

Crystal Structures of 1,3-Calix[4]-*bis*-crown-6·3CH₃CN and 1,3-Calix[4]-*bis*-(benzo-crown-6)·3 CH₃CN

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Abstract. The crystal structures of a new solvate of the ditopic receptor 1,3-calix[4]-*bis*-crown-6, *Bis*-C6, and of 1,3-calix[4]-*bis*-(benzo-crown-6), *Bis*-benzoC6, are reported. *Bis*-C6·3 CH₃CN (**1**) crystallizes in the monoclinic space group $P2_1/n$, $a = 14.388(3)$, $b = 26.947(8)$, $c = 14.707(4)$ Å, $\beta = 113.19(3)^\circ$, $V = 5241(5)$ Å³, $Z = 4$. Refinement led to a final conventional R value of 0.092 for 2723 reflections. The structure of (**1**) differs from the previously reported structure of *Bis*-C6·4 CH₃CN by the conformation of one crown ether chain. Two acetonitrile molecules are in the close neighbourhood of the crown ether cavities. *Bis*-benzoC6·3 CH₃CN (**2**) crystallizes in the monoclinic space group $P2_1/c$, $a = 10.391(4)$, $b = 17.264(11)$, $c = 30.426(9)$ Å, $\beta = 94.62(3)^\circ$, $V = 5440(7)$ Å³, $Z = 4$. Refinement led to a final conventional R value of 0.106 for 2965 reflections. Two acetonitrile molecules are located near the crown ether cavities, as in (**1**). One of the crown ether conformations is the same as in the binuclear caesium complex of *Bis*-benzoC6, supporting the hypothesis of a preorganization of this ligand towards the complexation of this ion; the second crown ether chain is partially disordered.

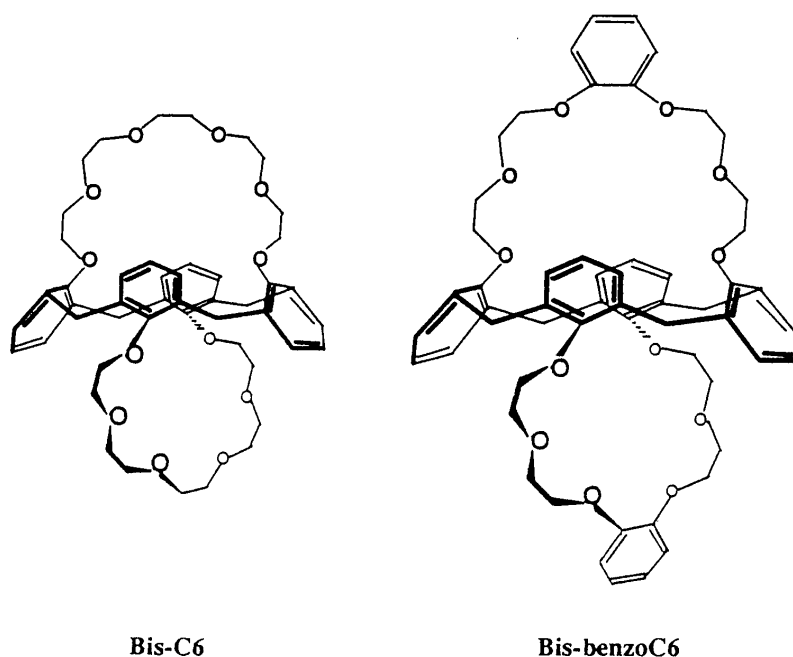
Key words: Bridged calix[4]arene, ditopic receptor, crystal structure.

Supplementary data related to this article (atomic coordinates, anisotropic displacement parameters, selected bond distances and angles and observed and calculated structure factors) are deposited with the British Library as Supplementary Publication No. SUP XXXX (42 pages).

