	C(24)—C(29)	1.499(3)
O(25)—C(26)	1.441(3)	O(27)—C(28)	1.409(4)
C(29)—C(30)	1.394(5)	C(29)—C(34)	1.371(4)
C(30)—C(31)	1.364(4)	C(31)—C(32)	1.345(6)
C(32)—C(33)	1.375(7)	C(33)—C(34)	1.396(5)
N—B	1.571(6)		

Table IX. Bond angles (deg.) in $BH_3NH_3 \cdot \mathbf{1}$

C(2)—O(1)—C(18)	114.9(2)	O(1)—C(2)—C(3)	112.0(4)
O(1)—C(2)—C(3′)	107.1(4)	C(2)—C(3)—O(4)	111.0(5)
C(2)—C(3′)—O(4′)	101.9(5)	C(3)—O(4)—C(5)	107.0(5)
C(3′)—O(4′)—C(5)	101.7(5)	O(4)—C(5)—C(6)	103.0(5)
O(4′)—C(5)—C(6)	129.9(6)	C(5)—C(6)—O(7)	111.6(4)
C(6)—O(7)—C(8)	113.0(4)	O(7)—C(8)—C(9)	110.0(3)
C(8)—C(9)—O(10)	109.3(4)	C(9)—O(10)—C(11)	112.5(3)
O(10)—C(11)—C(12)	108.9(3)	C(11)—C(12)—O(13)	108.8(3)
C(12)—O(13)—C(14)	113.9(2)	O(13)—C(14)—C(15)	108.3(2)
C(14)—C(15)—O(16)	109.7(3)	C(15)—O(16)—C(17)	114.6(2)
O(16)—C(17)—C(18)	108.8(2)	O(16)—C(17)—C(26)	112.0(2)
C(18)—C(17)—C(26)	110.2(2)	O(1)—C(18)—C(17)	108.2(2)
O(1)—C(18)—C(19)	111.8(2)	C(17)—C(18)—C(19)	110.1(2)
C(18)—C(19)—O(20)	110.4(2)	C(18)—C(19)—O(27)	108.5(2)
O(20)—C(19)—O(27)	111.5(2)	C(19)—O(20)—C(21)	113.1(2)
O(20)—C(21)—C(22)	107.6(2)	O(20)—C(21)—C(26)	111.5(2)
C(22)—C(21)—C(26)	109.7(2)	C(21)—C(22)—O(23)	112.3(2)
C(22)—O(23)—C(24)	109.4(2)	O(23)—C(24)—O(25)	110.3(2)
O(23)—C(24)—C(29)	110.5(2)	O(25)—C(24)—C(29)	110.1(2)
C(24)—O(25)—C(26)	108.4(2)	C(17)—C(26)—C(21)	111.9(2)
C(17)—C(26)—O(25)	108.5(2)	C(21)—C(26)—O(25)	109.9(2)
C(19)—O(27)—C(28)	114.0(3)	C(24)—C(29)—C(30)	121.0(2)
C(24)—C(29)—C(34)	119.9(3)	C(30)—C(29)—C(34)	118.9(3)
C(29)—C(30)—C(31)	120.7(3)	C(30)—C(31)—C(32)	120.3(4)
C(31)—C(32)—C(33)	120.8(3)	C(32)—C(33)—C(34)	119.6(4)
C(29)—C(34)—C(33)	119.7(4)		

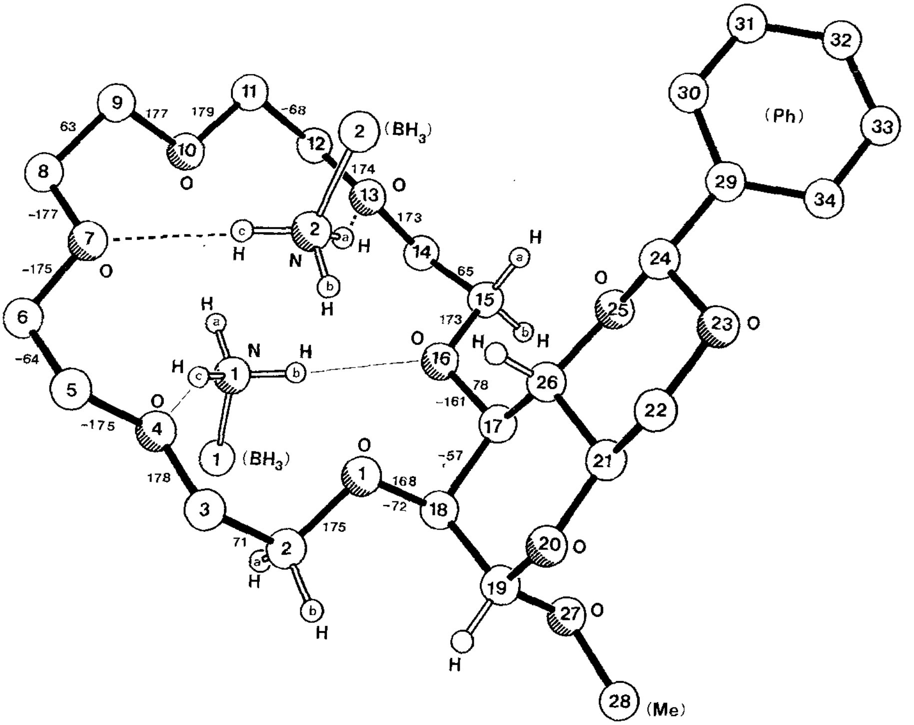


Fig. 2. The supramolecular structure of $(BH_3NH_3)_2 \cdot \mathbf{2}$ showing selected hydrogen atoms involved in steric interactions between the pyranosidic and macrocyclic rings. The torsional angles (°) around the macrocyclic ring are indicated beside the relevant C—C and C—O bonds. The ring experiences four [N—H···O] contacts within hydrogen bonding distance. Hydrogen bond distances R[N···O], R[H···O] (Å), angles (θ_N and θ_H °) between COC planes and (a) NO vectors and (b) HO vectors, N—H···O angles (°) at H atoms: [N(1)···O(4)] 3.07, [H_c···O] 2.16, (a) 2.9, (b) 2.9, H_c 157°; [N(1)···O(16)] 3.15, [H_b···O] 2.19, (a) 11.2, (b) 12.0, H_b 177°; [N(2)···O(7)] 3.09, [H_b···O] 2.13, (a) 6.6, (b) 5.8, H_b 173°; [N(2)···O(13)] 3.11, [H_a···O] 2.23, (a) 17.9, (b) 19.2, H_a 153°. Nonbonded [N(1)···O] (Å) distances: 3.42, 3.53, 3.36, and 3.36 to O(1), O(7), O(10), and O(13), respectively. Nonbonded [N(2)···O] (Å) distances: 3.41, 3.42, 3.24, and 3.29 to O(1), O(4), O(10), and O(16), respectively. Distances of N(1) and N(2) from the mean plane of six O atoms, 1.80 and 1.69 Å, respectively. The B(1)—N(1) and B(2)—N(2) bonds are inclined respectively by 23° and 25° to the normal to this plane.

shown in Figure 2. Tables X and XI give the bond lengths and angles, respectively. In the case of both BH_3NH_3 guest molecules, the NH_3 groups are involved in two-point binding via the perching arrangement [12]. As in the major occupancy conformation (A) of $BH_3NH_3 \cdot \mathbf{1}$, the macrocyclic ring in $(BH_3NH_3)_2 \cdot \mathbf{2}$ adopts an all-*gauche* conformation with local pseudo D_{3d} symmetry. However, it is interesting to note that, whilst there is an analogous short intramolecular H···H contact (2.10 Å) between one (H_b) of the methylene hydrogen atoms on C(2) and the anomeric hydrogen atom on C(19), there is no associated disorder of the macrocyclic ring in this case. This observation may be a result of the stabilising constraint of the hydrogen bond formed between N(1) and O(4). The only other intramolecular contact (2.40 Å) of significance is that between O(25) on the pyranosidic ring and H_a on C(15). There are no short nonbonded contacts between the BH_3 group attached to N(2) and the benzylidene ring of the host.

