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Structure of host-guest molecular complexes of dicyclohexano-18-crown-6 cis-isomers with 4-aminobenzoic acid

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The structure of 1:2 molecular complexes (*I* and *II*) of *cis-syn-cis* and *cis-anti-cis* isomers of dicyclohexano-18-crown-6 with 4-aminobenzoic acid have been defined by X-ray diffraction techniques. The experimental data for *I* has been obtained at two temperatures (293 and 203 K), while for *II* at a room temperature (293 K). Crystals of *I* are orthorhombic, space group $P2_12_12$, a = 17.923(2), b = 20.228(8), c = 9.455(8) Å (at 203 K), Z = 4. Crystals of complex *II* are monoclinic, space group $P2_1/c$, a = 12.611(4), b = 12.980(3), c = 10.940(6) Å, $\beta = 75.22(3)°$, Z = 2. The complexes are stabilized by host-guest NH...O hydrogen bonds. OH...O hydrogen bonds uniting the complexes in ribbons (*I*) and chains (*II*) have been found between the carboxylic groups of the guest molecules.

INTRODUCTION

In a number of papers[1–5] it has been shown that the stereomers of dicyclohexano-18-crown-6 (DCH-6) form stable host-guest complexes with neutral organic molecules in a different way. Many small molecules interact with both of the *cis*-isomers of DCH-6 (*cis-syn-cis*, isomer A, DCH-6^A, and *cis-anti-cis*, isomer B, DCH-6^B). Table 1 presents the list of these complexes. Their composition and structure were confirmed by X-ray crystallography. The compounds are stabilized by NH...O and CH...O hydrogen bonds. At the same time, only DCH-6^B forms stable associates with 2,4-dinitroaniline,[1] 4-aminobenzenesulphamide,[2] maleic anhydride,[3] 2-methylbenzenesulphamide,[4] 4-bromobenzenesulphamide,[5] and 4-nitrobenzenesulphamide.[5]

The geometry of the NH_3^+-group (complexes *III* and *IV* where the guest is present in the form of zwitterion, $NH_3^+SO_3^-$) corresponds to the symmetry of the complexed 18-membered cavity and stipulates the participation of every second oxygen atom of the macrocycle in NH...O hydrogen bonds. As a rule, both hydrogen atoms of the NH_2-proton donor centre (NH_2 and SO_2NH_2 groups) take part in complex formation. Two oxygen atoms separated by the oxyethylene fragment participate in the host-guest interactions. In complex *V* the guest NH_2 group forms hydrogen bonds with the neighbouring oxygen atoms of the crown ether, and this results in an unusual host conformation. The participation of only one proton of the NH_2 group in complexation was found in complex *X* and in the complexes of 18-crown-6[12] and DCH-6^B[13] with 6-chloro-7-sulphamido-3,4-dihydro-1,2,4-benzothiadiazine-1,1-dioxide (hypothiazide).

In the case of DCH-6^A host-guest interactions usually occur at the face of the ring shielded by the cyclohexano-substituents, but complex *III* is an exception. DCH-6^B coordinates the same guest molecules at the equivalent faces of the ring. The usual host:guest stoichiometry of the complexes is 1:1 for DCH-6^A and 1:2 for DCH-6^B. Complexes *VII* and *X* are the exceptions to this rule. Although the formal ratio in complex *VII* is 1:2, its actual composition is [DCH-6^B.sg].sg,* where the second guest molecule might be considered as a solvate. The unusual host-guest stoichiometry in *X* is stipulated by the 1,4-position of

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* sg: 4-aminobenzenesulphamidine (sulphaguanidine).

Table 1 Host-guest complexes of DCH-6 *cis*-isomers

		DCH-6^A			*DCH-6^B*	
No.	*Guest*	*H:G*	*Ref.*	*No.*	*H:G*	*Ref.*
I.	4-$NH_2PhCOOH$	1:2	[dc]	*II.*	1:2	[dc]
III.	NH_2SO_2OH	1:1	[6]	*IV.*	1:1	[6]
V.	4-$CH_3PhSO_2NH_2$	1:1	[7]	*VI.*	1:2	[7]
VII.	4-$NH_2PhSO_2NC(NH_2)_2$	1:2	[8]	*VIII.*	1:2	[8]
IX.	3,5-Cl_2-4-NH_2-$PhSO_2NH_2$	1:1	[9]	*X.*	1:1	[10]
XI.	$CNCH_2CN$	1:1	[11]	*XII.*	1:2	[11]

Table 2 Crystal and experimental data for complexes *I* and *II*

Complex	*I*		*II*
Formula	$C_{34}H_{50}N_2O_{10}$		$C_{34}H_{50}N_2O_{10}$
M.W.	646.8		646.8
Sp. group	$P2_12_12$		$P2_1/c$
a, Å	18.240(1)	17.923(2)	12.611(4)
b, Å	20.169(5)	20.228(8)	12.980(3)
c, Å	9.556(6)	9.455(8)	10.940(6)
β, °	90	90	75.22(3)
V, Å^3	3515.5	3427.9	1731.5
Z	4	4	2
D_{calc}, gcm^{-3}	1.222	1.253	1.243
Specimen dimensions (mm)	0.3 × 0.4 × 0.4		0.25 × 0.50 × 0.50
μ (cm^{-1})	7.005	7.184	0.98
T, K	293	203	293
Scan speed range (°/min)	1–20		8
Radiation	CuK_α	CuK_α	MoK_α
Scan mode		θ/2θ	ω
No. refl.	1344	3997	1820
Condition for obs.		$I > 3\sigma$	$I > 3\sigma$
No. ref. refl.		3011	1166
R	0.11	0.059	0.059
R_w		0.053	0.044
w		4.8345/σ^2(F)	2.7659/σ^2(F)

the H-donor groups in the guest molecule and its entering the complex as a bridge.