1. Introduction

We have recently reported the crystal structures of some alkali metal ion complexes of the ditopic receptors 1,3-calix[4]-*bis*-crown-6, *Bis*-C6, and 1,3-calix[4]-*bis*-(benzo-crown-6), *Bis*-benzoC6, represented in Scheme 1 [1–4]. Both ligands have been shown to present a high complementarity with the caesium ion. Moreover, the crystal structure of the free ligand *Bis*-C6 provides evidence of a preorganization of this ligand for the complexation of caesium nitrate [2]. These properties could be

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Scheme 1. 1,3-Calix[4]-bis-crown-6 (*Bis-C6*) and 1,3-Calix[4]-bis-(benzo-crown-6) (*Bis-benzoC6*).

at the origin of the high complexing selectivity observed for caesium with respect to sodium ions, in a nitric medium, during extraction experiments [5, 6].

We report here the crystal structures of new acetonitrile solvates of the ligand *Bis-C6* (another one has previously been described in [2]) and of *Bis-benzoC6*.

2. Experimental

2.1. SYNTHESIS

Slow evaporation of acetonitrile/chloroform solutions (1 : 1) of *Bis-C6* or [*Bis-benzoC6*] afforded colourless single crystals of *Bis-C6*·3 CH₃CN (**1**) and [*Bis-benzoC6*·3 CH₃CN (**2**)] suitable for X-ray crystallography.

2.2. CRYSTAL DATA

The diffraction experiments were performed with an Enraf-Nonius CAD4 diffractometer using MoK_α radiation. The crystals (0.60 × 0.60 × 0.50 mm for **(1)**, 0.65 × 0.60 × 0.50 mm for **(2)**) were examined in glass capillaries. The lattice parameters were determined from the least-squares refinement of the setting angles of 25 reflections (8 < θ < 12°). The data were collected in the range 1 < θ < 20°, in the ω/2θ scan mode for **(1)** and ω/θ scan mode for **(2)**, at 295 K for **(1)** and

243 K for (2). The intensity decay was estimated from three standard reflections, measured every 60 min (−4.8% in 45 h for (1), −3.8% in 52 h for (2), linearly corrected). The data were corrected for Lorentz-polarization effects, but not for absorption.

Both structures were solved by direct methods with SHELXS-86 [7] and refined by full-matrix least-squares on F . Hydrogen atoms were located at their ideal positions (C—H 0.95 Å, B 6 Å²), disordered carbon atoms in (2), and constrained to ride on their parent carbon atom. Analytical scattering factors for neutral atoms [8] were corrected for the anomalous dispersion terms $\Delta f'$ and $\Delta f''$. All calculations have been performed on a Vax 4000-200 computer, with the Enraf-Nonius MoIEN system [9].

Bis-C6.3 CH₃CN (1). Formula C₅₄N₃O₁₂H₆₉, formula weight 952.16; monoclinic, space group $P2_1/n$, $a = 14.388(3)$, $b = 26.947(8)$, $c = 14.707(4)$ Å $\beta = 113.19(3)^\circ$, $V = 5241(5)$ Å³, $Z = 4$, $D_x = 1.21$, $\mu = 0.79$ cm^{−1}.

2723 observations were used with $I > 3\sigma(I)$, out of 4876 unique reflections measured. 382 parameters were refined (anisotropic thermal parameters for oxygen atoms and nitrogen and carbon atoms of the solvent molecules). The final R values were $R = 0.092$ and $R_w = 0.088$ (unit weights) and the maximum residual density 0.35 e Å^{−3}.

Bis-benzoC6.3 CH₃CN (2). Formula C₆₂N₃O₁₂H₆₉, formula weight 1048.25; monoclinic, space group $P2_1/c$, $a = 10.391(4)$, $b = 17.264(11)$, $c = 30.426(9)$ Å, $\beta = 94.62(3)^\circ$, $V = 5440(7)$ Å³, $Z = 4$, $D_x = 1.28$, $\mu = 0.83$ cm^{−1}.