Table X. Bond lengths (Å) in $(BH_3NH_3)_2 \cdot \mathbf{2}$

O(1)—C(2)	1.431(3)	O(1)—C(18)	1.414(3)
C(2)—C(3)	1.477(4)	C(3)—O(4)	1.410(4)
O(4)—C(5)	1.417(4)	C(5)—C(6)	1.481(5)
C(6)—O(7)	1.396(3)	O(7)—C(8)	1.409(4)
C(8)—C(9)	1.472(4)	C(9)—O(10)	1.418(4)
O(10)—C(11)	1.415(3)	C(11)—C(12)	1.476(5)
C(12)—O(13)	1.425(4)	O(13)—C(14)	1.408(3)
C(14)—C(15)	1.486(4)	C(15)—O(16)	1.432(3)
O(16)—C(17)	1.422(3)	C(17)—C(18)	1.526(3)
C(17)—C(26)	1.500(4)	C(18)—C(19)	1.525(4)
C(19)—O(20)	1.416(5)	C(19)—O(27)	1.402(4)
O(20)—C(21)	1.423(3)	C(21)—C(22)	1.499(5)
C(21)—C(26)	1.516(4)	C(22)—O(23)	1.427(3)
O(23)—C(24)	1.411(3)	C(24)—O(25)	1.416(3)
C(24)—C(29)	1.503(4)	O(25)—C(26)	1.440(3)
O(27)—C(28)	1.416(5)	C(29)—C(30)	1.357(4)
C(29)—C(34)	1.382(4)	C(30)—C(31)	1.375(4)
C(31)—C(32)	1.351(5)	C(32)—C(33)	1.343(6)
C(33)—C(34)	1.394(5)	N(1)—B(1)	1.606(6)
N(2)—B(2)	1.596(5)		

Table XI. Bond angles (deg.) in $(BH_3NH_3)_2 \cdot \mathbf{2}$

C(2)—O(1)—C(18)	113.5(2)	O(1)—C(2)—C(3)	109.1(2)
C(2)—C(3)—O(4)	110.1(3)	C(3)—O(4)—C(5)	112.4(2)
O(4)—C(5)—C(6)	109.2(3)	C(5)—C(6)—O(7)	109.7(3)
C(6)—O(7)—C(8)	112.7(2)	O(7)—C(8)—C(9)	108.9(3)
C(8)—C(9)—O(10)	108.2(3)	C(9)—O(10)—C(11)	112.0(2)
O(10)—C(11)—C(12)	109.5(2)	C(11)—C(12)—O(13)	108.9(3)
C(12)—O(13)—C(14)	112.0(2)	O(13)—C(14)—C(15)	109.5(2)
C(14)—C(15)—O(16)	109.4(2)	C(15)—O(16)—C(17)	115.0(2)
O(16)—C(17)—C(18)	108.1(2)	O(16)—C(17)—C(26)	114.1(2)
C(18)—C(17)—C(26)	108.2(2)	O(1)—C(18)—C(17)	107.5(2)
O(1)—C(18)—C(19)	110.9(2)	C(17)—C(18)—C(19)	109.9(2)
C(18)—C(19)—O(20)	111.8(2)	C(18)—C(19)—O(27)	106.6(3)
O(20)—C(19)—O(27)	112.8(3)	C(19)—O(20)—C(21)	111.7(2)
O(20)—C(21)—C(22)	110.5(2)	O(20)—C(21)—C(26)	112.2(2)
C(22)—C(21)—C(26)	107.9(2)	C(21)—C(22)—O(23)	109.0(2)
C(22)—O(23)—C(24)	111.7(2)	O(23)—C(24)—O(25)	111.7(2)
O(23)—C(24)—C(29)	109.6(2)	O(25)—C(24)—C(29)	108.5(2)
C(24)—O(25)—C(26)	110.2(2)	C(17)—C(26)—C(21)	112.1(2)
C(17)—C(26)—O(25)	111.3(2)	C(21)—C(26)—O(25)	106.1(2)
C(19)—O(27)—C(28)	113.1(3)	C(24)—C(29)—C(30)	120.1(2)
C(24)—C(29)—C(34)	121.5(3)	C(30)—C(29)—C(34)	118.3(3)
C(29)—C(30)—C(31)	121.0(3)	C(30)—C(31)—C(32)	120.6(3)
C(31)—C(32)—C(33)	119.8(3)	C(32)—C(33)—C(34)	120.5(3)
C(29)—C(34)—C(33)	119.8(3)		

Table XII. Bond lengths (Å) in $BH_3NH_3 \cdot$ **3**

O(1)—C(2′)	1.326(18)	O(1)—C(2)	1.634(17)
O(1)—C(18)	1.388(8)	C(2′)—C(3)	1.398(23)
C(2)—C(3)	1.306(19)	C(3)—O(4)	1.387(12)
O(4)—C(5)	1.358(11)	C(5)—C(6)	1.483(13)
C(6)—O(7)	1.277(10)	O(7)—C(8)	1.391(8)
C(8)—C(9)	1.519(10)	C(8)—C(27)	1.471(9)
C(9)—O(10)	1.398(9)	C(9)—C(34)	1.519(11)
O(10)—C(11)	1.386(10)	C(11)—C(12)	1.432(12)
C(12)—O(13)	1.387(10)	O(13)—C(14)	1.337(10)
C(14)—C(15)	1.417(15)	C(15)—O(16)	1.290(12)
O(16)—C(17)	1.419(7)	C(17)—C(18)	1.542(10)
C(17)—C(26)	1.493(9)	C(18)—C(19)	1.502(10)
C(19)—O(20)	1.413(8)	C(19)—O(35)	1.395(8)
O(20)—C(21)	1.417(7)	C(21)—C(22)	1.476(9)
C(21)—C(26)	1.534(9)	C(22)—O(23)	1.422(8)
O(23)—C(24)	1.396(9)	C(24)—O(25)	1.421(8)
C(24)—C(37)	1.485(11)	O(25)—C(26)	1.419(7)
C(27)—O(28)	1.444(7)	C(27)—C(32)	1.508(9)
O(28)—C(29)	1.408(7)	C(29)—O(30)	1.397(8)
C(29)—C(43)	1.501(8)	O(30)—C(31)	1.433(8)
C(31)—C(32)	1.509(10)	C(32)—O(33)	1.443(8)
O(33)—C(34)	1.411(10)	C(34)—O(49)	1.406(10)
O(35)—C(36)	1.435(9)	C(37)—C(38)	1.374(15)
C(37)—C(42)	1.398(15)	C(38)—C(39)	1.408(15)
C(39)—C(40)	1.312(18)	C(40)—C(41)	1.324(18)
C(41)—C(42)	1.410(13)	C(43)—C(44)	1.372(9)
C(43)—C(48)	1.390(9)	C(44)—C(45)	1.384(10)
C(45)—C(46)	1.374(13)	C(46)—C(47)	1.360(11)
C(47)—C(48)	1.365(9)	O(49)—C(50)	1.421(10)
N—B	1.556(11)		

