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The first molecular complex of the unusual host: benzo,cyclohexano-18-crown-6. Crystal and molecular structure of its 1:1 complex with 4-aminobenzenesulphamide

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Complex *I* between benzo,cyclohexano-18-crown-6 (host, *H*) and 4-aminobenzenesulphamide (guest, *G*) was synthesized. Its structure was defined by X-ray analysis at 223 K. In the crystal a chain structure of the -*H-G-H*- type is realized. The guest serves as a single bridge between crown ether molecules connected by the symmetry operation (x, $1/2 - y$, $-1/2 + z$). H...O distances in NH...O hydrogen bonds are 2.35 – 2.50 Å for the amino group and 2.05 – 2.31 Å for the sulphamidic one. Unlike the majority of the molecular complexes of 18-membered crown ethers, here the etherial host oxygen atoms divided by two oxyethylene fragments participate in hydrogen bonds. Host symmetry is irregular: C-C bonds are in a favourable *gauche*-configuration except the one belonging to the aromatic moiety which is *cis*. One C-O bond is also in the *gauche*-configuration with the formations in the cycle of a corner fragment, while all the others are *anti*-.

INTRODUCTION

Molecular host-guest type complexes of the crown ethers serve as models for the study of the mechanisms of neutral molecule recognition and binding by receptors. They are also widely used for extraction from a mixture of small molecules based on the definite geometry of donor groups.[1,2] The general regularities of the molecular complexes of the simplest 18-membered crown ether, 18-crown-6, are fully described.[3,4] The peculiar feature of this macrocycle is its high conformational flexibility. It acts as an equal-sided receptor. As a consequence, it shows low selectivity in host-guest complexation. Dibenzo-18-crown-6 is characterized by conformational rigidity, which increases its selectivity, but the stability of the complexes falls.

We have made an attempt to carry out a systematic investigation of the structural aspects of crown-ether complexation. Neutral H-donor molecules serve as the guests, and as the hosts there are crown ethers with different cavity sizes, conformational flexibility and possessing rigid fragments to hinder the guest approach. *Cis-syn-cis* (*A*) and *cis-anti-cis* (*B*) isomers of dicyclohexano-18-crown-6 (DCH-6) serve the examples of the latter ones.

In the system crown ether—aminosulfuric acid (NH_2SO_2OH) the structural information concerning 12, 15, and 18-membered crown ethers is available. Complexes with host:guest stoichiometry 1:1 are stable in the crystalline state for 18-crown-6,[5,6] monobenzo-18-crown-6,[6] DCH-6^A,[7] DCH-6^B,[7] 15-crown-5[8] and benzo-15-crown-5.[8] For 12-crown-4 the complex is characterized by a 1:1.5 ratio. However, X-ray analysis showed[9] that only one guest molecule has direct N-H...O contacts with the host.

The complexes of 18-crown-6[10] and DCH-6^B[11] with 4-aminobenzenesulphamide have 1:2 stoichiometry. This ratio is typical for equal-sided host molecules. The attempts to synthesize the corresponding complexes of DCH-6^A and benzo-18-crown-6 have failed.

Another system described previously is the complexes of 18-membered crown ethers (18-crown-6, benzo-18-crown-6, DCH-6(A,B)[12,13]) with 3,5-dichloro-4-aminobenzenesulphamide. The aggregates are unusual by their stoichiometry. The trivial 1:2 ratio is noted for the equal-faced 18-crown-6, whereas 1:1 complexes are formed not only with different-faced DCH-6^A,[12] benzo-18-crown-6, but also with the equal-faced

DCH-6^B.[13] In this case the guest enters the cavity as a bridge with the formation of a -host-guest-host- chain motive.

In the present paper the results of the synthesis and X-ray analysis of title compound are described. The interest in this system is aroused by the host peculiarities manifested in the fusing of the macrocyclic cavity with aromatic and cyclohexyl-substituents which cause special impediments and restrict host conformational flexibility.

EXPERIMENTAL

Synthesis of the complex I

Liquid-phase hydrogenation of dibenzo-18-crown-6 is the main method of preparation of dicyclohexano-18-crown-6. The hydrogenation of the aromatic rings goes by steps and during incomplete conversion benzo,cyclohexano-18-crown-6 is separated. It can be separated with the A and B isomers of DCH-6 from the mixture in the form of their 1:1 complexes with aminosulfuric acid. Because of the difference in melting points, the host is separated from the proper complexes by treatment with NaOH or Na_2CO_3.[14,15] For the compound described here the host was prepared according to ref 14. Benzo,cyclohexano-18-crown-6 (3.66, 0.01 mol) and 4-aminobenzenesulphamide (1.72 g, 0.01 mol) were dissolved in 10 mL of methanol at 64 °C. After cooling, the crystals were filtered off. Crystals suitable for X-ray investigation were obtained by recrystallization from ethylacetate. The transparent, colourless crystals are soluble in acetone, methanol, ethanol: m.p. 150–151 °C, NMR (Bruker, $(CD_3)_2CO$, σ 1.34–1.97 m and 3.68–4.29 m (26H, CH, CH_2, CH_2O), 5.50 s (2H, NH), 6.33 s (2H, HNS), 6.82–7.24 m (8H, Ar). Calcd. for $C_{26}H_{38}N_2O_8S$, N-5.22, S-5.97; Found, N-5.31, S-5.92.