2965 observations were used with $I > 3\sigma(I)$, out of 5024 unique reflections measured. 382 parameters were refined (anisotropic thermal parameters for oxygen atoms (except O(11) which has two positions, see below) and nitrogen atoms of two solvent molecules, the other solvent molecule [N(2)—C(59)—C(60)] was not stable on refinement and was fixed in the last refinement cycles). Two parts of crown 2 [corresponding to O(7)—O(12)] are disordered and atoms C(17), C(18), C(26), C(27) and O(11) have been modeled by two positions with equal occupation factors. The final R values were $R = 0.106$ and $R_w = 0.139$ ($w = 1/\sigma(F)^2$) and the maximum residual density 0.64 e Å^{−3}.

3. Discussion of Results

3.1. CRYSTAL STRUCTURES

ORTEPII [10] drawings of the molecular unit of (1) are represented in Figures 1 and 2 along with the stereodrawing of the packing of compound (1) represented in Figure 3. The molecule does not possess any symmetry element, in contrast to that of *Bis-C6.4* CH₃CN (3) described previously [2]. The most noticeable feature of this structure is the presence of two acetonitrile molecules located inside the cavity defined by the crown ether chains and the aromatic rings. The main axis

of the N(1)—C(49)—C(50) and N(2)—C(51)—C(52) acetonitrile molecules are nearly perpendicular to the mean plane of the crown ether chains, the CH₃ group being directed towards the inside and occupying a position very near to that of the caesium or potassium ions in the complexes already described [1–4]. In spite of some departure from the normal values, the interatomic distances in the acetonitrile molecules leave no doubt about the localisation of the nitrogen atom (N(1)—C(49) = 1.10(2), C(49)—C(50) = 1.41(2) Å in one molecule and N(2)—C(51) = 1.10(2), C(51)—C(52) = 1.39(2) Å in the other one, to be compared to the usual values of 1.136 and 1.470 Å [11]). The C(methyl)···O distances range from 3.27(1) to 3.54(1) (mean value 3.4(1)) Å for crown 1 [O(1) to O(6)] and from 3.43(1) to 3.75(1) (mean value 3.5(1)) Å for crown 2 [O(7) to O(12)] [in the caesium and potassium complexes, the mean alkali-metal–oxygen distances were 3.33(9) (mean value for five complexes) and 3.3(2) Å respectively]. The six oxygen atoms define a plane within ±0.41(1) and 0.22(1) Å for crowns 1 and 2, respectively, the terminal carbon atoms of the CH₃CN molecules being at 0.98(1) and 1.27(1) Å from these mean planes [the caesium and potassium ions were nearer to the corresponding mean planes, with distances of 0.7(2) (mean value for five complexes) and 0.831(5) Å respectively]. The shorter contacts between the acetonitrile molecules and the aromatic rings are 3.35(2) and 3.31(2) Å for the methyl carbon atoms C(50) and C(52) respectively: they are comparable to, or even shorter than, the values reported for the inclusion complexes of acetonitrile in *p*-*tert*-butylcalix[4]arene [12], its tetracarboxylate derivative [13] and in *p*-*tert*-butylcalix[6]arene [14], which may indicate some interactions between the acetonitrile molecules and the aromatic π -clouds; in all those cases, the nitrogen atom is *exo* with respect to the calixarene cavity, which is consistent with dipole–dipole interactions. A third acetonitrile molecule occupies an intermolecular void in the packing of **(1)**, as frequently observed in the structures already reported [2–4].

