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Crystal structure of the 1:1 complex between the cis-anti-cis- isomer of dicyclohexano-18-crown-6 and 6-chloro-7-sulphamido-3, 4-dihydro-1, 2, 4-benzo-thiadiazine-1, 1-dioxide

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Crystal structure of the 1:1 complex between the cis-anti-cis- isomer of dicyclohexano-18-crown-6 and 6-chloro-7-sulphamido-3, 4-dihydro-1, 2, 4-benzo-thiadiazine-1, 1-dioxide

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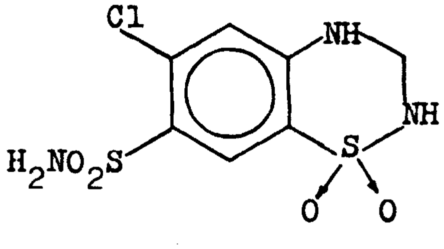
Single crystal X-ray analysis of the 1:1 complex (*I*) between the *cis-anti-cis-* isomer of dicyclohexano-18-crown-6 (*DCH-6B*, host—*H*) and 6-chloro-7-sulphamido-3,4-dihydro-1,2,4-benzo-thiadiazine-1, 1-dioxide (hypothiazide, guest—*G*) is reported. Crystals of (*I*) are triclinic, space group $P\bar{1}$, a=17.838(4), b=14.164(3), c=14.332(3)Å; α=90.51(4), β=110.82(4), γ=97.61(3)° and D_{calc}=1.387 gom^{-3} for Z=4. The final R-factor is 0.087 for 8886 reflections. The crystal packing is characterized by two types of chains where hydrogen bonding joins crown ether and guest entities. The chains differ by acetone molecule inclusion which is H-bonded to one of the guest imino groups. Between the individual chains there are only van der Waals interactions. Host molecules adopt D_{3d} and C_i conformations in the complex.

INTRODUCTION

Hydrogen bond interactions have served as the basis for a multiplicity of novel receptor systems. Crown ethers are among the earliest such models which use directed hydrogen bonds. X-H...O (X=O,N,C) contacts stabilize the proper host-guest complexes or supramolecular assemblies. Host-guest complexes on the base of 18-crown-6 have been studied and described thoroughly enough. A number of the molecular assemblies obtained with its substituted analogue, the *cis-anti-cis* isomer of dicyclohexano-18-crown-6 (*DCH-6B*), have been prepared and analyzed by X-ray crystallography recently[1–3]. At the beginning stage of investigation of the *DCH-6B* complexes with neutral organic molecules, the simplest benzenesulphamide derivatives or its close analogues which contain one[4] or more often two[5–7] H-donor groups to provide the effective functional complementarity between the components were chosen as the guests.

As a rule the sulphamidic H-donor group forms two NH...O hydrogen bonds with the host oxygen atoms divided by the oxyethylene-O-$(CH_2\text{-}CH_2)_2$- moiety. It is the usual mode of coordination[6,7]. Then we tried to complicate the guest entity using bulky molecules. A suitable example, 6-chloro-7-sulphamido-3,4-dihydro-1,2,4-benzo-thiadiazine-1,1-dioxide, consists of two fused six-membered cycles; the aromatic one bearing sulphamidic and chloro-substituents and another heterocyclic moiety where two NH-groups are separated by the methylene fragment (scheme 1).



Scheme 1

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Previously[8] we have discussed the structure of the 1:1 complex between this guest and 18-crown-6 (complex *II*). In *II* the guest fulfills the bridge function and is connected to the host through the sulphamidic SO_2NH_2 and the two imino-groups of -NH-CH_2-NH- moiety. Two host oxygen atoms divided by the oxyethylene fragment participate in the H-bonds with the guest sulphamidic group. The geometric parameters of these interactions are N1A(SO_2NH_2)...O(10) 2.925Å, H1(N1A)...O(10) 1.99Å, angle N1A-H1...O(10) 179°; N1A (SO_2NH_2) ...O(16) 2.935Å, H2(N1A)...O(16) 2.04Å, angle N1A-H2...O(16) 156° (the atomic numbering scheme is that of ref 8). Both imino groups interact with two other oxygen atoms also separated by the oxyethylene fragment: N3A...O(1) 2.936Å, H(N3A)...O(1) 2.04Å, angle N(3A)-H...O(1) 152°; N2A...O(7) 2.901Å, H(N2A)...O(7) 1.90Å, angle N(2A)-H...O(7) 151°. Thus, four of the six host oxygen atoms take part in host-guest interactions with the formation of four single H-bonds. The guest molecule unites two asymmetric 18-crown-6 molecules as a "head (SO_2NH_2) to tail (NH)" type in accordance to scheme: ...*G*(head) - *H* - *G*(tail) - *H* - *G*(head)... Two imino groups separated by the methylene moiety do not fit the 18-membered host cavity exactly. It causes a topological host-guest discrepency manifesting itself in the conformational changes of the heterocyclic framework. The conformation of the heterocyclic ring is characterized by the set of torsion angles *g+g+ag+g+aag +aag+aag+aag+a*, not having been described earlier. This complex to some extent might serve as a predecessor for the title compound.