Compexes of 4-aminobenzoic acid are of particular interest because physiological importance of the guest as a simple receptor model.[14] It forms a 1:2 crystalline complex with 18-crown-6.[15] However, only a preliminary X-ray investigation of this compound has been done (space group $P2_1/n$, $Z = 3$). Here, we present the results of the X-ray study of the molecular complexes of DCH-6 *cis*-isomers with 4-aminobenzoic acid. The coordination peculiarities and crown ether conformations are discussed.

EXPERIMENTAL

Synthesis of the complexes *I* and *II*

0.002 mol (0.744 g) of the corresponding DCH-6 isomer and 0.002 mol (0.548 g) of 4-aminobenzoic acid were dissolved in 8 mL of isopropanol at 82 °C. Crystals suitable for X-ray analysis were obtained by the recrystallization from propanol. The complexes are soluble in methanol, ethanol, acetone, water and are destroyed by hypochloric acid. Crystals of complex *I* are colourless, transparent, mp 159–161 °C. IR, KBr, ν cm^{-1}: 3480, 3390 (N-H), 2970–2850 (C-H), 1590 (C=O), 1095 (C-O-C). NMR, CF_3COOH, σ: 0.83–1.70 m and 3.40 s (36H, CH, CH_2, CH_2O-DCH-6), 7.20–7.87 c (8H, Ph). Anal. Found: N, 4.22. Calcd: N, 4.33. Crystals of complex *II* are colourless, transparent, mp 156–158 °C. IR, KBr ν, cm^{-1}: 3460, 3375 (N-H), 2970–2850 (C-H), 1630, 1590 (C=O), 1095 (C-O-C). NMR, CF_3COOH, σ: 0.83–1.60 m and 3.37 s (36H, CH, CH_2, CH_2O-DCH-6), 7.27–7.90 c (8H, Ph). Anal. Found: N, 4.41. Calcd: N, 4.33.

X-ray data collection and structure solution

Complex *I*. The experimental material for complex *I* has been obtained at a room (293 K) and a low temperature (203 K). A summary of the data collection parameters for complex *I* (at the both temperatures) and for complex *II* is given in Table 2, and atomic fractional coordinates for *I* (203 K) and *II* are given in Tables 3 and 4 respectively. Experimental data obtained for *I* at room temperature could not provide adequate least-squares refinement. Therefore the X-ray experiment for complex *I* was repeated at low temperature. The low temperature data refinement for *I* is used in the discussion below. Preliminary examination and data collection for *I* were performed with CuK_α-radiation on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite crystal incident beam monochromator. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using 25 reflections in the range of $20 < \theta < 30°$. As a check on crystal and electric stability, three reflections were measured every 60 min. The initial structural model was obtained by direct methods using the CRYSRULLER system of programs.[16] The structure model was refined by

Table 3 Atomic fractional coordinates ($\times 10^4$) and B_{eq} ($\times 10^2$) for complex *I*

Atom	*x/a*	*y/b*	*z/c*	B_{eq}
O(1G1)	9008(1)	4895(1)	2651(3)	373(8)
O(2G1)	9978(2)	4205(1)	2635(3)	384(8)
N(1G1)	7296(2)	2177(2)	2348(5)	516(12)
C(1G1)	9300(2)	4307(2)	3632(4)	309(11)
C(2G1)	8765(2)	3758(2)	2591(4)	297(10)
C(3G1)	8000(2)	3867(2)	2525(5)	322(11)
C(4G1)	7503(2)	3351(2)	2468(5)	339(11)
C(5G1)	7767(2)	2700(2)	2458(5)	340(10)
C(6G1)	8529(2)	2583(2)	2555(5)	341(11)
C(7G1)	9019(2)	3105(2)	2616(5)	326(11)
O(1G2)	9539(2)	4477(2)	−3753(3)	459(9)
O(2G2)	9452(2)	4572(2)	−1405(3)	482(10)
N(1G2)	7297(4)	2126(3)	−2330(6)	661(20)
C(1G2)	9267(2)	4295(2)	−2569(5)	361(11)
C(2G2)	8743(2)	3734(2)	−2527(5)	321(10)
C(3G2)	8564(3)	3377(3)	−3744(4)	384(13)
C(4G2)	8089(3)	2850(3)	−3698(5)	454(15)
C(5G2)	7753(3)	2662(2)	−2421(5)	429(13)
C(6G2)	7924(3)	3028(3)	−1213(5)	504(16)
C(7G2)	8399(3)	3551(2)	−1243(5)	398(13)
O(1)	5899(2)	2235(2)	53(3)	386(8)
C(2)	5598(3)	1612(3)	362(6)	384(14)
C(3)	6094(3)	1076(2)	−143(5)	364(14)
O(4)	6768(2)	1075(2)	641(4)	453(9)
C(5)	7241(3)	533(3)	335(6)	468(16)
C(6)	7972(3)	641(3)	1063(6)	440(16)
O(7)	7911(2)	762(1)	2575(4)	392(8)
C(8)	7598(3)	237(2)	3393(6)	370(12)
C(9)	7522(3)	503(3)	4923(6)	388(14)
O(10)	7094(2)	1096(2)	5020(4)	423(9)
C(11)	6335(3)	1043(3)	4578(6)	442(15)
C(12)	5904(3)	1612(3)	5139(6)	513(18)
O(13)	6227(2)	2206(2)	4634(4)	663(12)
C(14)	5871(4)	2821(4)	4940(8)	752(25)
C(15)	5250(5)	2936(4)	3973(7)	741(25)
O(16)	5572(2)	2989(1)	2525(4)	442(9)
C(17)	4998(2)	2866(2)	1524(5)	381(13)
C(18)	5371(3)	2768(2)	65(6)	375(12)
C(19)	5759(4)	3383(3)	−422(6)	460(16)
C(20)	5208(4)	3968(3)	−517(7)	528(19)
C(21)	4830(4)	4073(3)	919(7)	481(17)
C(22)	4453(3)	3442(3)	1407(8)	501(16)
C(23)	8272(4)	644(4)	5581(8)	559(20)
C(24)	8782(4)	34(4)	5557(8)	646(22)
C(25)	8858(3)	−225(3)	4020(7)	527(17)
C(26)	8090(4)	−370(3)	3421(8)	516(17)

full-matrix least squares techniques, with anisotropic thermal parameters for non-H atoms and isotropic ones for H atoms. the geometrical calculations were performed by PARST.[17] The drawings were made by PLUTO in the CRYSRULLER package.[16]