The two crown ether chains present different conformations, which can be described by the torsion angles reported in Table 1. In crown 1, the O—C—C—O angles present the sequence $g^+g^-g^+g^-g^+$ (in the notation of Fyles and Gandour [15]) identical to the one already encountered in **(3)** and in some caesium complexes [1, 2, 4] as well as in the potassium complex [3]. On the other hand, crown 2 possesses the unusual conformation $g^+g^-0g^+g^-$ (the angle defined by the central C—C bond is $-5(3)^\circ$, not significantly different from 0, hence the notation adopted): such a conformation is also observed in **(2)** (see below) and in the binuclear caesium complex of *Bis-benzoC6* [1], but in those cases, the zero angle is a necessary consequence of the presence of the phenyl substituent. In the present compound, the origin of this conformation does not obviously result from the interactions with the solvent molecules nor from crystal packing effects: it can be noted, however, that some short contacts (3.25 Å for the shorter one) exist between the nitrogen atom of the acetonitrile molecule included in crown 1 and some carbon atoms of crown 2 from another molecule. It must be noted that, although the more frequent conformation encountered so far is that observed

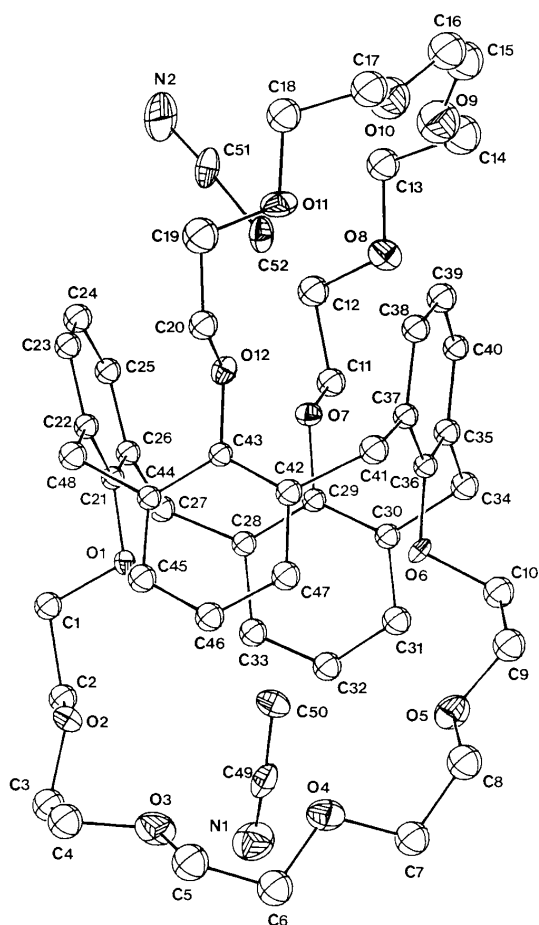


Figure 1. Molecular unit of *Bis-C6.3* CH₃CN (**1**); only the two solvent molecules nearer to the macrocycle are shown. Thermal ellipsoids drawn at 20% probability level.

for crown 1, other conformations have been found in caesium complexes with monodentate counterions [1, 2] and in the sodium complex [3] of *Bis-C6*. The crown ether chains thus appear to have some flexibility, in spite of their bonding to the calixarene 'platform'. As a result of these differences in solvent content and in conformations, the crystal packing of (**1**) is different from that of (**3**).

ORTEP [10] drawings of the molecular unit of (**2**) are represented in Figures 4 and 5. The molecule does not possess any symmetry element. As in the structure of (**1**) two acetonitrile molecules are located inside the cavity defined by the crown ether chains and the aromatic rings, with the same geometric features. The C(methyl)···O distances range from 3.38(1) to 3.59(1) (mean value 3.46(8)) Å for crown 1 [O(1) to O(6)] and from 3.05(2) to 4.25(2) (mean value 3.5(4)) Å for crown 2 [O(7) to O(12), including disordered O(11)]. The six oxygen atoms define a

Table I. Torsion angles ($^{\circ}$) of the crown ether chains in (1) and (2). The two values given for some bonds of crown 2 of (2) correspond to the disordered parts.