X-ray data collection, structure determination and refinement

A colourless, prismatic crystal of the title compound with the dimensions of 0.55 × 0.30 × 0.15 mm was used for X-ray analysis. Preliminary examination and data collection were performed with CuK_α radiation ($\lambda = 1.54184$ Å) on an Enraf-Nonius CAD-4 diffractometer at 223 ± 1 K. Cell constants and orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections in range $17 < \theta < 25°$. The intensity data were collected using the ω-2θ technique. Crystallographic and experimental details are given in Table 1. The initial structural model was obtained by direct methods. The structure was solved by use of SHELXS-86[16] and refined with the SHELX-76[17] computer programs. All non-hydrogen atoms for the structural model were obtained from an E-map. Hydrogen atoms were found by analyzing the difference Fourier-maps. The structural model was refined by full matrix least-squares where the function minimized was $w(/F_o/-/F_c/)^2$ and $w = 1/\sigma(F)^2$ with anisotropic thermal parameters for non-hydrogen atoms and isotropic ones for H atoms. Maximal and minimal heights in final difference map are 0.40 and -0.46 eÅ^{-3}. All the figures were made using ORTEP.[18] The final fractional coordinates are given in Table 2, and interatomic distances and bond angles, Tables 3 and 4.

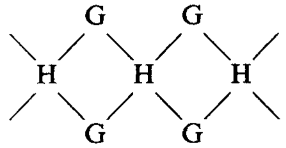
Table 1 Data collection and structure analysis parameters

Formula	$C_{26}H_{38}N_2O_8S$
Temperature	223(1)K
Space group	Pbca
Cell constants	
a(Å)	13.260(2)
b(Å)	20.627(3)
c(Å)	19.427(3)
Cell volume, Å^3	5313.5
Z	8
D(calc) (gcm^{-3})	1.347(1)
μ (cm^{-1})	14.98
Radiation	CuK_α
Number of reflections	
measured	6183
unique	4020
Final R-values	
unweighted	0.041
$w = 1/(F^2)$	0.039

RESULTS AND DISCUSSION

Bonding mode of benzo,cyclohexano-18-crown-6 to the guest molecule

Figure 1 shows the fragment of the chain structure of the title compound with the coordination of both guest donor groups by the host molecules. In **I** the host:guest ratio is 1:1. It is differed from that found in the complexes of the same guest with DCH-6^B (complex **II**) and 18-crown-6 (complex **III**; the host:guest stoichiometry is 1:2). The asymmetry of benzo,cyclohexano-18-crown-6 can cause asymmetry in its environment, since on the both sides of the macrocyclic cavity there are different guest donor groups. The NH_2-moiety, being part of the sulphamidic group, forms two hydrogen bonds with NH...O distances of N(1G)-H...O(4) = 2.938(2) and N(1G)-H...O(13) = 2.996(2) Å. The geometric parameters of the hydrogen bonds in I are given in Table 5. The guest NH_2-group is coordinated on the other side of the cavity with NH...O distances of N(2G)-H...O(1) = 3.115(3) and N(2G)-H...O10) = 3.264(3) Å. The chain structure of -H-G-H- type differs from complexes II[11] and III.[10] In II the guest serves as a double-bridge uniting by both donor groups host molecules connected by the inversion center. The



chain motive is formed.