EXPERIMENTAL

Synthesis of the complex *I*

0.744 g(0.002 mol) *DCH-6B* in 10 mL of acetone was mixed with the solution of hypothiazide (0.297 g, 0.001 mol) at 56°C. Crystals precipitated after cooling to 20°C, were filtered off and air dried. Crystals suitable for X-ray investigation were obtained by recrystallization from acetone. They are soluble in methanol, ethanol, acetone, DMFA, DMSO; mp 172 – 174°C (with the decomposition); ^{1}H NMR, σ 1.49 m and 3.60s (36H, *DCH-6B*) 4.47s (2H, CH2N). Anal. Calc. for (*I*): C, 48.95; H, 6.78; Cl, 5.07; N, 6.01; S, 9.17. Found, C, 49.05; H, 6.69; Cl, 5.01; N, 6.14; S, 9.25.

X-ray data collection, structure determination and refinement

Colourless single crystals were used for X-ray analysis. Preliminary cell parameters were obtained as a part of the alignment process of the crystal on the diffractometer using the angular values of 30 reflections automatically well-centered with a routine which repeatedly improves the angular values to reach the maximum of the peaks until the angles change by not more than 0.001°. The intensity data were collected at room temperature in the range $3<\theta<28°$ on a Siemens AED single crystal diffractometer equipped with a IBM PS2/30 personal computer through a modified version of the Lehmann and Larsen procedure[9 - 10]. MoK_α radiation (λ=0.71069) was employed. One standard reflection was monitored for the compound at regular intervals without significant variations in intensity. Crystal and experimental data are summarized in Table 1. The intensities were corrected for Lorentz and polarization effects but not for absorption. All the calculations were performed with the SHELX76[11] system of programs through the CRYSRULER package[12] using an IBM PS2/80 personal computer. Scattering factors were those of SHELX. The structure was solved by direct methods and refined using the block-matrix least-squares technique. The geometrically constrained hydrogen atoms of the crown ethers, aromatic guest moieties and solvate molecule were placed in calculated positions at 0.95Å from the bonded carbon atoms and refined isotropically, all the rest were not included in the final refinement. The final agreement factor was R=0.087. Final positional parameters are collected in Table 2, bond distances and angles, in Tables 3 and 4. The atomic numbering scheme in the molecules forming the complex (*I*) is given in Figs. 1a-f.

Table 1 Crystal Data and Summary of Intensity Data Collection and Structure Refinement for Complex I

Chemical Formula	$C_{27}O_{10}H_{44}S_2N_3Cl.0.5(CH_3)_2CO$
M.W.	699.3
Space group	$P\bar{1}$
a(Å)	17.838(4)
b(Å)	14.164(3)
c(Å)	14.332(3)
α(deg)	90.51(4)
β(deg)	110.82(4)
γ(deg)	97.61(3)
V(Å^3)	3348.7(3)
Z	4
D_{calc}(gcm^{-3})	1.387(1)
Diffractometer	Siemens AED
Radiation	MoK_α
μ(cm^{-1})	2.99
Scan speed range (°/min)	0.3 – 1.2
Scan width (°)	1.40+0.35tanθ
h-range	-18/16
k-range	-14/10
l-range	0/15
F(000)	1488
No. measured reflections	9969
Condition for obs.	$I>3\sigma(I)$
No. refining reflections	8886
R(hkl)	0.087

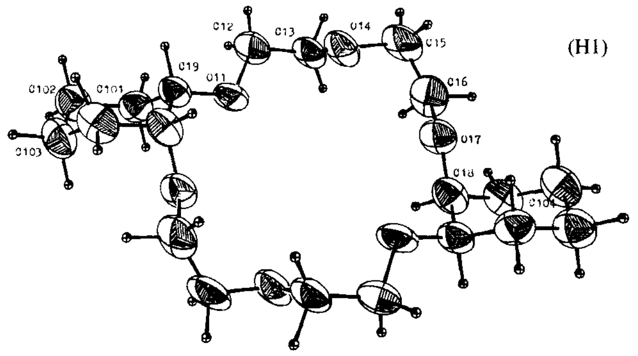

Figure 1a ORTEP diagram of the H1 molecule with the atomic numbering scheme.