Crown 1		Crown 2	
<i>Compound (1)</i>			
C(22)—C(21)—O(1)—C(1)	93(1)	C(30)—C(29)—O(7)—C(11)	93(1)
C(26)—C(21)—O(1)—C(1)	-89(1)	C(28)—C(29)—O(7)—C(11)	-86(1)
C(21)—O(1)—C(1)—C(2)	176(1)	C(29)—O(7)—C(11)—C(12)	178(1)
O(1)—C(1)—C(2)—O(2)	74(1)	O(7)—C(11)—C(12)—O(8)	69(1)
C(1)—C(2)—O(2)—C(3)	161(1)	C(11)—C(12)—O(8)—C(13)	171(1)
C(2)—O(2)—C(3)—C(4)	169(1)	C(12)—O(8)—C(13)—C(14)	-178(1)
O(2)—C(3)—C(4)—O(3)	-77(1)	O(8)—C(13)—C(14)—O(9)	-77(1)
C(3)—C(4)—O(3)—C(5)	-168(1)	C(13)—C(14)—O(9)—C(15)	-143(2)
C(4)—O(3)—C(5)—C(6)	166(1)	C(14)—O(9)—C(15)—C(16)	175(2)
O(3)—C(5)—C(6)—O(4)	69(1)	O(9)—C(15)—C(16)—O(10)	-5(3)
C(5)—C(6)—O(4)—C(7)	-170(1)	C(15)—C(16)—O(10)—C(17)	180(2)
C(6)—O(4)—C(7)—C(8)	-171(1)	C(16)—O(10)—C(17)—C(18)	152(2)
O(4)—C(7)—C(8)—O(5)	-79(1)	O(10)—C(17)—C(18)—O(11)	72(2)
C(7)—C(8)—O(5)—C(9)	-176(1)	C(17)—C(18)—O(11)—C(19)	-174(1)
C(8)—O(5)—C(9)—C(10)	-177(1)	C(18)—O(11)—C(19)—C(20)	-168(1)
O(5)—C(9)—C(10)—O(6)	67(1)	O(11)—C(19)—C(20)—C(12)	-73(1)
C(9)—C(10)—O(6)—C(36)	128(1)	C(19)—C(20)—O(12)—C(43)	-178(1)
C(10)—O(6)—C(36)—C(35)	70(1)	C(20)—O(12)—C(43)—C(44)	92(1)
C(10)—O(6)—C(36)—C(37)	-111(1)	C(20)—O(12)—C(43)—C(42)	-89(1)
<i>Compound (2)</i>			
C(30)—C(29)—O(1)—C(1)	91(1)	C(54)—C(55)—O(7)—C(15)	88(1)
C(34)—C(29)—O(1)—C(1)	-91(1)	C(50)—C(55)—O(7)—C(15)	-89(1)
C(29)—O(1)—C(1)—C(2)	-179(1)	C(55)—O(7)—C(15)—C(16)	173(1)
O(1)—C(1)—C(2)—O(2)	-71(1)	O(7)—C(15)—C(16)—O(8)	73(1)
C(1)—C(2)—O(2)—C(3)	-173(1)	C(15)—C(16)—O(8)—C(17)	179(1)/-113(1)
C(2)—O(2)—C(3)—C(4)	-179(1)	C(16)—O(8)—C(17)—C(18)	-179(2)/-164(1)
O(2)—C(3)—C(4)—O(3)	82(1)	O(8)—C(17)—C(18)—O(9)	-86(2)/-161(2)
C(3)—C(4)—O(3)—C(5)	175(1)	C(17)—C(18)—O(9)—C(19)	-166(1)/-173(2)
C(4)—O(3)—C(5)—C(6)	-180(1)	C(18)—O(9)—C(19)—C(20)	169(1)/173(2)
O(3)—C(5)—C(6)—O(4)	1(1)	O(9)—C(19)—C(20)—O(10)	1(2)
C(5)—C(6)—O(4)—C(11)	177(1)	C(19)—C(20)—O(10)—C(25)	-177(1)
C(6)—O(4)—C(11)—C(12)	180(1)	C(20)—O(10)—C(25)—C(26)	176(1)/175(1)
O(4)—C(11)—C(12)—O(5)	-81(1)	O(10)—C(25)—C(26)—O(11)	62(2)171(1)
C(11)—C(12)—O(5)—C(13)	-177(1)	C(25)—C(26)—O(11)—C(27)	-78(2)1171(2)
C(12)—O(5)—C(13)—C(14)	173(1)	C(26)—O(11)—C(27)—C(28)	-153(2)/-178(1)
O(5)—C(13)—C(14)—O(6)	75(1)	O(11)—C(27)—C(28)—O(12)	-172(1)-88(2)
C(13)—C(14)—O(6)—C(48)	170(1)	C(27)—C(28)—O(12)—C(41)	177(1)/-155(1)
C(14)—O(6)—C(48)—C(43)	91(1)	C(28)—O(12)—C(41)—C(36)	-89(1)
C(14)—O(6)—C(48)—C(47)	-90(1)	C(28)—O(12)—C(41)—C(40)	91(1)