Table 2 Fractional atomic coordinates (× 10^4) for compound I

Atom	*x/a*	*y/b*	*z/c*	B_{eq}
S(1G)	3129(1)	3700(1)	339(1)	2.26(1)
O(1G)	3968(1)	4137(1)	390(1)	3.68(5)
O(2G)	2122(1)	3970(1)	344(1)	1.00(5)
N(1G)	3231(1)	3267(1)	−335(1)	2.76(5)
N(2G)	3237(2)	2027(1)	2804(1)	3.52(6)
C(1G)	3217(2)	3167(1)	1039(1)	1.86(5)
C(2G)	3167(2)	2500(1)	983(1)	2.19(5)
C(3G)	3179(2)	2115(1)	1567(1)	2.28(5)
C(4G)	3224(2)	2387(1)	2220(1)	2.27(6)
C(5G)	3276(2)	3066(1)	2272(1)	2.43(6)
C(6G)	3280(2)	3445(1)	1688(1)	2.24(5)
O(1)	2239(1)	4330(1)	−2022(1)	2.51(4)
C(2)	1657(2)	4394(1)	−1409(1)	2.76(7)
C(3)	901(2)	3850(1)	−1383(1)	3.02(7)
O(4)	1383(1)	3265(1)	−1168(1)	2.95(5)
C(5)	847(2)	2700(1)	−1368(2)	3.77(8)
C(6)	1118(2)	2146(1)	−917(2)	3.42(8)
O(7)	2158(1)	2002(1)	−1035(1)	2.73(5)
C(8)	2568(2)	1512(1)	−649(1)	2.62(6)
C(9)	3639(2)	1483(1)	−658(1)	2.51(6)
O(10)	4092(1)	1959(1)	−1045(1)	2.58(4)
C(11)	5173(2)	1997(1)	−1002(1)	2.98(7)
C(12)	5491(2)	2564(1)	−1424(1)	3.10(7)
O(13)	5179(1)	3151(1)	−1106(1)	2.58(4)
C(14)	5689(2)	3699(1)	−1393(1)	2.86(6)
C(15)	5144(2)	4313(1)	−1248(1)	2.74(7)
O(16)	4311(1)	4356(1)	−1712(1)	2.46(4)
C(17)	3746(2)	4945(1)	−1652(1)	2.48(6)
C(18)	2865(2)	4884(1)	−2159(1)	2.41(6)
C(19)	3250(2)	4814(1)	−2892(1)	2.90(6)
C(20)	3933(2)	5384(1)	−3093(1)	3.41(7)
C(21)	4781(2)	5480(1)	−2569(1)	3.19(7)
C(22)	4356(2)	5542(1)	−1845(1)	2.94(6)
C(23)	4132(2)	1005(1)	−300(1)	3.43(8)
C(24)	3580(3)	551(1)	68(1)	4.41(9)
C(25)	2541(3)	580(1)	83(1)	4.46(10)
C(26)	2042(2)	1065(1)	−269(1)	3.45(8)

Table 3 Bond distances (Å) in I

Atoms	*d*, Å	*Atoms*	*d*, Å
S(1G)-O(1G)	1.435(1)	O(1)-C(2)	1.427(2)
S(1G)-O(2G)	1.448(1)	O(1)-C(18)	1.435(3)
S(1G)-N(1G)	1.592(2)	C(2)-C(3)	1.505(3)
S(1G)-C(1G)	1.753(2)	C(3)-O(4)	1.425(3)
N(2G)-C(4G)	1.358(2)	O(4)-C(5)	1.419(3)
C(1G)-C(2G)	1.382(3)	C(5)-C(6)	1.484(4)
C(1G)-C(6G)	1.390(2)	C(6)-O(7)	1.428(3)
C(2G)-C(3G)	1.383(2)	O(7)-C(8)	1.372(2)
C(3G)-C(4G)	1.388(2)	C(8)-C(9)	1.420(3)
C(4G)-C(5G)	1.408(3)	C(8)-C(26)	1.372(3)
C(5G)-C(6G)	1.376(2)	C(9)-O(10)	1.372(2)
C(9)-C(23)	1.374(3)	O(10)-C(11)	1.439(3)
C(11)-C(12)	1.488(3)	C(12)-O(13)	1.423(2)
O(13)-C(14)	1.429(2)	C(14)-C(15)	1.487(3)
C(15)-C(16)	1.429(2)	O(16)-C(17)	1.429(3)
C(17)-C(18)	1.533(3)	C(17)-C(22)	1.523(3)
C(18)-C(19)	1.520(2)	C(19)-C(20)	1.537(3)
C(20)-C(21)	1.528(3)	C(21)-C(22)	1.521(2)
C(23)-C(24)	1.388(3)	C(24)-C(25)	1.380(5)
C(25)-C(26)	1.381(3)		