After establishing its stoichiometry as 1 : 1 in the absence of an elemental analysis, the first point which emerged from the X-ray analysis of the 1 : 1 complex of the $\alpha\alpha$-DD-bismannosido-18-crown-6 (**3**) is that binding of BH_3NH_3 occurs to the sterically congested β-face of the macrocycle through three-point [N—H···O] hydrogen bonding. In common with $BH_3NH_3 \cdot$ **1**, $BH_3NH_3 \cdot$ **3** exhibits disorder in the macrocyclic component of the host. The supramolecular structures A and B and the relevant atomic numbering schemes are shown in Figure 3. Tables XII and XIII give the bond lengths and angles, respectively. In view of the configurationally-enforced absence [3,6,12] of local pseudo D_{3d} symmetry in the macrocyclic conformations of $BH_3NH_3 \cdot$ **3**, it is not realistic to discuss the binding of the BH_3NH_3 guest in terms of perching or nesting modes [13]. However, nonbonded intramolecular interactions between the macrocyclic rings and fused carbohydrate moieties once again influence the conformation adopted by the macrocyclic ring. In this context, the principle regions on the ring for consideration are those associated with the methylene groups at C(2), C(2′), C(6), C(11), and C(15). There is a short intramolecular H···H contact (2.11 Å) between H_b on C(2′) and the anomeric hydrogen atom on C(19) in conformation A, which is relieved in conformation B by the adoption of an alternative orientation [C(2)] of the methylene group. In this alternative conformation (B), the shortest intramolecular H···H contact to H(19)

Table XIII. Bond angles (deg.) in $BH_3NH_3 \cdot \mathbf{3}$

C(2′)—O(1)—C(18)	128.2(10)	C(2)—O(1)—C(18)	101.8(8)
O(1)—C(2′)—C(3)	121.7(15)	O(1)—C(2)—C(3)	107.5(12)
C(2′)—C(3)—O(4)	111.8(12)	C(2)—C(3)—O(4)	121.3(11)
C(3)—O(4)—C(5)	115.6(8)	O(4)—C(5)—C(6)	111.4(8)
C(5)—C(6)—O(7)	117.0(8)	C(6)—O(7)—C(8)	116.8(6)
O(7)—C(8)—C(9)	106.7(5)	O(7)—C(8)—C(27)	113.3(5)
C(9)—C(8)—C(27)	108.8(6)	C(8)—C(9)—O(10)	110.5(6)
C(8)—C(9)—C(34)	111.5(6)	O(10)—C(9)—C(34)	109.5(6)
C(9)—O(10)—C(11)	113.5(6)	O(10)—C(11)—C(12)	114.0(7)
C(11)—C(12)—O(13)	114.4(8)	C(12)—O(13)—C(14)	116.0(7)
O(13)—C(14)—C(15)	116.7(9)	C(14)—C(15)—O(16)	120.4(9)
C(15)—O(16)—C(17)	119.2(6)	O(16)—C(17)—C(18)	107.6(5)
O(16)—C(17)—C(26)	113.4(5)	C(18)—C(17)—C(26)	109.7(5)
O(1)—C(18)—C(17)	108.5(5)	O(1)—C(18)—C(19)	111.0(6)
C(17)—C(18)—C(19)	111.6(6)	C(18)—C(19)—O(20)	114.3(6)
C(18)—C(19)—O(35)	108.4(6)	O(20)—C(19)—O(35)	111.4(5)
C(19)—O(20)—C(21)	112.6(5)	O(20)—C(21)—C(22)	110.8(5)
O(20)—C(21)—C(26)	111.4(5)	C(22)—C(21)—C(26)	108.8(5)
C(21)—C(22)—O(23)	110.0(5)	C(22)—O(23)—C(24)	111.4(5)
O(23)—C(24)—O(25)	110.9(6)	O(23)—C(24)—C(37)	111.3(7)
O(25)—C(24)—C(37)	108.2(6)	C(24)—O(25)—C(26)	110.3(5)
C(17)—C(26)—C(21)	109.0(5)	C(17)—C(26)—O(25)	111.4(5)
C(21)—C(26)—O(25)	108.7(5)	C(8)—C(27)—O(28)	111.9(5)
C(8)—C(27)—C(32)	111.7(5)	O(28)—C(27)—C(32)	106.7(5)
C(27)—O(28)—C(29)	109.9(4)	O(28)—C(29)—O(30)	112.6(5)
O(28)—C(29)—C(43)	107.6(5)	O(30)—C(29)—C(43)	107.7(5)
C(29)—O(30)—C(31)	111.8(5)	O(30)—C(31)—C(32)	107.2(5)
C(27)—C(32)—C(31)	109.6(6)	C(27)—C(32)—O(33)	111.0(5)
C(31)—C(32)—O(33)	107.4(5)	C(32)—O(33)—C(34)	111.4(6)
C(9)—C(34)—O(33)	113.2(6)	C(9)—C(34)—O(49)	106.1(7)
O(33)—C(34)—O(49)	111.9(6)	C(19)—O(35)—C(36)	115.5(5)
C(24)—C(37)—C(38)	120.4(9)	C(24)—C(37)—C(42)	120.8(8)
C(38)—C(37)—C(42)	118.8(8)	C(37)—C(38)—C(39)	119.6(10)
C(38)—C(39)—C(40)	119.9(12)	C(39)—C(40)—C(41)	123.2(11)
C(40)—C(41)—C(42)	119.7(12)	C(37)—C(42)—C(41)	118.8(11)
C(29)—C(43)—C(44)	120.6(6)	C(29)—C(43)—C(48)	121.2(6)
C(44)—C(43)—C(48)	118.2(6)	C(43)—C(44)—C(45)	120.5(7)
C(44)—C(45)—C(46)	120.0(8)	C(45)—C(46)—C(47)	120.0(7)
C(46)—C(47)—C(48)	120.1(7)	C(43)—C(48)—C(47)	121.2(6)
C(34)—O(49)—C(50)	113.3(7)		

increases to 2.64 Å. For the methylene group at C(11), a similar conformation is adopted where the shortest intramolecular H···H to H(34) is 2.71 Å. There are qualitatively similar 1,5-interactions between C(6) and O(28) and between C(15) and O(25) in which the H_a atoms approach these oxygen atoms at distances of 2.54 and 2.65 Å, respectively. There are no short nonbonded contacts between the BH_3 group in the guest and either of the benzylidene rings in the host.