Complex *II*. The crystal data for complex *II* were collected on a RED-4 diffractometer by the ω scan technique using MoK_α-radiation. The intensities were corrected for background and Lp effects but not for absorption. The structure was solved by direct methods using MULTAN.[18] Hydrogen atoms of the amino- and carboxylic groups were located on the difference Fourier map, the positions of all the other H-atoms were calculated (C-H = 1.05 Å, H-C-H 109°) and their positional parameters were not varied.

RESULTS AND DISCUSSION

The guest molecules in complexes *I* and *II* are characterized by two H-donor centres located in the 1,4-positions of the aromatic ring: the NH_2 and COOH groups. The previous investigations[19,20] show that the guest NH_2 group topologically matches the 18-membered cycle and easily interacts with it. In the molecular complexes described below only the amino-group of the guest molecule takes part in host-guest interactions, forming N-H…O_{cr} hydrogen bonds. At the same time, the COOH group is capable of creating systems of intramolecular and intermolecular H-bonds,[19,20] including those which unite molecules in dimers of the following type:

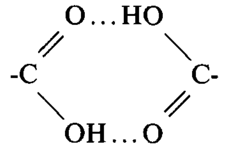


Table 4 Atomic fractional coordinates ($\times 10^4$) and B_{eq} ($\times 10^2$) for complex *II*

Atom	*x/a*	*y/b*	*z/c*	B_{eq}
O(1G1)	1312(3)	301(3)	4328(4)	550(21)
O(2G1)	242(3)	838(3)	6156(4)	570(20)
N(1G1)	4473(3)	3571(4)	5867(5)	542(26)
C(1G1)	1163(4)	850(5)	5310(5)	424(29)
C(2G1)	2019(4)	1531(5)	5499(5)	335(26)
C(3G1)	3048(4)	1471(4)	4658(5)	334(29)
C(4G1)	3868(4)	2157(4)	4788(5)	339(30)
C(5G1)	3663(4)	2909(5)	5746(6)	423(33)
C(6G1)	2620(4)	2914(5)	6593(5)	401(30)
C(7G1)	1821(4)	2229(5)	6471(5)	424(30)
O(1)	6946(3)	4164(3)	5778(4)	440(19)
C(2)	6961(5)	4907(5)	6732(6)	553(39)
C(3)	6013(4)	4713(5)	7901(6)	514(32)
O(4)	4984(3)	5029(3)	7682(4)	452(19)
C(5)	4820(5)	6116(4)	7831(6)	511(38)
C(6)	6343(5)	3650(5)	2246(5)	476(36)
O(7)	6424(3)	3856(3)	3489(3)	503(20)
C(8)	7511(4)	3644(5)	3621(5)	462(29)
C(9)	7743(4)	4368(5)	4593(6)	462(31)
C(10)	8912(4)	4188(5)	4711(6)	608(30)
C(11)	9091(5)	3096(6)	4998(7)	799(35)
C(12)	8816(5)	2329(6)	4046(6)	663(37)
C(13)	7643(4)	2509(5)	3940(6)	517(33)

Complex [DCH-6^A.2(4-NH_2PhCOOH)] (complex *I*) Figure 1 shows the structure of complex *I*. The arrangement is unusual by its 1:2 stoichiometry. The nature of the *H*:*G1* and *H*:*G2* (*H* is the host, *G1* and *G2* are symmetrically independent guest molecules) interactions is essentially different. All short NH...O and OH...O distances are given in Table 5. *G1* is connected by the H-bonds with the face of the crown ether shielded by the bulky cyclohexano groups. Four N...O contacts (in the range 2.889–3.315 Å) were found for the guest NH_2 group. Two of them, with O(1) and O(7), are in accordance with the classic scheme of host-guest interactions in systems with crown ethers. The macrocycle oxygen atoms separated by the oxyethylene fragment take part in these interactions. N(1G1)...O_{cr} contacts (distances, 2.899 and 2.910 Å) with two other oxygen atoms, O(4) and O(13), are a little shorter than those mentioned above (Table 5). Nitrogen atom N(1G1) is at a distance of 1.58 Å from the mean plane of the crown ether heteroatoms. The reciprocal *H*:*G1* arrangement is characterized by the dihedral angle between the planes defined by the heteroatoms of the crown ether and the aromatic fragment of the guest and is 81.6°. The arrangement of this moiety in complex *I* is similar to other 1:1 DCH-6^A associates with organic molecules.[7,11]

The close packing is due to the presence of the second guest molecule *G2* in voids in the crystal. However, in contrast to complex *VII* where the second guest molecule took part in *G*-*G* interactions and might be considered as a solvate, in this case direct *H*-*G2* contacts were found. The weak NH...O hydrogen bonds (3.279–3.377 Å) with N(1G2) are characterized by the geometric parameters given in Table 5 and consist of (a) contact with the basic host molecule through O(1) and (b) contact with the host molecule translated along c axis through O(10). Thus, *G2* serves as a bridge uniting *H*-*G1* associates in chains:

-G2- H -G2- H -G2-
| |
G1 G1

Note, that *H*:*G1* interactions occur at the face of the macrocycle loaded with bulky substituents and a proximal complex[11] is formed, while the *G2* molecule approaches the host somewhat from the side. N(1G2)