Table 4 Bond angles (deg) for I

Angle		*Angle*	
N(1G)-S(1G)-C(1G)	106.4(1)	O(2G)-S(1G)-C(1G)	107.3(1)
O(2G)-S(1G)-N(1G)	107.4(1)	O(1G)-S(1G)-C(1G)	106.7(1)
O(1G)-S(1G)-N(1G)	110.2(1)	O(1G)-S(1G)-O(2G)	118.3(2)
S(1G)-C(1G)-C(6G)	116.7(2)	S(1G)-C(1G)-C(2G)	124.2(2)
C(2G)-C(1G)-C(6G)	119.0(2)	C(1G)-C(2G)-C(3G)	120.5(2)
C(2G)-C(3G)-C(4G)	121.1(2)	N(2G)-C(4G)-C(3G)	123.0(2)
C(3G)-C(4G)-C(5G)	118.1(2)	N(2G)-C(4G)-C(5G)	119.0(2)
C(4G)-C(5G)-C(6G)	120.5(2)	C(1G)-C(6G)-C(5G)	120.8(2)
C(2)-O(1)-C(18)	113.2(2)	O(1)-C(2)-C(3)	108.7(2)
C(2)-C(3)-O(4)	110.0(2)	C(3)-O(4)-C(5)	113.0(2)
O(4)-C(5)-C(6)	110.5(2)	C(5)-C(6)-O(7)	107.5(2)
C(6)-O(7)-C(8)	116.7(2)	O(7)-C(8)-C(26)	125.9(2)
O(7)-C(8)-C(9)	114.8(2)	C(9)-C(8)-C(26)	119.3(2)
C(8)-C(9)-C(23)	119.9(2)	C(8)-C(9)-O(10)	114.6(2)
O(10)-C(9)-C(23)	125.5(2)	C(9)-O(10)-C(1)	116.4(2)
O(10)-C(11)-C(12)	107.2(2)	C(11)-C(12)-O(13)	110.3(2)
C(12)-O(13)-C(14)	111.5(2)	O(13)-C(14)-C(15)	111.7(2)
C(14)-C(15)-O(16)	108.1(2)	C(15)-O(16)-C(17)	114.1(2)
O(16)-C(17)-C(22)	113.0(2)	O(16)-C(17)-C(18)	106.2(2)
C(18)-C(17)-C(22)	108.3(2)	O(1)-C(18)-C(17)	112.9(2)
C(17)-C(18)-C(19)	110.6(2)	O(1)-C(18)-C(19)	106.9(2)
C(18)-C(19)-C(20)	111.3(2)	C(19)-C(20)-C(21)	111.4(2)
C(20)-C(21)-C(22)	110.6(2)	C(17)-C(22)-C(21)	110.8(2)
C(9)-C(23)-C(24)	119.7(3)	C(23)-C(24)-C(25)	120.5(2)
C(24)-C(25)-C(26)	120.1(3)	C(8)-C(26)-C(25)	120.6(3)

Table 5 Intermolecular hydrogen bonds (Å) and angles (deg) in compound I

H-group	*H...O*, Å		*N...O*, Å		*NH...O*, *deg*	
SO_2NH_2	H(1G)..O(13)	2.31	N(1G)..O(13)	2.996(2)	N(1G)-H(1G)..O(13)	178
	H(2G)..O(4)	2.05	N(1G)..O(4)	2.938(2)	N(1G)-H(2G)..O(4)	169
NH_2	H(3G)..O(1)	2.35	N(2G)..O(1)	3.115(3)	N(2G)-H(3G)..O(1)	152[a]
	H(4G)..O(10)	2.50	N(2G)..O(10)	3.264(3)	N(2G)-H(4G)..O(10)	142[a]

[a] Symmetry operation for atoms N(2G), H(3G), H(4G) is x, 1/2 − y, −1/2 + z.