It should be noted that in all three complexes [$BH_3NH_3 \cdot \mathbf{1}$, $(BH_3NH_3)_2 \cdot \mathbf{2}$, and $BH_3NH_3 \cdot \mathbf{3}$] containing methyl α-D-pyranosidic residues, the axial methoxyl groups at the anomeric centres adopt the *gauche* orientations about their exocyclic C—O bonds with respect

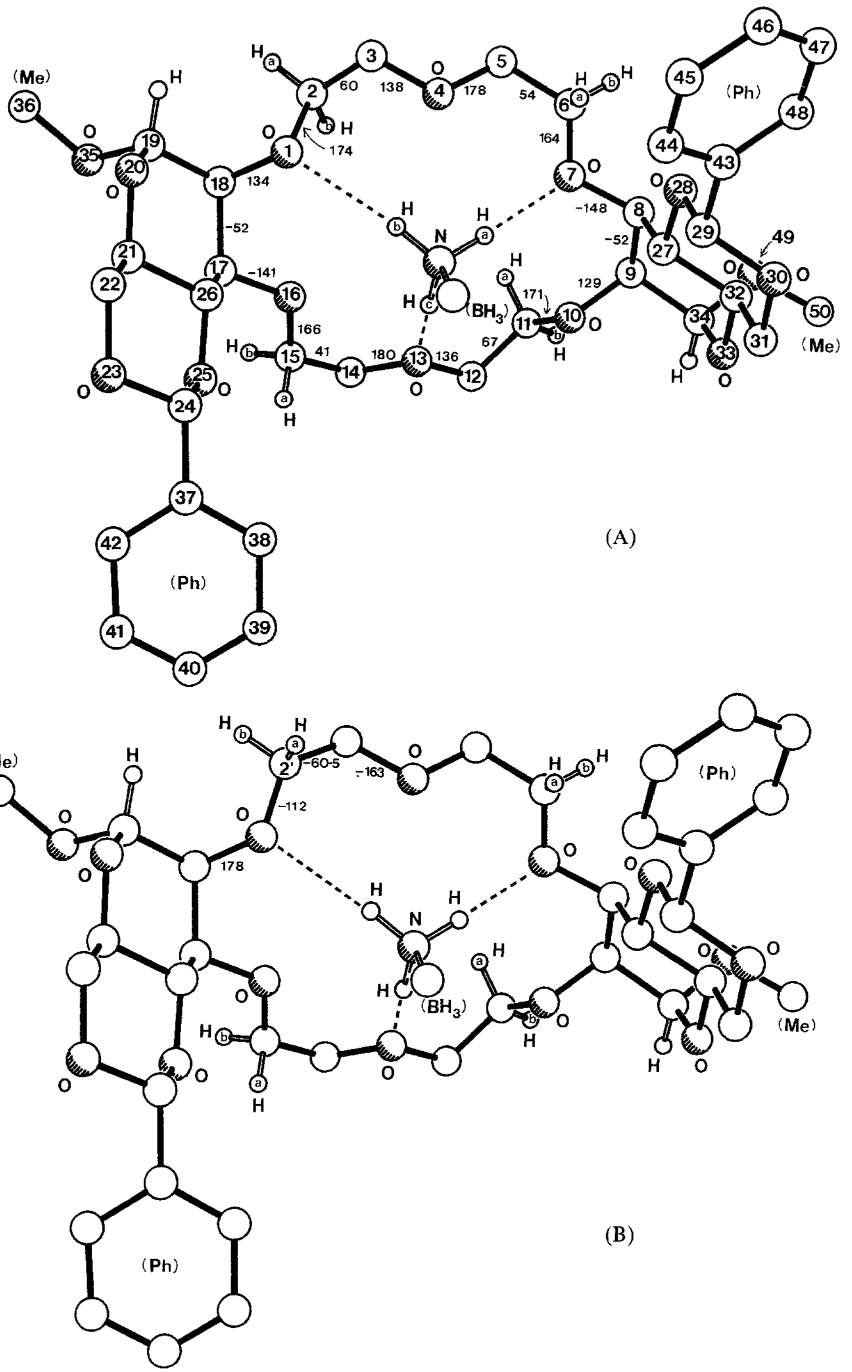


Fig. 3. The supramolecular structures of the two alternative equal occupancy conformations, (A) and (B), of $BH_3NH_3 \cdot \mathbf{3}$ showing selected hydrogen atoms involved in steric interactions between the pyranosidic and macrocyclic rings. The torsional angles (°) around the macrocyclic ring of (A) are indicated beside the relevant C—C and C—O bonds. The sequence of torsional angles in the region with different geometries are shown in (B). Hydrogen bond distances $R[\mathrm{N}\cdots\mathrm{O}]$ (Å), $R[\mathrm{H}\cdots\mathrm{O}]$, angles ($\theta_\mathrm{N}$ and θ_H°) between COC planes (in geometries A and B) and (a) NO vectors and (b) HO vectors, N—H···O angles (°) at H atoms: [N···O(1)] 3.29, [$\mathrm{H_b}\cdots$O], 2.34, ($\mathrm{a_A}$) 44, ($\mathrm{b_A}$) 47, ($\mathrm{a_B}$) 15, ($\mathrm{b_B}$) 12, $\mathrm{H_b}$ 169, [N···O(7)] 3.11, [$\mathrm{H_a}\cdots$O] 2.17, (a) 41, (b) 45, $\mathrm{H_a}$ 167; [N···O(13)] 3.12, [$\mathrm{H_c}\cdots$O] 2.21, (a) 13, (b) 6, $\mathrm{H_c}$ 157. Nonbonded [N···O] (Å) distances: 3.08, 3.48, and 3.07 to O(4), O(10), and O(16), respectively. Distance of N from mean plane of six O atoms, 1.59 Å. The B—N bond is inclined by 1° to the normal to this plane.