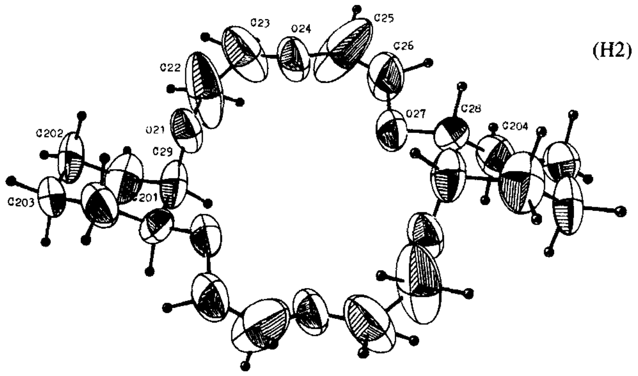

Figure 1b ORTEP diagram of the H2 molecule, with the atomic numbering scheme.

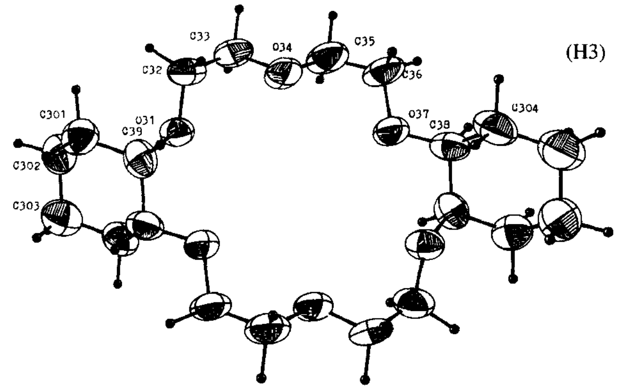

Figure 1c ORTEP diagram of the H3 molecule with the atomic numbering scheme.

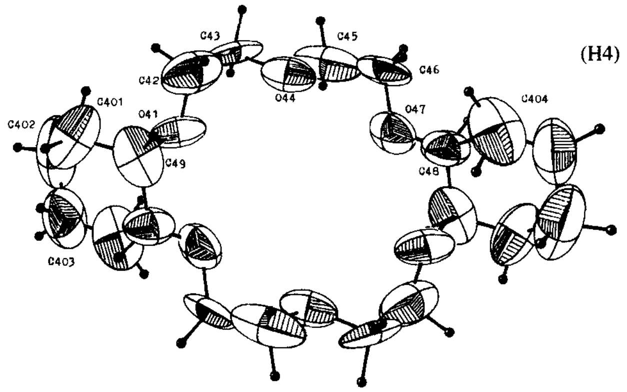

Figure 1d ORTEP diagram of the H4 molecule with the atomic numbering scheme.

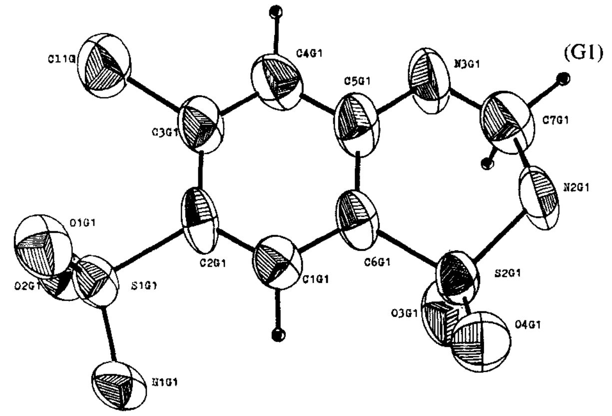

Figure 1e ORTEP diagram of the G1 molecule with the atomic numbering scheme.