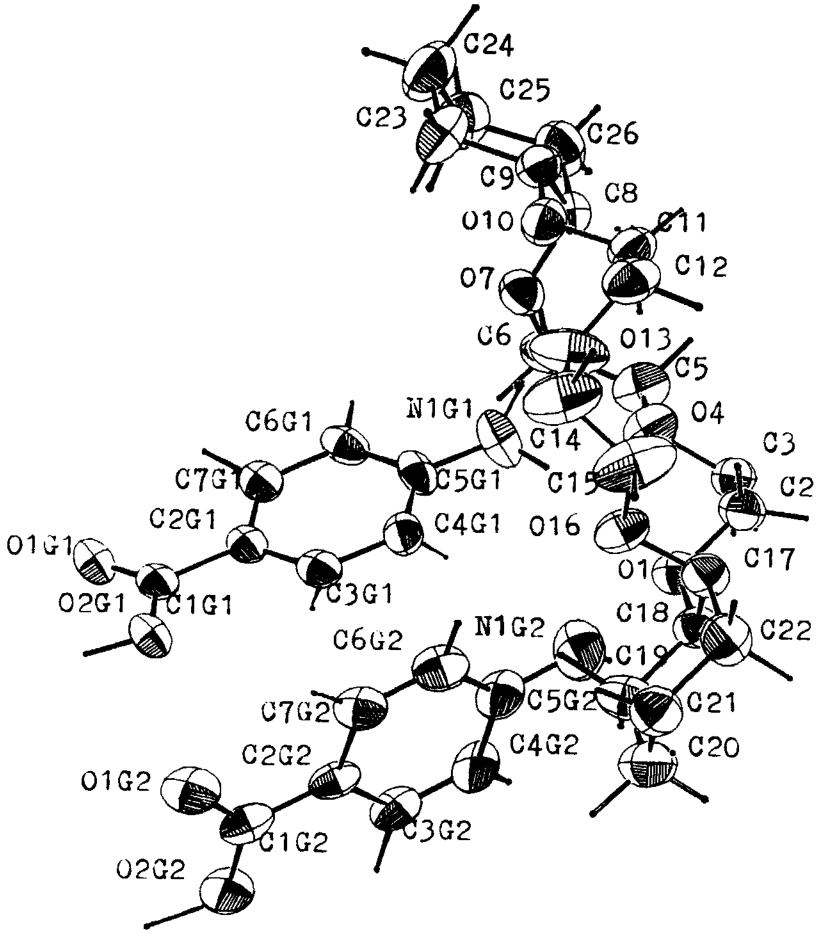


Figure 1 ORTEP diagram of molecular complex *I*.

Table 5 Geometric parameters of H-bonds *I* and *II*

Complex *I*

N...O, Å		*H...O*, Å		*N-H...O, deg*	
N(1G1)...O(1)	3.315	H(1N1)...O(1)	2.56	N(1G1)-H(1N1)...O(1)	141
N(1G1)...O(7)	3.075	H(2N1)...O(7)	1.78	N(1G1)-H(2N1)...O(7)	162
N(1G1)...O(4)	2.910	H(2N1)...O(4)	2.22	N(1G1)-H(2N1)...O(4)	108
N(1G1)...O(13)	2.889	H(1N1)...O(13)	2.61	N(1G1)-H(1N1)...O(13)	99
N(1G2)...O(10)	3.279	H(4N1)...O(10)	2.69	N(1G2)-H(4N1)...O(10)	163
O...O, Å		*H...O*, Å		*O-H...O, deg*	
O(1G1)...O(2G1*)	2.572	H(01)...O(2G1*)	1.59	O(1G1)-H(01)...O(2G1*)	166
O(1G2)...O(1G2*)	2.685				
O(2G2)...O(2G2*)	2.619				
O(1G2)...O(2G2*)	3.450				

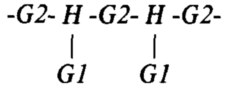
* Symmetry code is -x, -y, z

Complex *II*

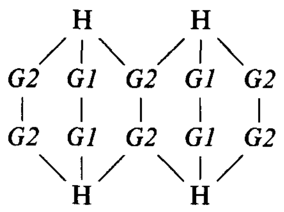
N...O, Å		*H...O*, Å		*N-H...O, deg*	
N(1G1)...O(4)	2.931	H(1N1)...O(4)	1.82	N(1G1)-H(1G1)...O(4)	153
N(1G1)...O(7)	3.113	H(2N1)...O(7)	2.07	N(1G1)-H(2N1)...O(7)	161
O...O, Å		*H...O*, Å		*O-H...O, deg*	
O(1G1)...O(2G1)*	2.615	O(1G1)...H1	1.31	O(1G1)...H1...O(2G1)*	180
		O(2G1)*...H1	1.30		

* Symmetry code is -x, -y, -z

is at a distance of 1.95 Å from the mean plane of the host heteroatoms. The dihedral angle between the mean planes defined by the host heteroatoms and the *G2* aromatic ring is 80.1°. It should be stressed that the *G1* and *G2* aromatic moieties are in practically perpendicular planes: the dihedral angle between them is 81.2°. In the unit cell the two-fold axis is parallel to [001] and the orientation of *G1* and *G2* is different about it. The aromatic moiety and carboxylic group of *G2* lie in a plane, while the corresponding flat fragment of *G1* is practically perpendicular to it. This defines the nature of the >C=O...HO- contacts between carboxylic groups: for *G1* they are between differently denoted oxygen atoms, O(1G1) and O(2G1); for *G2* they appeared to be between atoms denoted in the same way. In the carboxylic group of *G1*, carbonyl and carboxylic oxygen atoms are distinguished, the bond distances are: for C=O: O(2G1)-C(1G1) = 1.233; for C-O: (O1G1)-C(1G1) = 1.299 Å. The hydrogen atom is well localized and the OH...O hydrogen bond is directed: O(1G1)...O(2G1)* = 2.572 Å (Table 5). Besides that there is also one shortened diagnonal contact, O(2G1)...O(2G1*) = 3.217 Å (the symmetry code for O(2G1)* is -x,-y,z). In the carboxylic group of the *G2* entity the C-O distances are similar: O(1G2)-C(1G2) = 1.275; O(2G2)-C(1G2) = 1.279 Å. The hydrogen atom occupies a migrating position between O(1G2) and O(2G2); the shortened contacts defined as H-bonds are given in Table 5: O(1G2)... O(1G2*) = 2.685, O(2G2)...O(2G2*) = 2.619, O(1G2)...O(2G2*) = 3.450 Å (the symmetry code for the dependent guest molecule is -x,-y,z). These contacts unite the chains