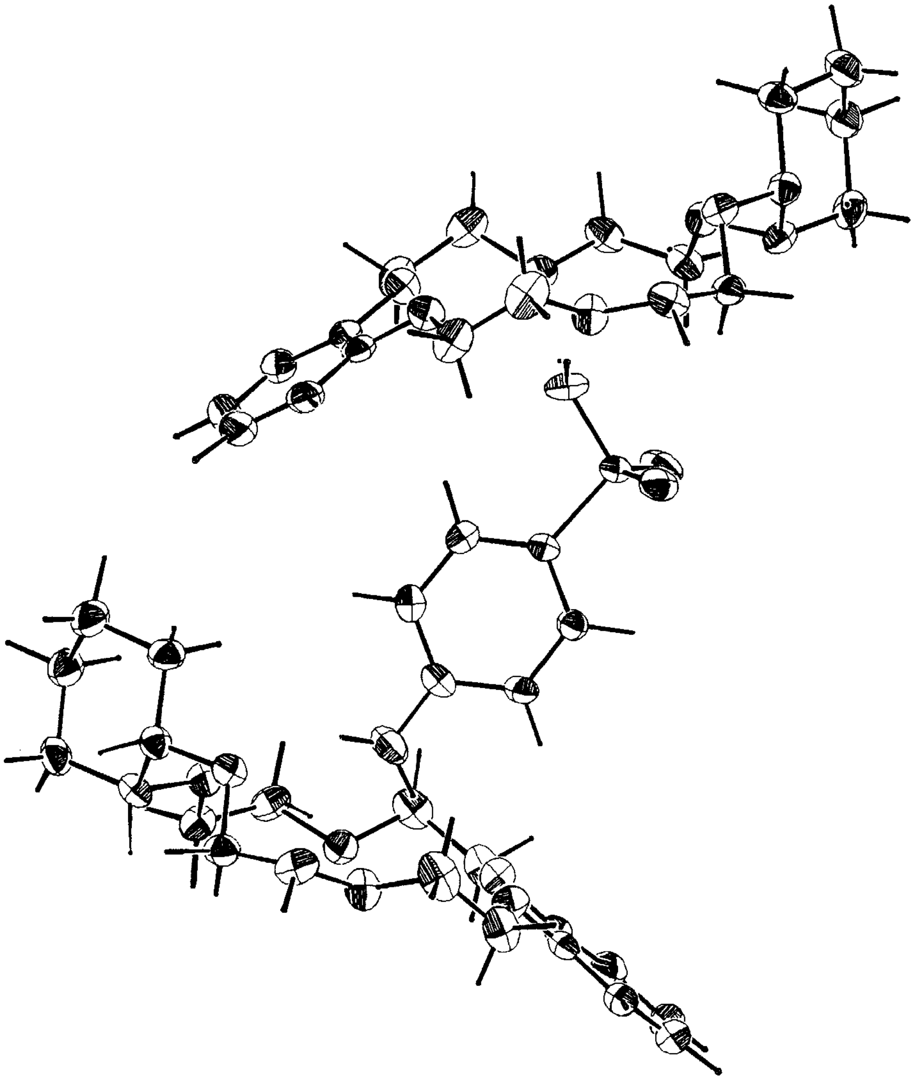


Figure 1 ORTEP diagram of the elementary fragment of the -H-G-H-G-H- chain in I.

NH...O distances in **II** are 3.02 Å for the SO_2NH_2-group and 3.13–3.22 Å for the NH_2-group. Both H-donor groups interact with two sides of the host cavity simultaneously. In **III** only the sulphamidic group participates in NH...O contacts with the crown ether, of the 'head to head' type, while the amino group is responsible for the uniting -G-H-G- entities in the network. The host-guest NH...O contacts are in the range 2.92–3.05 Å.

Ordinarily, host oxygen atoms, divided by one oxyethylene fragment, enter into guest binding. Such coordination was found in the majority of 18-crown-6 complexes,[3,4] in the complexes of DCH-6^A with 4-methylbenzenesulphamide,[19] 4-aminobenzenesulphamidine,[20] DCH-6^B with 3,5-dichloro-4-aminobenzenesulphamide,[13] 2-methylbenzenesulphamide.[21] In **I** the hydrogen bonds are practically linear and carried out with oxygen atoms separated not by one (as a rule), but two oxyethylene fragments (Figs 2–3). The reciprocal H-G arrangement is characterized by the dehidral angle between the average plane of crown ether heteroatoms and guest aromatic moiety of 84.4° for the structure fragment presented in Fig 2 and 86.0° for the structure fragment presented in Fig 3. The N-atoms of the guest donor groups are 1.92(N1G) and 1.69 Å(N2G) on opposite sides of the plane of the host ring.

Crown ether peculiarities

In **I** the peculiarities of the host conformation are stipulated by its structure: the conjunction of the macrocyclic framework with cyclohexyl and aromatic fragments. In the part of the host including the aromatic entity, the macrocycle conformation is