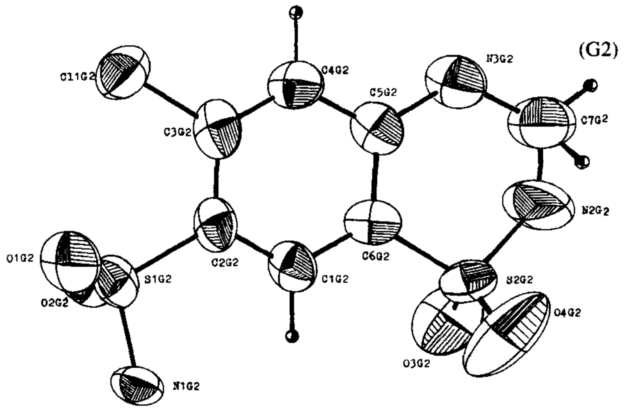

Figure 1f ORTEP diagram of the G2 molecule with the atomic numbering scheme.

Figure 1 ORTEP diagram of the molecules forming complex I. The atoms are represented with 50% probability ellipsoids.

Table 2 Fractional atomic coordinates [x10^4] and Beq for non-hydrogen atoms

Atom	*x/a*	*y/b*	*z/c*	*B[eq]*
S(1G1)	8828(1)	2982(2)	76(2)	4.6(.1)
S(2G1)	6930(1)	2888(2)	-3887(2)	5.1(.1)
Cl(1G1)	7566(2)	1238(2)	311(2)	7.5(.1)
O(1G1)	8543(3)	3264(4)	839(5)	5.8(.3)
O(2G1)	9398(3)	2316(4)	288(5)	6.1(.2)
O(3G1)	7444(3)	2583(5)	-4354(5)	6.8(.3)
O(4G1)	6930(4)	3883(4)	-3738(4)	6.5(.3)
N(1G1)	9225(4)	3921(5)	-289(5)	5.0(.3)
N(2G1)	5989(4)	2401(5)	-4507(5)	5.7(.3)
N(3G1)	5986(5)	1118(5)	-3409(6)	6.7(.4)
C(1G1)	7791(5)	2793(6)	-1894(7)	4.5(.3)
C(2G1)	7969(5)	2460(7)	-980(7)	4.7(.4)
C(3G1)	7419(6)	1678(7)	-852(7)	5.4(.4)
C(4G1)	6791(6)	1254(6)	-1658(8)	5.9(.4)
C(5G1)	6625(6)	1571(7)	-2619(8)	5.5(.4)
C(6G1)	7148(5)	2400(6)	-2728(6)	4.4(.3)
C(7G1)	5846(6)	1351(7)	-4431(8)	6.5(.4)
S(1G2)	6292(1)	-2975(2)	-253(2)	5.2(.1)
S(2G2)	8180(1)	-2741(2)	3720(2)	5.1(.1)
Cl(1G2)	7509(1)	-1184(2)	-515(2)	6.4(.1)
O(1G2)	6590(3)	-3355(5)	-962(5)	6.5(.3)
O(2G2)	5762(3)	-2275(4)	-568(5)	7.2(.3)
O(3G2)	7555(5)	-2632(6)	4072(6)	10.2(.4)
O(4G2)	8414(5)	-3643(5)	3700(5)	9.2(.3)
N(1G2)	5846(4)	-3835(5)	173(5)	5.1(.3)
N(2G2)	9014(7)	-2076(9)	4397(7)	14.0(.6)
N(3G2)	9075(4)	-956(5)	3228(6)	5.6(.3)
C(1G2)	7332(5)	-2743(6)	1719(7)	4.5(.3)
C(2G2)	7135(5)	-2422(6)	778(6)	4.4(.4)
C(3G2)	7670(5)	-1605(7)	644(7)	4.9(.4)
C(4G2)	8281(5)	-1143(6)	1455(7)	4.9(.4)
C(5G2)	8463(5)	-1454(6)	2431(7)	4.4(.4)
C(6G2)	7961(5)	-2282(6)	2542(7)	4.2(.3)
C(7G2)	9243(7)	-1234(10)	4226(8)	8.0(.5)
O(11)	10360(3)	4066(4)	-1324(4)	5.5(.2)
C(12)	11061(6)	3596(8)	-944(8)	6.3(.4)
C(13)	11294(5)	3486(7)	120(8)	5.4(.4)
O(14)	11571(3)	4397(5)	637(5)	5.7(.2)
C(15)	11926(6)	4347(8)	1691(10)	7.2(.5)
C(16)	11352(7)	4158(7)	2195(8)	7.2(.5)
O(17)	10945(4)	4984(4)	2199(4)	5.4(.2)
C(18)	10219(6)	4763(7)	2442(7)	5.4(.3)
C(19)	9844(5)	5648(7)	2329(7)	4.7(.3)
C(101)	10341(6)	6432(6)	3084(8)	5.1(.4)
C(102)	10563(6)	6125(7)	4169(8)	6.2(.4)
C(103)	10928(6)	5223(8)	4268(8)	6.1(.4)
C(104)	10419(6)	4429(6)	3492(8)	5.9(.4)