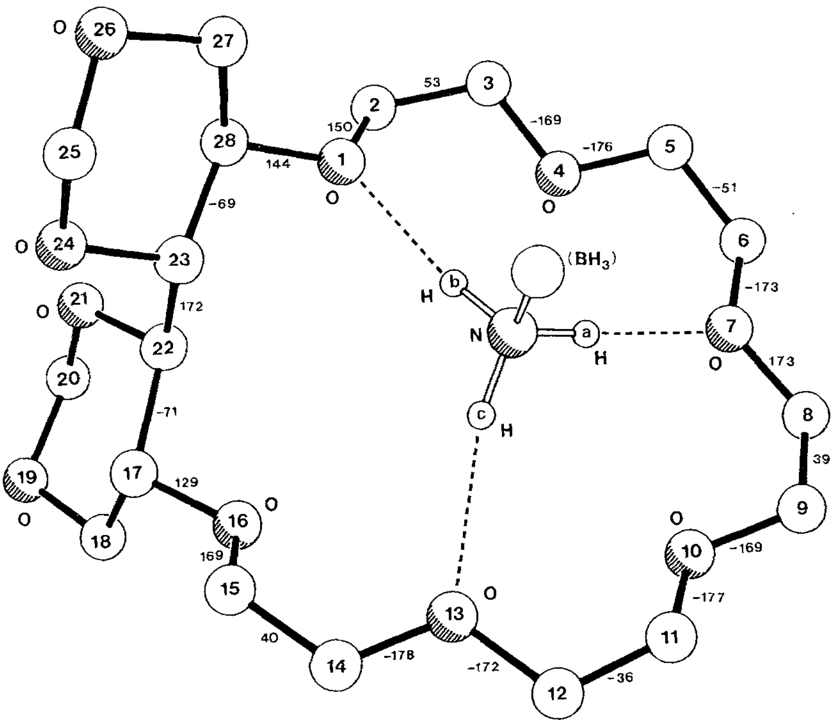


Fig. 4. The supramolecular structure of $BH_3NH_3 \cdot \mathbf{4}$. The torsional angles (°) around the macrocyclic ring are indicated beside the relevant C—C and C—O bonds. Hydrogen bond distances, $R[N \cdots O]$ (Å), $R[H \cdots O]$ (Å), angles (θ_N and θ_H°) between COC planes and (a) NO vectors and (b) HO vectors, N—H···O angles (°) at H atoms: $[N \cdots O(1)]$ 3.14, $[H_b \cdots O]$ 2.18, (a) 3, (b) 3, H_b 172; $[N \cdots O(7)]$ 3.05, $[H_a \cdots O]$ 2.09, (a) 3, (b) 3, H_a 176; $[N \cdots O(13)]$ 3.12, $[H_c \cdots O]$ 2.18, (a) 19, (b) 17, H_c 167. Nonbonded $[N \cdots O]$ (Å) distances: 3.27, 3.15, and 3.78 to O(4), O(10), and O(16), respectively. Distance of N from mean plane of six O atoms, 1.18 Å. The B—N bond is inclined by 4° to the normal to this plane.

to the pyranosidic ring oxygen atoms that are expected on the basis of the *exo*-anomeric effect [14].

In the absence of an elemental analysis, X-ray analysis of the BH_3NH_3 complex with the D-mannitolo-20-crown-6 derivative (**4**) established that it has 1 : 1 stoichiometry. The supramolecular structure and atomic numbering scheme are shown in Figure 4. Tables XIV and XV give the bond lengths and angles, respectively. The BH_3NH_3 guest molecule in $BH_3NH_3 \cdot \mathbf{4}$ occupies a quasi-perching position in its three-point binding mode to the 20-membered ring. The three hydrogen bonds are of similar length as reflected in the near normal relationship between the axis of the B-N bond and the plane of the six oxygen atoms in the macrocyclic polyether ring. The torsional angles associated with the macrocyclic rings in the host molecules of $BH_3NH_3 \cdot \mathbf{4}$, $Me_2CHNH_3 \cdot \mathbf{4} \cdot ClO_4$, and $PhCH_2NH_3 \cdot \mathbf{6} \cdot ClO_4$★ are given in Table XVI. As expected, there are close similarities between the conformations adopted by the two acetal rings in the mannitolo component of the macrocyclic ring. With two exceptions [the torsional angles about O(13)—C(14) and about C(14)—C(15)], the confor-

---

★ Compound **6** is the analogue of **4** derived from 1,3 : 4,6-di-*O*-benzylidene-D-mannitol.

Table XIV. Bond lengths (Å) in $\mathrm{BH_3NH_3}\cdot\mathbf{4}$

O(1)—C(2)	1.357(9)	O(1)—C(28)	1.423(7)
C(2)—C(3)	1.414(13)	C(3)—O(4)	1.376(10)
O(4)—C(5)	1.369(10)	C(5)—C(6)	1.410(16)
C(6)—O(7)	1.336(12)	O(7)—C(8)	1.322(12)
C(8)—C(9)	1.357(16)	C(9)—O(10)	1.372(12)
O(10)—C(11)	1.298(13)	C(11)—C(12)	1.354(15)
C(12)—O(13)	1.386(10)	O(13)—C(14)	1.349(10)
C(14)—C(15)	1.404(12)	C(15)—O(16)	1.359(10)
O(16)—C(17)	1.408(8)	C(17)—C(18)	1.534(10)
C(17)—C(22)	1.519(11)	C(18)—O(19)	1.388(9)
O(19)—C(20)	1.386(12)	C(20)—O(21)	1.413(8)
O(21)—C(22)	1.427(7)	C(22)—C(23)	1.486(8)
C(23)—O(24)	1.430(7)	C(23)—C(28)	1.500(10)
O(24)—C(25)	1.415(8)	C(25)—O(26)	1.388(12)
O(26)—C(27)	1.398(9)	C(27)—C(28)	1.531(9)
N—B	1.594(10)		

Table XV. Bond angles (deg.) in $\mathrm{BH_3NH_3}\cdot\mathbf{4}$

C(2)—O(1)—C(28)	118.5(6)	O(1)—C(2)—C(3)	113.3(7)
C(2)—C(3)—O(4)	115.9(7)	C(3)—O(4)—C(5)	115.4(6)
O(4)—C(5)—C(6)	115.1(8)	C(5)—C(6)—O(7)	119.6(11)
C(6)—O(7)—C(8)	121.4(9)	O(7)—C(8)—C(9)	121.3(10)
C(8)—C(9)—O(10)	119.8(9)	C(9)—O(10)—C(11)	123.7(8)
O(10)—C(11)—C(12)	126.8(10)	C(11)—C(12)—O(13)	116.9(9)
C(12)—O(13)—C(14)	118.3(6)	O(13)—C(14)—C(15)	119.0(8)
C(14)—C(15)—O(16)	117.3(8)	C(15)—O(16)—C(17)	118.8(6)
O(16)—C(17)—C(18)	109.9(6)	O(16)—C(17)—C(22)	107.7(5)
C(18)—C(17)—C(22)	109.0(6)	C(17)—C(18)—O(19)	112.3(6)
C(18)—O(19)—C(20)	108.8(6)	O(19)—C(20)—O(21)	111.5(7)
C(20)—O(21)—C(22)	111.6(5)	C(17)—C(22)—O(21)	110.6(5)
C(17)—C(22)—C(23)	114.4(5)	O(21)—C(22)—C(23)	109.1(5)
C(22)—C(23)—O(24)	108.1(5)	C(22)—C(23)—C(28)	114.6(5)
O(24)—C(23)—C(28)	110.0(5)	C(23)—O(24)—C(25)	109.6(5)
O(24)—C(25)—O(26)	112.5(6)	C(25)—O(26)—C(27)	109.2(6)
O(26)—C(27)—C(28)	111.2(6)	O(1)—C(28)—C(23)	107.0(5)
O(1)—C(28)—C(27)	109.3(5)	C(23)—C(28)—C(27)	109.9(6)

mations of the polyether components of $\mathrm{BH_3NH_3}\cdot\mathbf{4}$ and $\mathrm{PhCH_2NH_3}\cdot\mathbf{6}\cdot\mathrm{ClO_4}$ are comparable whilst differing from that of the polyether component of $\mathrm{Me_2CHNH_3}\cdot\mathbf{4}\cdot\mathrm{ClO_4}$. A notable feature of $\mathrm{BH_3NH_3}\cdot\mathbf{4}$, however, is a significant flattening of the polyether component as reflected in the magnitudes of the five C—C torsional angles. This may be a consequence of the difference in formal charge on the two types of guest species, i.e., $\mathrm{BH_3NH_3}$ is neutral and both $\mathrm{Me_2CHNH_3^+}$ and $\mathrm{PhCH_2NH_3^+}$ are cationic.