in ribbons along the c axis (Fig 2):



Complex [$DCH\text{-}6^B$.2(4-NH_2PhCOOH)] (complex *II*) Figure 3 shows the structure of complex *II*. Its 1:2 stoichiometry is typical for $DCH\text{-}6^B$ associates with the guest molecules arranged at both equal faces of the centrosymmetric host molecule. As in *I*, the NH_2-group coordinates the crown ether and the proper associate is stabilized by NH...O contacts of 2.931–3.113 Å. The corresponding geometric parameters of the NH...O interactions are given in Table 5.

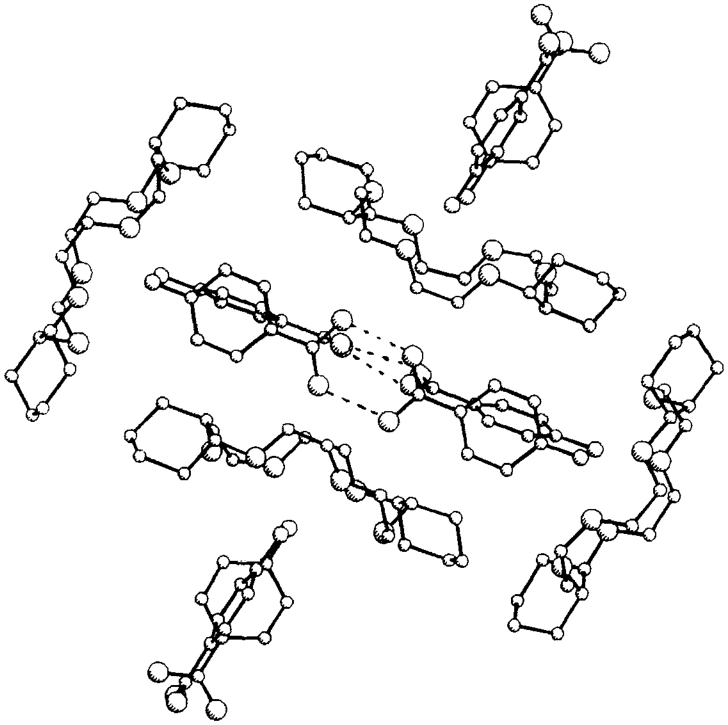


Figure 2 Packing of *I* in the crystal.

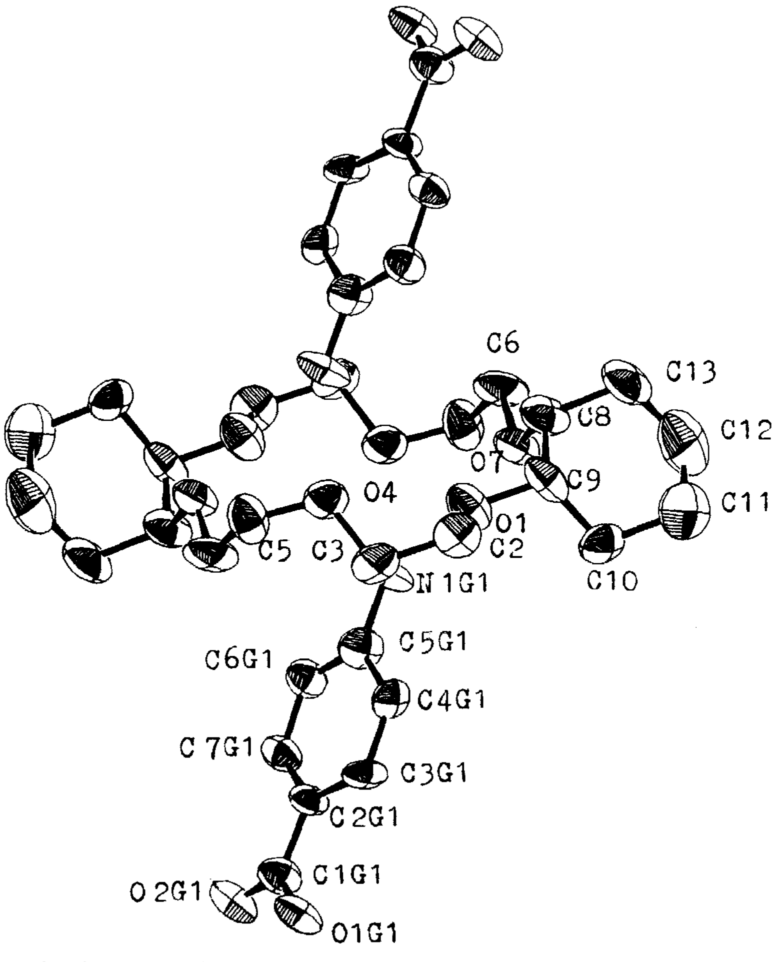


Figure 3 ORTEP diagram of molecular complex *II*.