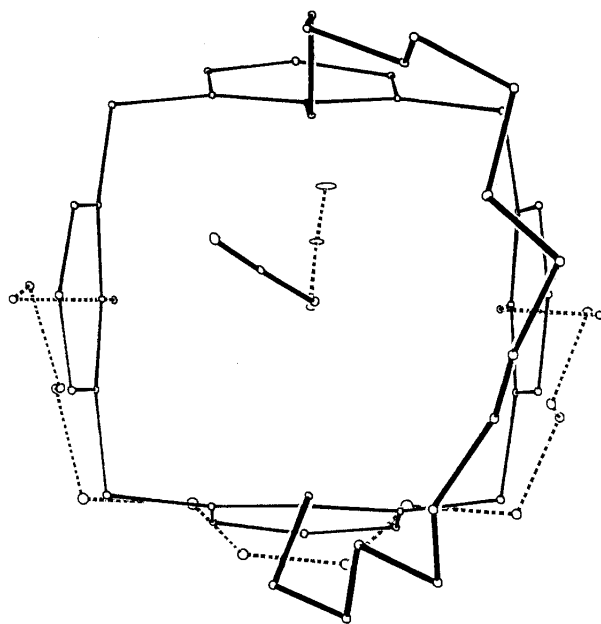


Figure 2. Molecular unit of *Bis-C6*·3 CH₃CN (**1**); view orthogonal to that of Figure 1. Upper crown and solvent molecule in bold lines, lower ones in dashed lines. For clarity, atoms are represented as small spheres of arbitrary radii.

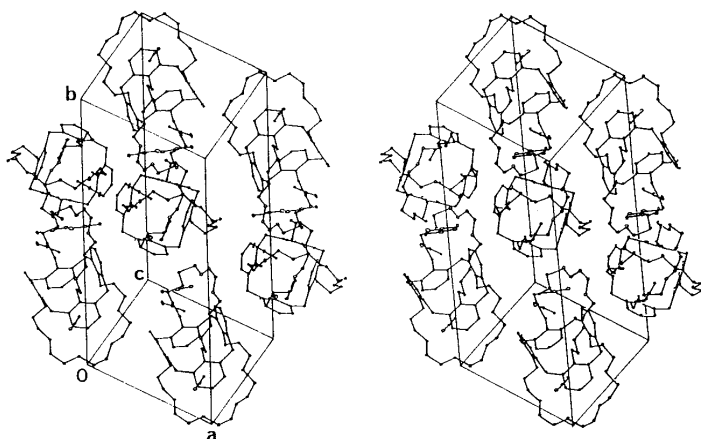


Figure 3. Stereodrawing of the packing of compound (**1**).