The X-ray analysis of $\mathrm{(BH_3NH_3)_2}\cdot\mathbf{5}$ revealed that the two $\mathrm{BH_3NH_3}$ guest molecules bind to opposite faces of the macrocycle in the 2 : 1 complex *via* a total of one bifurcated and four single [N—H···O] hydrogen bonds. In one instance [N(2)], all three $\mathrm{NH_3}$ hydrogen atoms are involved, whilst in the case of the other [N(1)], only two $\mathrm{NH_3}$ hydrogen atoms are utilised

Table XVI. A comparison of the torsional angles (°) in $BH_3NH_3 \cdot \mathbf{4}$, $Me_2CHNH_3 \cdot \mathbf{4} \cdot ClO_4$, and $PhCH_2NH_3 \cdot \mathbf{6} \cdot ClO_4$

Torsional angle	$BH_3NH_3 \cdot \mathbf{4}$	$Me_2CHNH_3 \cdot \mathbf{4} \cdot ClO_4$	$PhCH_2NH_3 \cdot \mathbf{6} \cdot ClO_4$
C(28)—O(1)—C(2)—C(3)	150	- 87	164
O(1)—C(2)—C(3)—O(4)	53	- 67	70
C(2)—C(3)—O(4)—C(5)	- 169	170	180
C(3)—O(4)—C(5)—C(6)	- 176	174	- 164
O(4)—C(5)—C(6)—O(7)	- 51	66	- 65
C(5)—C(6)—O(7)—C(8)	- 173	172	179
C(6)—O(7)—C(8)—C(9)	173	179	177
O(7)—C(8)—C(9)—O(10)	39	- 72	63
C(8)—C(9)—O(10)—C(11)	- 169	170	168
C(9)—O(10)—C(11)—C(12)	- 177	- 77	- 179
O(10)—C(11)—C(12)—O(13)	- 36	- 64	- 71
C(11)—C(12)—O(13)—C(14)	- 172	180	- 168
C(12)—O(13)—C(14)—C(15)	- 178	- 75	- 66
O(13)—C(14)—C(15)—O(16)	40	- 51	- 54
C(14)—C(15)—O(16)—C(17)	169	- 165	- 160
C(15)—O(16)—C(17)—C(22)	129	159	167
O(16)—C(17)—C(22)—C(23)	- 71	- 68	- 70
C(17)—C(22)—C(23)—C(28)	172	167	175
C(22)—C(23)—C(28)—O(1)	- 69	- 73	- 67
C(23)—C(28)—O(1)—C(2)	144	151	125

Table XVII. Bond lengths (Å) in $(BH_3NH_3)_2 \cdot \mathbf{5}$

O(1)—C(2)	1.412(4)	O(1)—C(30)	1.413(3)
C(2)—C(3)	1.505(5)	C(3)—O(4)	1.419(4)
O(4)—C(5)	1.411(4)	C(5)—C(6)	1.481(6)
C(6)—O(7)	1.417(4)	O(7)—C(8)	1.415(5)
C(8)—C(9)	1.521(5)	C(8)—C(12)	1.518(5)
C(9)—O(10)	1.427(5)	O(10)—C(11)	1.415(4)
C(11)—C(12)	1.529(6)	C(11)—C(15)	1.562(6)
C(12)—O(13)	1.419(5)	O(13)—C(14)	1.433(5)
C(14)—C(15)	1.517(6)	C(15)—O(16)	1.412(4)
O(16)—C(17)	1.420(5)	C(17)—C(18)	1.495(6)
C(18)—O(19)	1.417(5)	O(19)—C(20)	1.411(4)
C(20)—C(21)	1.457(5)	C(21)—O(22)	1.412(4)
O(22)—C(23)	1.407(4)	C(23)—C(24)	1.510(4)
C(23)—C(27)	1.522(4)	C(24)—O(25)	1.413(4)
O(25)—C(26)	1.446(3)	C(26)—C(27)	1.524(4)
C(26)—C(30)	1.538(4)	C(27)—O(28)	1.426(3)
O(28)—C(29)	1.435(4)	C(29)—C(30)	1.529(5)
N(1)—B(1)	1.614(5)	N(2)—B(2)	1.604(8)

in binding. The supramolecular structure and atomic numbering scheme are shown in Figure 5. Tables XVII and XVIII give the bond lengths and angles, respectively. In Table XIX, the torsional angles associated with the polyether chains in $(BH_3NH_3)_2 \cdot \mathbf{5}$ are compared with those adopted by the polyether chains in (*S*)-$PhMeCHNH_3 \cdot H_2O \cdot \mathbf{5} \cdot ClO_4$ [8]. In the adoption of face-to-face geometries, the gross conformations of the macrocycles in the host