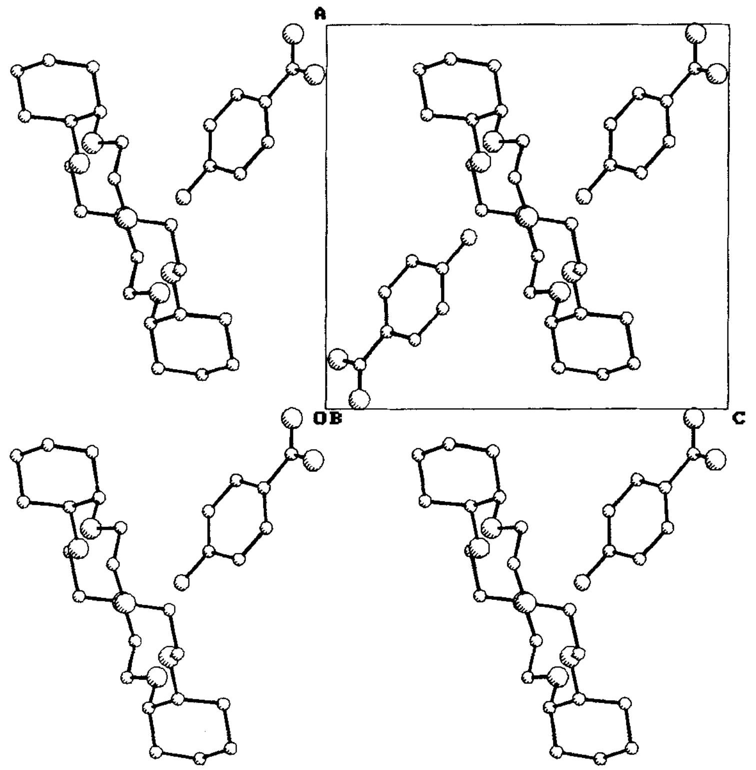


Figure 4 Packing of *II* in the crystal.

Oxygen atoms divided by the oxyethylene moiety take part in NH...O hydrogen bonds. Atom N(1G1) is 1.97 Å from the mean plane of the host heteroatoms. According to Cram,[21] the both associates (*I* and *II*) might be called perching complexes. The dihedral angle between the mean average planes defined by the host heteroatoms and the aromatic moiety of *G1* is 63.5°. The 1:2 complexes are united in chains -H-G-G-H- by means of OH...O hydrogen bonds. Carboxylic groups of the two guest molecules connected by the inversion centre participate in these interactions. The O...O distance is O(1G1)...O(2G1)* = 2.615 Å. The H-atom occupies the migrating position between the oxygen atoms. The geometric parameters of the corresponding OH...O interactions are given in Table 5. This type of binding is known for the crystal 4-aminobenzoic acid[19,20] and other carbonic acids.[22] The crystal packing of the complexes in the unit cell is shown in Fig 4. Between the individual chains there are no contacts shorter than van der Waals ones.

Conformational peculiarities of DCH-6^A

Two types of symmetry are trivial for DCH-6^A in its complexes both with the metals and neutral molecules. They are C_s-symmetry with the mirror plane crossing the central oxygen atoms of the macrocycle and C_2-symmetry with the two-fold axis which is perpendicular to the plane of the crown ether oxygen atoms.[23] As a rule, in both cases the macrocycle conformation is described by 8 *gauche* bonds (all C-C and 2 C-O, complexes *VII* and *XI*, for example). The participation in the guest coordination of two neighbouring host oxygen atoms as in complex *V* stipulates the unusual asymmetric ring conformation with 9 *gauche* bonds: 5 C-C and 4 C-O. C_s-symmetry for DCH-6^A was found in *IX*. The cycle is characterized by 10 *gauche* bonds (6 C-C and 4 C-O). The remaining C-O bonds not mentioned above are in an *anti*-configuration.

In complex *I* the host is asymmetric and characterized by an unusual conformation. It is probably connected with the participation of two guest molecules in the host coordination. The number of *gauche*-bonds is 10 (6 C-C and 4 C-O). The cycle is described by the following set of *anti*, *gauche* torsion angles: **g** + **g** + **ag** + **aag** + **g** + **ag** + **g** + **ag** + **ag** − **g** − **aa**. The meaning of the torsion angles in the heterocyclic host framework in *I* and *II* are given in Table 6. For DCH-6^A it is the so-called four-angle conformation with the corner fragments fixed at the atoms C(6), C(9), C(14), and C(18). The fragments O(4)...O(7) and O(13)...O(16) of the cycle are asymmetric with respect to one another. If in the first one an anti-torsion angle is at the inner (nearer the centre of macrocyclic cavity) side of the OCH_2CH_2O fragment, along the O(4)-C(5) bond, then

Table 6 Torsion angles (deg) in the crown ethers framework *I* and *II*

Atoms	*I*	*II*
C(2)-O(1)-C(18)-C(17)	61.4	—
C(18)-O(1)-C(2)-C(3)	160.4	—
C(9)-O(1)-C(2)-C(3)	—	−173.4
O(1)-C(2)-C(3)-O(4)	67.1	74.5
C(2)-C(3)-O(4)-C(5)	173.4	80.5
C(3)-O(4)-C(5)-C(6)	171.9	172.6
O(4)-C(5)-C(6)-O(7)	54.1	67.1
C(5)-C(6)-O(7)-C(8)	62.2	−179.8
C(6)-O(7)-C(8)-C(9)	−174.8	−149.1
O(7)-C(8)-C(9)-O(10)	56.0	—
O(7)-C(8)-C(9)-O(1)	—	−61.6
C(8)-C(9)-O(10)-C(11)	62.1	—
C(8)-C(9)-O(1)-C(2)	—	−170.5
C(9)-O(10)-C(11)-C(12)	162.4	—
O(10)-C(11)-C(12)-O(13)	58.7	—
C(11)-C(12)-O(13)-C(14)	174.9	—
C(12)-O(13)-C(14)-C(15)	−80.3	—
O(13)-C(14)-C(15)-O(16)	−63.5	—
C(14)-C(15)-O(16)-C(17)	159.6	—
C(15)-O(16)-C(17)-C(18)	−167.5	—
O(16)-C(17)-C(18)-O(1)	58.5	—