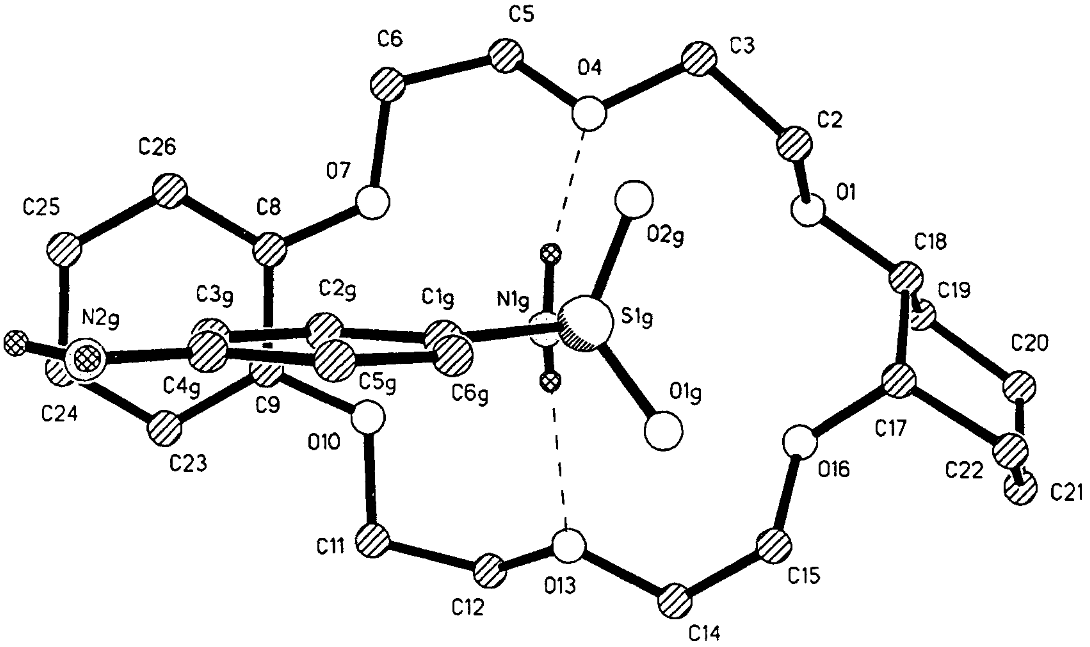


Figure 2 Scheme of the guest sulphamidic group interaction with the host (H-atoms except those belonging to the donor groups are omitted for clarity).

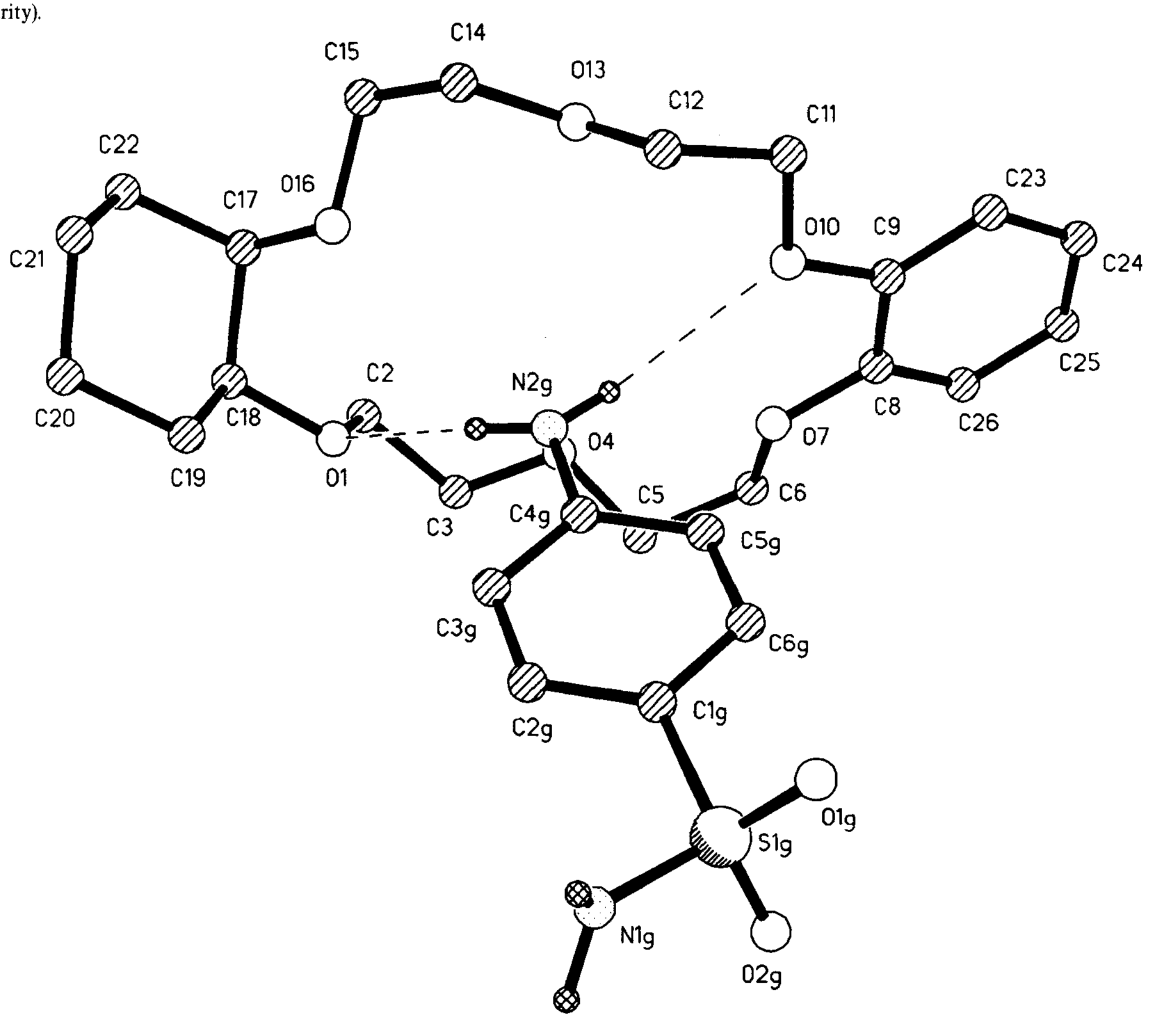


Figure 3 Scheme of the guest amino group interaction with the host (H-atoms except those belonging to the donor groups are omitted for clarity).