O(21)	6129(4)	-4909(6)	2071(5)	6.6(.3)
C(22)	5644(10)	-4632(16)	2569(12)	15(1)
C(23)	5231(11)	-3917(14)	2304(11)	11.8(.8)
O(24)	4896(4)	-3596(5)	1384(5)	7.1(.3)
C(25)	4077(10)	-3555(21)	1081(16)	22(1)
C(26)	3519(8)	-3802(13)	311(12)	11.0(.8)
O(27)	3668(4)	-4314(5)	-439(6)	7.7(.3)
C(28)	3357(7)	-3939(7)	-1395(9)	6.9(.4)
C(29)	3890(6)	-4101(10)	-1956(9)	7.0(.4)
C(201)	3547(8)	-3668(9)	-3001(10)	8.8(.5)
C(202)	2682(7)	-4070(8)	-3576(8)	7.6(.5)
C(203)	2179(7)	-3934(9)	-2980(9)	8.0(.5)
C(204)	2485(7)	-4347(8)	-1962(9)	7.3(.5)
O(31)	9988(3)	-772(4)	-2948(4)	5.0(.2)
C(32)	10314(7)	-1641(6)	-2906(8)	6.1(.4)
C(33)	11117(6)	-1449(8)	-3055(8)	6.7(.4)
O(34)	10956(4)	-1305(5)	-4072(5)	6.4(.3)
C(35)	11677(6)	-1081(8)	-4268(10)	7.8(.5)
C(36)	11525(6)	-1036(8)	-5333(9)	6.7(.5)
O(37)	11094(3)	-289(4)	-5773(5)	5.9(.3)
C(38)	11187(5)	-21(7)	-6674(9)	5.4(.4)
C(39)	10858(6)	925(7)	-6948(8)	5.4(.4)
C(301)	10956(6)	1277(7)	-7885(9)	6.0(.4)
C(302)	10585(6)	531(9)	-8752(8)	7.3(.5)
C(303)	10937(7)	-414(9)	-8500(10)	7.7(.5)
C(304)	10827(7)	-772(7)	-7542(10)	6.6(.5)
O(41)	4997(5)	-494(5)	7123(6)	8.7(.3)
C(42)	5253(13)	-1405(12)	7175(12)	12.6(.9)
C(43)	6025(10)	-1351(9)	7080(11)	9.6(.7)
O(44)	5920(4)	-1280(5)	6022(7)	8.2(.3)
C(45)	6600(10)	-1106(12)	5855(17)	13.4(.9)
C(46)	6528(9)	-1237(10)	4853(15)	10.3(.8)
O(47)	6085(5)	-504(6)	4275(8)	9.2(.5)
C(48)	6123(9)	-381(10)	3413(13)	8.8(.7)
C(49)	5893(9)	626(12)	2971(13)	10.9(.7)
C(401)	6051(10)	830(12)	1996(14)	11.7(.8)
C(402)	5605(13)	40(25)	1243(13)	18(1)
C(403)	5888(13)	-926(19)	1679(16)	14(1)
C(404)	5763(10)	-1154(12)	2542(18)	13.2(.9)
O(1A)	4620(4)	3486(5)	5343(6)	8.4(.4)
C(1A)	3325(6)	3883(8)	4566(9)	8.9(.6)
C(2A)	4144(7)	3774(7)	4589(9)	6.4(.5)
C(3A)	4320(8)	4047(9)	3700(11)	10.8(.7)

DISCUSSION

The overall system of interactions

The crystal is built of centrosymmetric *DCH-6B* molecules occupying in the unit cell four positions around the inversion centers: *(1,1/2,0)*, *(H1)*; *(1/2,-1/2,0)*, *(H2)*; *(1,0,-1/2)*, *(H3)*; *(1/2,0,1/2)*, *(H4)*. Hypothiazide and acetone molecules are in general positions in the ratio *H:G:sol.=1:1:0.5*. Two types of host-guest chains with alternating component locations are formed:

- H1 - G1 - H4 - (Fig.2)
|
OC $(CH_3)_2$

and - H2 - G2 - H3 - (Fig.3)

They are distinguished by the solvate acetone molecule being H-bonded with the guest (Fig. 2) in one of them (chain I). The N2G1...01A distance is 3.00(1)Å. The guest carries out a bridge function in both chains, joining to two crystallographically distinct host molecules by sulphamidic and one imino group, the character of the host-guest interactions being rather similar. Both chains are built by the "head to head" and "tail to tail" manner with alteration of the *G-H-G* moieties coordinated by these two types. This is the principal difference in the (*I*) and (*II*) architecture. The guest imino group forms one shortened N...O contact. The distances are N(3G1)...O(41)=2.97(1)Å (chain I) and N(3G2)... O(31)=2.981(9)Å (chain II) (Fig. 3). The sulphamidic group participates in three shortened N...O contacts with the same host O-atoms in both chains. The N...O distances are N(1G1)...O(11)=2.893(9)Å, N(1G1)...O(14)*

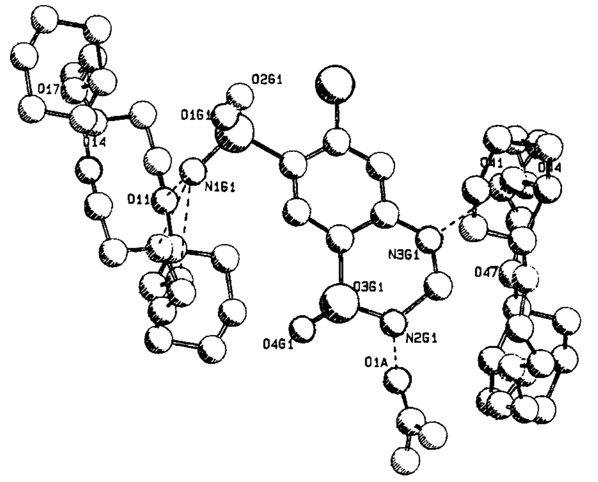

Figure 2 The fragment of the chain - *H1* - $\underset{OC(CH_3)_2}{G1}$ - *H4* - with the indicating of the shortest N. . .O contacts and the partial atom (N and O) denotement.

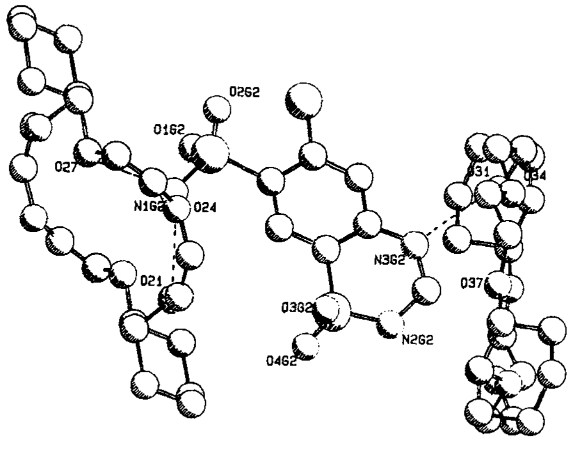

Figure 3 The fragment of the chain - *H2* - *G1* - *H3* - with the indicating of the shortest N. . .O contacts and the partial atom (N and O) denotement.

=2.89 (1)Å, and N(1G1)...O(17)*=3.099(9)Å in chain I and N(1G2)...O(21) = 3.04(1)Å, N(1G2)...O(24)* = 2.86(1)Å, and N(1G2)...O(27) = 2.85(1)Å in chain II (Fig. 3). The independent structural unit consists of two different host and one guest entities. Thus, if the $G\text{-}H_n\text{-}G$ moieties could be picked out from the chain, it appeared to be that for n=3,4 they were stabilized by only two N...O contacts, while for n=1,2 there were six such interactions. It could not be stated unequivocally which of them were the true hydrogen bonds because of the lack of localized H-atoms of guest functional groups. N...O distances for the sulphamidic group are rather similar in (*I*) and (*II*), while for the imino groups they are somewhat shorter in complex *II*. The reciprocal host-guest arrangement is characterized by dihedral angles between the average planes through the heteroatoms of the crown ether and guest aromatic rings collected in Table 5. Guest entities are in a perching mode above the proper cavity with which they are connected by the hydrogen bonds. The deviations of the N-atoms from the average