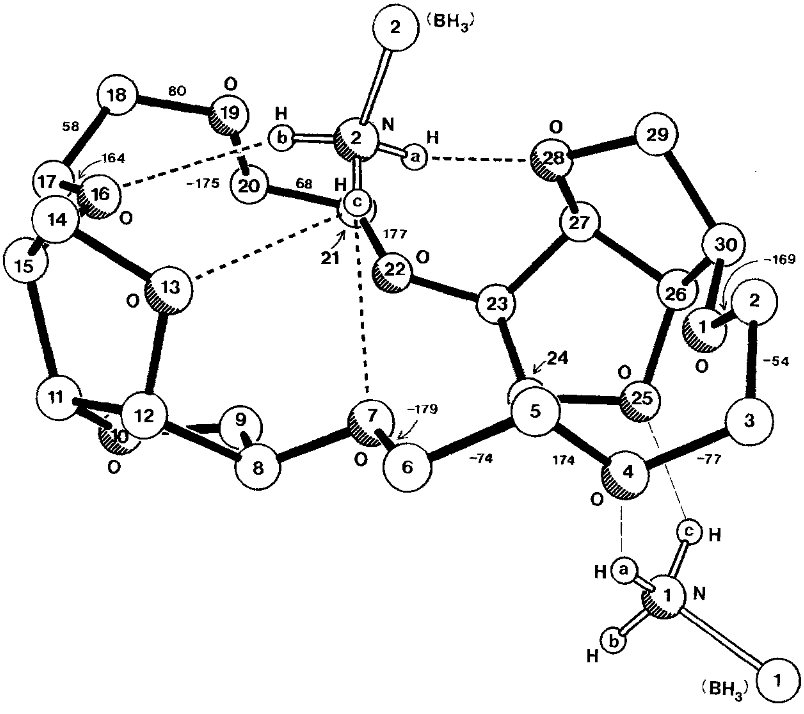


Fig. 5. The supramolecular structure of $(BH_3NH_3)_2 \cdot \mathbf{5}$. The torsional angles (°) associated with the polyether chains are indicated beside the relevant C—C and C—O bonds. Hydrogen bond distances, R[N···O] (Å), R[H···O] (Å), angles (θ_N and θ_H°) between COC planes and (a) NO vectors and (b) HO vectors, N—H···O angles (°) at H atoms: [N(1)···O(4)] 2.96, [H_a···O] 2.08, (a) 18, (b) 18, H_a 150; [N(1)···O(25)] 2.96, [H_c···O] 2.14, (a) 44, (b) 46, H_c 143; [N(2)···O(7)] 3.26, [H_c···O] 2.43, (a) 45, (b) 54, H_c 145, [N(2)···O(13)] 3.12, [H_c···O] 2.39, (a) 55, (b) 47, H_c 133; [N(2)···O(16)] 3.15, [H_b···O] 2.31, (a) 7, (b) 4, H_b 145; [N(2)···O(28)] 2.99, [H_a···O] 2.05, (a) 21, (b) 25, H_a 168. Nonbonded [N···O] (Å) distances less than 3.5 Å: [N(1)···O(1)] 3.12; [N(2)···O(19)] 3.42.

components of these two complexes are the same, *cf.* the face-to-back geometry of the uncomplexed host [8]. Moreover, the conformation of the polyether chain reflected by the torsional angles from O(16) to O(22) in $(BH_3NH_3)_2 \cdot \mathbf{5}$ match closely both in sign and magnitude those in one of the polyether chains in (*S*)-PhMeCHNH$_3$ · H$_2$O · **5** · ClO$_4$. It is interesting that the potential of **5** to bind two guest species within the same cavity created by the face-to-face geometry of the host observed in (*S*)-PhMeCHNH$_3$ · H$_2$O · **5** · ClO$_4$ is not realised in $(BH_3NH_3)_2 \cdot \mathbf{5}$. An associated consequence of the approach of one of the guest species to the opposite face of the host instead of being accommodated side by side with the other guest within the cavity is a directing of one [O(4)] of the polyether chain oxygen atoms to the largely hydrophobic exterior of the cavity, i.e., there is some destruction of the hydrophobic-hydrophilic balance observed in (*S*)-PhMeCHNH$_3$ · H$_2$O · **5** · ClO$_4$.

This investigation illustrates the fact that BH_3NH_3 is an excellent neutral guest species for forming crystalline complexes with a wide range of chiral crown ether hosts. This structural phenomenon is welcome particularly amongst the 18-crown-6 hosts (i.e., **1–3**) derived from asymmetric carbohydrate precursors which have previously resisted many attempts by us to

Table XVIII. Bond angles (deg.) in $(BH_3NH_3)_2 \cdot \mathbf{5}$

C(2)—O(1)—C(30)	114.7(2)	O(1)—C(2)—C(3)	108.5(3)
C(2)—C(3)—O(4)	113.3(3)	C(3)—O(4)—C(5)	114.2(3)
O(4)—C(5)—C(6)	109.0(3)	C(5)—C(6)—O(7)	109.5(3)
C(6)—O(7)—C(8)	113.2(2)	O(7)—C(8)—C(9)	109.7(3)
O(7)—C(8)—C(12)	115.0(3)	C(9)—C(8)—C(12)	103.6(3)
C(8)—C(9)—O(10)	103.9(3)	C(9)—O(10)—C(11)	108.1(3)
O(10)—C(11)—C(12)	107.9(3)	O(10)—C(11)—C(15)	114.8(3)
C(12)—C(11)—C(15)	103.9(3)	C(8)—C(12)—C(11)	103.5(3)
C(8)—C(12)—O(13)	110.7(3)	C(11)—C(12)—O(13)	106.5(3)
C(12)—O(13)—C(14)	105.9(3)	O(13)—C(14)—C(15)	103.7(3)
C(11)—C(15)—C(14)	101.2(3)	C(11)—C(15)—O(16)	112.8(3)
C(14)—C(15)—O(16)	107.0(3)	C(15)—O(16)—C(17)	114.6(3)
O(16)—C(17)—C(18)	107.4(4)	C(17)—C(18)—O(19)	115.8(4)
C(18)—O(19)—C(20)	113.6(3)	O(19)—C(20)—C(21)	110.8(3)
C(20)—C(21)—O(22)	110.7(3)	C(21)—O(22)—C(23)	113.5(2)
O(22)—C(23)—C(24)	111.4(2)	O(22)—C(23)—C(27)	116.1(2)
C(24)—C(23)—C(27)	100.5(3)	C(23)—C(24)—O(25)	103.8(2)
C(24)—O(25)—C(26)	107.1(2)	O(25)—C(26)—C(27)	105.8(2)
O(25)—C(26)—C(30)	113.7(2)	C(27)—C(26)—C(30)	105.2(2)
C(23)—C(27)—C(26)	104.2(2)	C(23)—C(27)—O(28)	110.0(2)
C(26)—C(27)—O(28)	106.4(2)	C(27)—O(28)—C(29)	105.8(2)
O(28)—C(29)—C(30)	105.0(3)	O(1)—C(30)—C(26)	108.4(2)
O(1)—C(30)—C(29)	114.3(2)	C(26)—C(30)—C(29)	102.2(3)

Table XIX. A comparison of the torsional angles (°) in $(BH_3NH_3)_2 \cdot \mathbf{5}$ and (S)-$PhMeCHNH_3 \cdot H_2O \cdot \mathbf{5} \cdot ClO_4$

Torsional angle	$(BH_3NH_3)_2 \cdot \mathbf{5}$	(S)-$PhMeCHNH_3 \cdot H_2O \cdot \mathbf{5} \cdot ClO_4$[a]
C(30)—O(1)—C(2)—C(3)	- 169	- 174
O(1)—C(2)—C(3)—O(4)	- 54	49
C(2)—C(3)—O(4)—C(5)	- 77	163
C(3)—O(4)—C(5)—C(6)	174	- 172
O(4)—C(5)—C(6)—O(7)	- 74	- 69
C(5)—C(6)—O(7)—C(8)	- 179	177
C(15)—O(16)—O(17)—C(18)	164	176
O(16)—C(17)—C(18)—O(19)	58	51
C(17)—C(18)—O(19)—C(20)	80	68
C(18)—O(19)—C(20)—C(21)	- 175	175
O(19)—C(20)—C(21)—O(22)	68	58
C(20)—C(21)—O(22)—C(23)	177	165

[a] Although the atomic numbering scheme employed previously [8] for (S)-$PhMeCHNH_3 \cdot H_2O \cdot \mathbf{5} \cdot ClO_4$ is different, this match of torsional angles represents the best relative one between the two complexes.

obtain good single crystals of complexes where the guest has been Group IA or IIA metal cations or alkylammonium ions★.