described by *anti,gauche*±,*anti* sequence of torsion angles except the *cis*-configuration along the C(8)-C(9) bond (the corresponding torsion angle is 1.0°). The torsion angles along the heterocyclic framework are given in Table 6. The part of the macrocyclic cavity conjugated with the cyclohexyl substituent is characterized by the conformation with the corner *gauche*+,*gauche*+ fragment at the C(18) bridge atom. The torsion angles are 70.4 and 58.3°. It is the expected conformation for similar macrocycles. The arrangement of H-atoms at the bridge C(17) and C(18) atoms corresponds to the *cis*-conformer: the deviations of H-atoms from the plane defined by the atoms O(1), C(17), C(18), O(16) are 1.30 and 0.06 Å, respectively; the torsion angle H17-C17-C18-H18 is 64°.

Table 6 Torsion angles (deg) in the crown ether framework of benzo,cyclohexano-18-crown-6 in compound I

Angle	ϕ, *deg*
C(2)-O(1)-C(18)-C(17)	70.4(3)
C(18)-O(1)-C(2)-C(3)	170.0(2)
O(1)-C(2)-C(3)-O(4)	78.0(2)
C(2)-C(3)-O(4)-C(5)	−158.2(2)
C(3)-O4)-C(5)-C(6)	−157.2(2)
O(4)-C(5)-C(6)-O(7)	−65.3(3)
C(5)-C(6)-O(7)-C(8)	178.1(2)
C(6)-O(7)-C(8)-C(9)	−165.7(2)
O(7)-C(8)-C(9)-O(10)	1.1(3)
C(8)-C(9)-O(10)-C(11)	172.7(2)
C(9)-O(10)-C(11)-C(12)	−176.8(2)
O(10)-C(11)-C(12)-O(13)	69.2(3)
C(11)-C(12)-O(13)-C(14)	164.7(2)
C(12)-O(13)-C(14)-C(15)	160.5(2)
O(13)-C(14)-C(15)-O(16)	−77.8(3)
C(14)-C(15)-O(16)-C(17)	−177.0(2)
C(15)-O(16)-C(17)-C(18)	−177.2(2)
O(16)-C(17)-C(18)-O(1)	58.3(3)

The heterocyclic cavity is elongated in the direction of the cyclic substituents. The transanular O...O distances are O(1)...O(10) = 5.793, O(4)...O(13) = 5.040, and O(7)...O(16) = 5.784 Å. The distances between the neighbouring oxygen atoms are in the range 2.566–2.981 Å. The macrocycle has a bath-like form. In distinction from the crown-like D_{3d} conformation of 18-crown-6 in host-guest complexes or even the more flattened C_i-conformation of DCH-6^{B} in similar complexes, benzo,cyclohexano-18-crown-6 in I is characterized by the relative non-coplanarity of its heteroatoms. Their deviations are O(1) −0.42, O(4) 0.51, O(7) −0.12, O(10) −0.30, O(13) 0.30, and O(16) 0.03 Å. The maximal deviations were found for the oxygen atoms participating in the hydrogen bonds (O(4), O(13) and O(1), O(10)) on the different sides of the cavity. The four peripheral oxygen atoms are coplanar within the limits ±0.16 Å, while the central heteroatoms deviate from this plane by 0.848(O4) and 0.349 Å(O13), respectively.

The cyclohexane moiety has a chair conformation with the average C-C distance 1.527(3) Å and C-C-C