plane within $\pm 0.198(7)$ and $\pm 0.28(1)$ Å for crowns 1 and 2, respectively (including disorder for crown 2), the terminal carbon atoms of the CH₃CN molecules being at 1.07(1) and 0.70(1) Å from these mean planes [in the binuclear caesium complex of *Bis-benzoC6*, the ions were at distances of 0.675(2) and 0.697(1) Å from the corresponding planes]. The shorter contacts between the acetonitrile molecules and

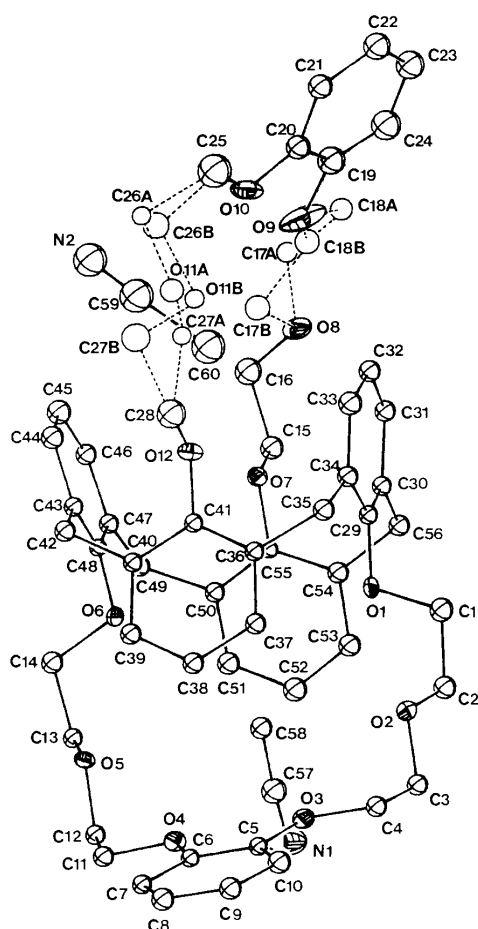


Figure 4. Molecular unit of *Bis-benzoC6-3* CH₃CN (**2**); only the two solvent molecules nearer to the macrocycle are shown. Disordered parts in dashed lines. Thermal ellipsoids drawn at 20% probability level.

the aromatic rings are 3.38(1) and 3.19(1) Å for the methyl carbon atoms C(58) and C(60) respectively. A third acetonitrile molecule occupies an intermolecular void in the packing, as in the structure of (**1**).

Crown 1 [corresponding to O(1)—O(6)] presents the $g^-g^+0g^-g^+$ conformation. The disorder in two parts of crown 2 prevents the assignment of a unique conformation; however, some *anti-gauche* permutations can be noticed. The $g^+g^-0g^+g^-$ conformation was also observed in the binuclear caesium complex of *Bis-benzoC6* [1]. The same trend has been found for *Bis-C6*: the chain conformation is not modified by the complexation of one or two caesium ions with bidentate nitrate counterions [2], or by the complexation of potassium ions [3], but it

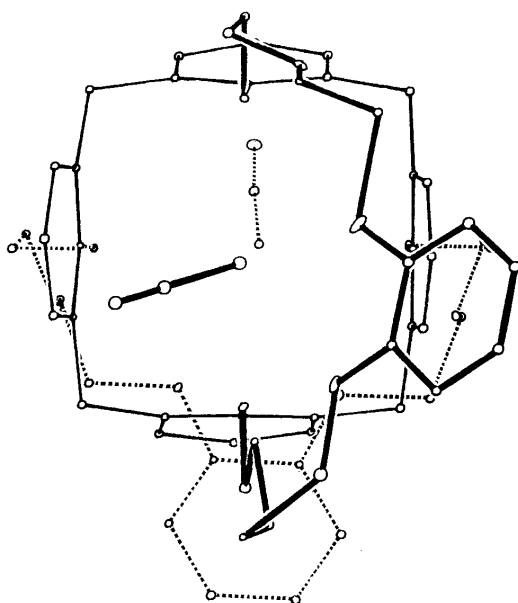


Figure 5. Molecular unit of *Bis-benzoC6-3* CH₃CN (**2**), view orthogonal to that of Figure 3. Upper crown and solvent molecule in bold lines, lower ones in dashed lines. For clarity, atoms are represented as small spheres of arbitrary radii. Only one of the disordered positions is represented.

may be modified when the complexed ion is too small and a good complementarity not achieved, as is the case for sodium ions [3].