in the second one the *anti*-torsion angle is at the exterior side of the corresponding fragment, along the C(15)-O(16) bond. The signs of the *gauche*-torsion angles are also different: $g + g +$ in the first and $g - g -$ in the second. The heterocyclic cavity is elongated in the direction of the cyclohexano substituents and is characterized by transanular O…O distances: O(1)…O(10) = 5.653, O(4)…O(13) = 4.520, and O(7)…O(16) = 6.154 Å. Maximum deviations from coplanarity are observed for the O(4) (−0.407) and O(7) (0.571 Å) atoms.

Conformational peculiarities of DCH-6^B

It is typical for DCH-6^B that in the complexes with neutral organic molecules it admits C_i-symmetry with 8 *gauche* bonds (6 C-C and 2 C-O) and two $g \pm g \pm$ corner fragments along the cycle. Their arrangement is different: in the complexes *VIII*, *X*, *XII* (Table 1) they are fixed at the bridge carbon atoms and the cycle is elongated in the direction of the cyclohexano-groups, shortened O…O distances being between the central oxygen atoms. In *VI*, and in the complex of DCH-6^B with 2-$CH_3PhSO_2NH_2$[7] as well, the corner fragments are in the central part of the heterocyclic framework, shortened O…O distances being between one pair of cyclohexanediol atoms.

In *II* the ring conformation is of the second type: the corner fragments are at the C(3) and C(3)* atoms, shortened transanular O…O distances being between O(7) and O(7)*, 5.157 Å. The other O…O distances are O(1)…O(1)* = 5.997 and O(4)…O(4)* = 5.858 Å. Host oxygen atoms are coplanar within 0.21? Å.

Geometric parameters of *I* and *II*

The general geometry for both host and guest is typical in *I* and *II*. The list of the bond distances (Å) and angles (deg) for them is given in Tables 7 and 8. For the

Table 7 Bond distances (Å) in *I* and *II*

Atoms	*293 K*	*d*, Å *203 K*	*d*, Å
O(1G1)-C(1G1)	1.27(2)	1.2996(45)	1.288(7)
O(2G1)-C(1G1)	1.26(3)	1.233(5)	1.262(7)
N(1G1)-C(5G1)	1.38(3)	1.357(6)	1.367(7)
C(1G1)-C(2G1)	1.46(3)	1.468(6)	1.450(8)
C(2G1)-C(3G1)	1.39(3)	1.390(5)	1.389(8)
C(2G1)-C(7G1)	1.44(2)	1.397(6)	1.370(8)
C(3G1)-C(4G1)	1.38(3)	1.373(6)	1.400(8)
C(4G1)-C(5G1)	1.42(3)	1.399(6)	1.407(8)
C(5G1)-C(6G1)	1.41(3)	1.389(5)	1.404(8)
C(6G1)-C(7G1)	1.38(3)	1.375(6)	1.376(8)
O(1G2)-C(1G2)	1.30(4)	1.275(6)	—
O(2G2)-C(1G2)	1.24(4)	1.279(6)	—
N(1G2)-C(5G2)	1.26(4)	1.361(8)	—
C(1G2)-C(2G2)	1.43(3)	1.474(6)	—
C(2G2)-C(3G2)	1.36(4)	1.386(7)	—
C(2G2)-C(7G2)	1.53(4)	1.411(7)	—
C(3G2)-C(4G2)	1.37(3)	1.365(8)	—
C(4G2)-C(5G2)	1.41(5)	1.402(7)	—
C(5G2)-C(6G2)	1.50(5)	1.395(7)	—
C(6G2)-C(7G2)	1.39(4)	1.358(7)	—
O(1)-C(2)	1.38(4)	1.402(7)	1.425(7)
O(1)-C(18)	1.45(3)	1.435(6)	—
C(2)-C(3)	1.45(4)	1.481(7)	1.533(8)
C(3)-O(4)	1.35(3)	1.417(6)	1.438(7)
O(4)-C(5)	1.32(5)	1.416(7)	1.429(7)
C(5)-C(6)	1.18(8)	1.496(8)	1.522(9)
C(6)-O(7)	1.57(8)	1.455(7)	1.415(7)
O(7)-C(8)	1.46(5)	1.429(6)	1.441(6)
C(8)-C(9)	1.63(6)	1.549(8)	1.502(8)
C(8)-C(13)	—	—	1.533(9)
C(8)-C(26)	1.63(5)	1.512(8)	—
C(9)-O(10)	1.44(4)	1.427(7)	—
C(9)-C(10)	—	—	1.531(8)
C(9)-C(23)	1.54(5)	1.508(9)	—
O(10)-C(11)	1.42(4)	1.427(7)	—
C(10)-C(11)	—	—	1.480(10)
C(11)-C(12)	1.48(5)	1.484(8)	1.540(10)
C(12)-O(13)	1.28(5)	1.417(7)	—
C(12)-C(13)	—	—	1.531(9)
O(13)-C(14)	1.45(7)	1.428(9)	—
C(14)-C(15)	1.08(10)	1.459(11)	—
C(15)-O(16)	1.77(8)	1.490(8)	—
O(16)-C(17)	1.38(4)	1.420(6)	—
C(17)-C(18)	1.46(4)	1.546(8)	—
C(17)-C(22)	1.59(4)	1.524(7)	—
C(18)-C(19)	1.57(4)	1.498(8)	—
C(19)-C(20)	1.56(5)	1.544(9)	—
C(20)-C(21)	1.46(5)	1.532(10)	—
C(21)-C(22)	1.53(5)	1.516(9)	—
C(23)-C(24)	1.59(6)	1.536(11)	—
C(24)-C(25)	1.39(5)	1.551(10)	—