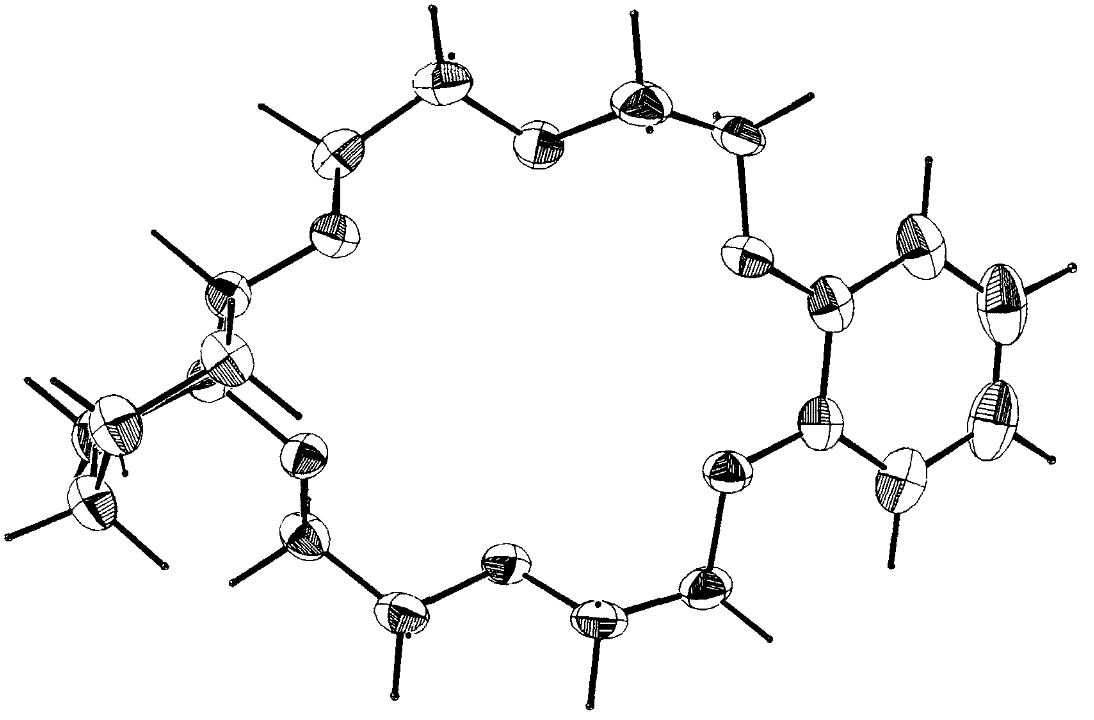


Figure 4 Structure of benzo,cyclohexano-18-crown-6 projected onto the plane of its heteroatoms.

Table 7 Some average characteristics for the host molecule in I and related compounds

Crown ether	*C-O$_{pyr}$*	*C-O$_{diol}$*	*C-O$_{cr}$*	*C-C*	*C-O-C$_{pyr}$*	*C-O-C$_{cr}$*	*C-C-O*	*Ref*
1	1.372	1.432	1.427	1.486	116.6	113.6	110.8	d.c.
2	1.364	1.430	1.426	1.496	117.3	114.3	111.1	[22]
3	1.388	—	1.425	1.467	117.0	113.9	110.8	[23]
4	—	1.437	1.430	1.501	—	111.9	109.3	[24]
	—	(1.440)	(1.422)	(1.492)	—	111.2	109.9	

1-benzo,cyclohexano-18-crown-6, 2-β-D-mannozido-naphtho-18-crown-6, 3-benzo-18-crown-6, 4-dicyclohexano-18-crown-6.

Table 8 Some geometric parameters for guest molecule in I and related compounds

Guest	*C-C-S-N*	*C-C(N)-C*	*C-C(S)-C*	*N-C*	*S-C*	*Ref*
4-$NH_2PhSO_2NH_2$	−12.1 172.0	118.1	119.0	1.358	1.753	d.c.
-"-	98.9 −77.3	121.3	122.0	1.408	1.737	[10]
-"-	87.1 −90.0	118.2	120.8	1.37	1.761	[11]
4-$NH_2(3,5\text{-}Cl_2)Ph\text{-}SO_2NH_2$	78.9 −99.1	115.9	120.3	1.39	1.767	[12]
-"-	110.9 −68.3	114.0	120.0	1.34	1.770	[13]

angle 110.5(2)°. The aromatic fragment is planar to within ±0.037 Å; the average C-C distance is 1.386(3) Å and the endocyclic angle is 120.0(2)°. The dihedral angle between the average plane defined by the macrocyclic heteroatoms and the aromatic moiety is 16°. The accuracy of the experiment is high enough (the final R-factor is 0.041 (R_w = 0.039)) to distinguish the three types of C-O distances in the macrocycle: in the heterocyclic framework (1.427(3) Å), in the cyclohexanediol fragment (1.432(3) Å), and in the pyrocatechol fragment (1.372(2) Å) which in comparison with the same distances in similar compounds are presented in Table 7.

Guest geometry

The guest molecule has an ordinary geometry and is characterized by the average metrical parameters coinciding in general with those found in this molecule in complexes **II** and **III** and in 3,5-dichloro-4-aminobenzenesulphamide (Table 8). The main distinction is found in the conformation of the sulphamidic entity, characterized by torsion angle ϕ along the S-C bond, 172.0°.

Between the individual chains in **I** there are only van der Waals interactions.

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