Finally, we examined the ability of the chiral crown ether derivatives **1**, **2**, and **5** to act as

---

★ However, note that in the case of methyl 4,6-*O*-benzylidene-2,3,-*O*-(1,2-bisethoxyethoxy)benzenediyl)-α-D-glucopyranoside, which contains a catechol unit, crystalline 1 : 1 complexes with KI and KSCN have been obtained [15,16] and subjected to successful X-ray analysis.

chiral auxiliaries in the enantioselective reduction of acetophenone by BH_3NH_3. The results in Table VII show that rather modest enantiomeric excesses (e.e.'s) of 5–13% were obtained compared with the e.e. of 26–28% achieved [9] when the chiral 2,3,11,12-tetraphenyl-18-crown-6 derivatives were employed as chiral auxiliaries. In chiral reagent complexes, such as $BH_3NH_3 \cdot \mathbf{1}$ and $BH_3NH_3 \cdot \mathbf{2}$ derived from asymmetric carbohydrate precursors, one problem is the presence of diastereoisomeric complexes in solution. Another problem, which is shared with $(BH_3NH_3)_2 \cdot \mathbf{5}$, is the design of suitable chiral crown ether hosts incorporating sugar residues in such a way that the chirality of the carbohydrate component expresses itself sterically and/or electronically towards the approach of a prochiral substrate. Clearly, a challenge exists to design and synthesise better chiral BH_3NH_3 complexes.

Acknowledgement

This research was supported by the Science and Engineering, and Agriculture and Food, Research Councils in the United Kingdom.

References

1. H. M. Colquhoun, G. Jones, J. M. Maud, J. F. Stoddart, and D. J. Williams: *J. Chem. Soc., Dalton Trans.* 63 (1984).
2. D. R. Alston, J. F. Stoddart, J. B. Wolstenholme, B. L. Allwood, and D. J. Williams: *Tetrahedron*, in press.
3. J. F. Stoddart: *Chem. Soc. Rev.* **8**, 85 (1979).
4. D. A. Laidler and J. F. Stoddart: *Carbohyd. Res.* **55**, C1 (1977); *J. Chem. Soc., Chem. Commun.* 481 (1977); A. C. Coxon, D. A. Laidler, R. B. Pettman, and J. F. Stoddart: *J. Am. Chem. Soc.* **100**, 8260 (1978).
5. R. B. Pettman and J. F. Stoddart: *Tetrahedron Lett.* 461 (1979).
6. D. A. Laidler, J. F. Stoddart, and J. B. Wolstenholme: *Tetrahedron Lett.* 465 (1979);
   L. Tõke, L. Fenichel, P. Bakó, and J. Szejtli: *Acta Chim. Acad. Sci. Hung.* **98**, 357 (1978);
   P. Bakó, L. Fenichel, L. Tõke, and M. Czugler: *Justus Liebigs Ann. Chem.* 1163 (1981);
   M. Czugler, *Cryst. Struct. Commun.* **10**, 511 (1981);
   P. Bakó, L. Fenichel, and L. Tõke, *Acta Chim. Acad. Sci. Hung.* **111**, 297 (1982);
   W. Hain, R. Lehnert, H. Rottele, and G. Schröder: *Tetrahedron Lett.* 625 (1978);
   W. Hain, R. Lehnert, B. Walz, and G. Schröder, *Justus Liebigs Ann. Chem.* 1046 (1984).
7. D. A. Laidler and J. F. Stoddart: *Tetrahedron Lett.* 453 (1979);
   S. E. Fuller, J. F. Stoddart, and D. J. Williams: *J. Chem. Soc., Chem. Commun.* 1093 (1982);
   S.E. Fuller, B. E. Mann, and J. F. Stoddart: *J. Chem. Soc., Chem. Commun.* 1096 (1982).
8. J. C. Metcalfe, J. F. Stoddart, G. Jones, T. H. Crawshaw, A. Quick, and D. J. Williams: *J. Chem. Soc., Chem. Commun.* 430 (1981);
   J. C. Metcalfe, J. F. Stoddart, G. Jones, T. H. Crawshaw, E. Gavuzzo, and D. J. Williams: *J. Chem. Soc., Chem. Commun.* 432 (1981).
9. B. L. Allwood, H. Shahriari-Zavareh, J. F. Stoddart, and D. J. Williams: *J. Chem. Soc., Chem. Commun.* 1461 (1984).
10. P. G. Jones: *Chem. Brit.* **17**, 222 (1981).
11. G. M. Sheldrick: SHELXTL, *An Integrated System for Solving, Refining, and Displaying Crystal Structures for Diffraction Data*, University of Gottingen, Federal Republic of Germany (1978). Revised version (1984).
12. J. F. Stoddart: *Proceedings of the Summer School on Bioenergetics and Thermodynamics: Model Systems* (21 May–1 June 1979, Tabiano, Italy, Ed. A. Braibanti), pp. 43–62. Reidel (1980); *Lectures in Heterocyclic Chemistry* (Vol. 5, Ed. R. N. Castle and S. W. Schneller), pp. S-47–S-60 (1980); *Progress in Macrocyclic Chemistry* (Vol. 2, Ed. R. M. Izatt and J. J. Christensen), pp. 173–250. Wiley-Interscience (1981);
    T. H. Crawshaw, D. A. Laidler, J. C. Metcalfe, R. B. Pettman, J. F. Stoddart, and J. B. Wolstenholme: *The Proceedings of the 26th OHOLO Biological Conference on Biomimetic Chemistry and Transition State Analogs as Approaches to Understanding Enzyme Catalysis* (Ed. B. S. Green, Y. Ashani, and D. Chipman) pp. 49–64. Elsevier (1982).

13. D. J. Cram and K. N. Trueblood: *Top. Curr. Chem.* **98**, 43 (1981);
K. N. Trueblood, C. B. Knobler, D. S. Lawrence, and R. V. Stevens: *J. Am. Chem. Soc.* **104**, 1355 (1982);
I. Goldberg: *Inclusion Compounds* (Structural Aspects of Inclusion Compounds Formed by Organic Host Lattices, Vol. 2, Ed. J. L. Atwood, J. E. D. Davies, and D. D. MacNicol), pp. 261–335, Academic Press (1984).
14. J. F. Stoddart, *Stereochemistry of Carbohydrates,* Wiley-Interscience (1971);
W. A. Szarek and D. Horton, *Anomeric Effect. Origin and Consequences*, ACS Symposium Series, 87 (1979);
P. Deslongchamps, *Stereoelectronic Effects in Organic Chemistry,* Pergamon Press (1983);
A. J. Kirby, *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen,* Springer-Verlag (1983).
15. K. Suwińska, M. Pietraszkiewicz, J. Lipkowski, J. Jurczak, G. D. Andreetti, and G. Bocelli: *J. Mol. Struct.* **75**, 221 (1981).
16. K. Suwińska and G. D. Andreetti: *J. Incl. Phenom.* **1**, 71 (1983/4).