In a recent publication Arnaud-Neu *et al.* [16] have studied the binding properties of calix[4]-bis-crowns towards alkali cations. In particular for *Bis-C6* they have observed a discrepancy between the entropic terms depending on the solvent in which the complexation was carried out: they noticed that $T\Delta S_c$ became more positive for the potassium complexation in acetonitrile as compared to methanol. This effect was attributed to: (i) a larger desolvation of the cation upon complexation in acetonitrile; and (ii) to the ligand being more solvated in acetonitrile than in methanol. The results presented in this paper are in agreement with assumption (ii).

Work is now directed towards evaluating the chemical complexation process through molecular mechanic calculations [2,3] taking these new results into account.

References

1. P. Thuéry, M. Nierlich, C. Bressot, V. Lamare, J.F. Dozol, Z. Asfari and J. Vicens: *J. Incl. Phenom.* **23**, 305 (1996).
2. Z. Asfari, C. Naumann, M. Nierlich, P. Thuéry, C. Bressot, V. Lamare, J. F. Dozol and J. Vicens: *New J. Chem.* **20**, 1183 (1996).

3. P. Thuéry, M. Nierlich, V. Lamare, J.F. Dozol, Z. Asfari and J. Vicens: submitted to *Supramol. Chem.*
4. P. Thuéry, M. Nierlich, V. Lamare, J.F. Dozol, Z. Asfari and J. Vicens: *Acta Crystallogr.*, **C52**, 2729 (1996).
5. Z. Asfari, C. Bressot, J. Vicens, C. Hill, J.F. Dozol, H. Rouquette, S. Eymard, V. Lamare and B. Tournois: *Anal. Chem.* **67**, 3133 (1995).
6. Z. Asfari, S. Wenger and J. Vicens: *J. Incl. Phenom.* **19**, 137 (1994); C. Hill, J.F. Dozol, V. Lamare, H. Rouquette, S. Eymard, B. Tournois, J. Vicens, Z. Asfari, C. Bressot, R. Ungaro and A. Casnati: *J. Incl. Phenom.* **19**, 399 (1994).
7. G.M. Sheldrick: SHELXS-86: *Program for the Solution of Crystal Structures*, University of Göttingen, Germany (1985).
8. *International Tables for X-ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, England (1974). Present distributor: Academic Publishers, Dordrecht, The Netherlands.
9. MoIEN: *An Interactive Structure Solution Procedure*, Enraf-Nonius, Delft, The Netherlands (1990).
10. C.K. Johnson: ORTEPII, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, USA (1976).
11. *International Tables for Crystallography*, Vol. C: The International Union of Crystallography, Kluwer Academic Publishers, Dordrecht, The Netherlands (1995), pp. 694, 698.
12. W. Xu, R.J. Puddephatt, L. Manoylovic-Muir, K.W. Muir and C.S. Frampton: *J. Incl. Phenom.* **19**, 277 (1994).
13. M.A. McKervey, E.M. Seward, G. Ferguson and B.L. Ruhl: *J. Org. Chem.* **51**, 3581 (1986).
14. P. Thuéry, N. Keller, M. Lance, J.D. Vigner and M. Nierlich: *J. Incl. Phenom.* **20**, 373 (1995).
15. T.M. Fyles and R.D. Gandour: *J. Incl. Phenom.* **12**, 313 (1992).
16. F. Arnaud-Neu, Z. Asfari, B. Souley and J. Vicens: *New J. Chem.* **20**, 453 (1996).