Table 8 Bond angles (deg) in *I* and *II*

Atoms		
O(1G1)-C(1G1)-O(2G1)	123.4(4)	121.0(5)
O(2G1)-C(1G1)-C(2G1)	121.2(3)	118.1(5)
O(1G1)-C(1G1)-C(2G1)	115.5(3)	120.7(5)
C(1G1)-C(2G1)-C(7G1)	120.1(3)	121.2(5)
C(1G1)-C(2G1)-C(3G1)	121.7(4)	118.3(5)
C(3G1)-C(2G1)-C(7G1)	118.2(4)	120.3(5)
C(2G1)-C(3G1)-C(4G1)	121.4(4)	119.1(5)
C(3G1)-C(4G1)-C(5G1)	119.8(3)	121.1(5)
N(1G1)-C(5G1)-C(4G1)	121.6(3)	120.5(5)
C(4G1)-C(5G1)-C(6G1)	119.5(4)	117.3(5)
N(1G1)-C(5G1)-C(6G1)	118.9(4)	122.0(5)
C(5G1)-C(6G1)-C(7G1)	120.0(4)	121.2(5)
C(2G1)-C(7G1)-C(6G1)	121.2(4)	120.6(5)
O(1G2)-C(1G2)-O(2G2)	122.0(4)	—
O(2G2)-C(1G2)-C(2G2)	118.7(4)	—
O(1G2)-C(1G2)-C(2G2)	119.3(4)	—
C(1G2)-C(2G2)-C(7G2)	120.3(4)	—
C(1G2)-C(2G2)-C(3G2)	121.5(4)	—
C(3G2)-C(2G2)-C(7G2)	118.2(4)	—
C(2G2)-C(3G2)-C(4G2)	121.4(4)	—
C(3G2)-C(4G2)-C(5G2)	120.5(5)	—
N(1G2)-C(5G2)-C(4G2)	121.9(5)	—
C(4G2)-C(5G2)-C(6G2)	117.8(5)	—
N(1G2)-C(5G2)-C(6G2)	120.2(5)	—
C(5G2)-C(6G2)-C(7G2)	122.3(5)	—
C(2G2)-C(7G2)-C(6G2)	119.8(4)	—
C(2)-O(1)-C(18)	114.8(4)	—
C(2)-O(1)-C(9)	—	113.3(4)
O(1)-C(2)-C(3)	111.1(5)	110.2(5)
C(2)-C(3)-O(4)	110.1(4)	111.0(5)
C(3)-O(4)-C(5)	113.9(4)	111.8(4)
O(4)-C(5)-C(6)	108.5(5)	107.7(5)
C(5)-C(6)-O(7)	114.3(4)	108.7(5)
C(6)-O(7)-C(8)	115.9(4)	111.3(4)
O(7)-C(8)-C(9)	106.4(4)	108.2(5)
C(9)-C(8)-C(13)	—	112.8(5)
O(7)-C(8)-C(26)	108.5(5)	—
C(9)-C(8)-C(26)	108.5(5)	—
C(8)-C(9)-O(10)	113.5(4)	—
C(8)-C(9)-C(19)	—	109.2(5)
C(8)-C(9)-O(1)	—	107.6(5)
O(10)-C(9)-C(23)	107.1(5)	—
C(9)-O(10)-C(11)	115.5(4)	—
C(9)-C(10)-C(11)	—	111.5(2)
O(10)-C(11)-C(12)	109.5(5)	—
C(10)-C(11)-C(12)	—	113.6(6)
C(11)-C(12)-O(13)	108.9(5)	—
C(11)-C(12)-C(13)	—	109.9(5)
C(12)-O(13)-C(14)	119.2(5)	—
O(13)-C(14)-C(15)	110.7(6)	—
C(14)-C(15)-O(16)	107.0(6)	—
C(15)-O(16)-C(17)	108.6(5)	—
O(16)-C(17)-C(22)	112.3(4)	—
O(16)-C(17)-C(18)	107.7(4)	—
C(18)-C(17)-C(22)	108.1(4)	—
O(1)-C(18)-C(17)	112.9(4)	—
C(17)-C(18)-C(19)	111.6(4)	—
O(1)-C(18)-C(19)	108.4(4)	—
C(18)-C(19)-C(20)	111.0(5)	—
C(19)-C(20)-C(21)	109.7(5)	—
C(20)-C(21)-C(22)	110.5(5)	—
C(17)-C(22)-C(21)	112.3(5)	—
C(9)-C(23)-C(24)	111.9(6)	—
C(23)-C(24)-C(25)	109.7(6)	—
C(24)-C(25)-C(26)	109.6(6)	—
C(8)-C(26)-C(25)	112.3(5)	—

Symmetry code for atoms C(5) and C(6) is 1 − x, 1 − y, 1 − z.

Table 9 Some average distances (Å) and angles (deg) *I* and *II*

Host	*C-C*	*C-C$_{cr}$*	*C-C$_{cycl}$*	*C-O-C-*	*C-C-O*	*C-C-C*
DCH-6^{A}	1.430	1.480	1.528	114.7	110.1	110.6
DCH-6^{B}	1.433	1.528	1.520	112.1	108.9	111.0
Guest	*C-C*	*C-N*	*C-C-C*	*C-C(N)-C*	*C-C(COOH)-C*	
G1 (I)	1.387	1.357	120.0	119.5	118.2	
G2 (I)	1.388	1.361	120.0	117.8	118.2	
G1 (II)	1.391	1.367	119.9	117.3	120.3	

estimation of the experiment accuracy Table 7 contains the meanings of bond distances at both temperatures. Some average values for the corresponding compounds are collected in Table 9.

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