Table 3 Bond distances (Å)

Hypothiazide molecules

Atoms	*N=1*	*N=2*
S(1GN) – O(1GN)	1.434(8)	1.434(8)
S(1GN) – O(2GN)	1.432(6)	1.427(6)
S(1GN) – N(1GN)	1.606(7)	1.611(7)
S(1GN) – C(2GN)	1.795(7)	1.775(7)
S(2GN) – O(3GN)	1.419(7)	1.401(10)
S(2GN) – O(4GN)	1.424(6)	1.400(8)
S(2GN) – N(2GN)	1.643(6)	1.622(10)
S(2GN) – C(6GN)	1.736(9)	1.747(10)
Cl (1N) – C(3GN)	1.73(1)	1.70(1)
N(2GN) – C(7GN)	1.48(1)	1.26(2)
N(3GN) – C(5GN)	1.36(1)	1.37(1)
N(3GN) – C(7GN)	1.44(1)	1.42(1)
C(1GN) – C(2GN)	1.33(1)	1.36(1)
C(1GN) – C(6GN)	1.37(1)	1.38(1)
C(2GN) – C(3GN)	1.43(1)	1.45(1)
C(3GN) – C(4GN)	1.35(1)	1.36(1)
C(4GN) – C(5GN)	1.39(2)	1.40(1)
C(5GN) – C(6GN)	1.44(1)	1.42(1)

Dicyclohexano-18-crown-6 molecules

Atoms	*N=1*	*N=2*	*N=3*	*N=4*
O(N1) – C(N2)	1.43(1)	1.39(2)	1.42(1)	1.41(2)
C(N2) – C(N3)	1.44(2)	1.31(3)	1.51(2)	1.42(3)
C(N3) – O(N4)	1.41(1)	1.35(1)	1.40(1)	1.46(2)
O(N4) – C(N5)	1.42(1)	1.37(2)	1.41(2)	1.31(2)
C(N5) – C(N6)	1.44(2)	1.20(2)	1.45(2)	1.40(3)
C(N6) – O(N7)	1.45(1)	1.41(2)	1.41(1)	1.46(2)
O(N7) – C(N8)	1.45(1)	1.42(1)	1.40(2)	1.27(2)
C(N8) – C(N9)*	1.48(1)	1.48(2)	1.53(1)	1.60(2)
C(N8) – C(NO4)	1.51(1)	1.50(1)	1.52(2)	1.54(2)
C(N9) – C(N01)	1.49(1)	1.56(2)	1.49(2)	1.54(3)
C(N9) – O(N1)	1.43(1)	1.40(2)	1.45(1)	1.53(2)
C(N01) – C(N02)	1.54(2)	1.49(2)	1.51(2)	1.47(3)
C(N02) – C(N03)	1.49(2)	1.46(2)	1.54(2)	1.58(4)
C(N03) – C(N04)*	1.52(1)	1.51(2)	1.53(2)	1.36(4)
O(1A) – C(2A)	1.22(1)			
C(1A) – C(2A)	1.47(2)			

*symmetry operations: 2-x,1-y,-z for H1; 1-x,-1-y,-z for H2; 2-x,-y,-1-z for H3; 1-x,-y,1-z for H4 planes of the six O-atoms are given in Table 5, as well. Between the chains only van der Waals interactions are realized. The complex crystal packing is shown in Fig. 4.

Conformational host peculiarities

DCH-6B, as the substituted analogue of 18-crown-6, adopts as a rule similar conformations in host-guest complexes. Frequently, they are pseudo-D_{3d} and C_i-symmetry. Pseudo-D_{3d}-symmetry is described by the following set of torsion angles: $(ag{+}aag{-}aag{+}a)_2$. It has been found for *DCH-6B* in its complexes with metals[13,14], aminosulfuric acid zwitter-ion[15], hydroxonium ion[16] etc. C_i-symmetry for 18-crown-6 and *DCH-6B* is characterized by two corner fragments (the place of the meeting of two *gauche*-bonds) with the set of torsion angles: *ag-ag-g-aag+aag+ag+g+aag-a*. Contrary to 18-crown-6, in the *DCH-6B* moiety there are the "principal points" in the form of cyclohexano-substituents. So the positions of the corner fragments with reference to these moieties could be different. In complex *I DCH-6B* conformations are trivial for that complex type: C_i and D_{3d} (Figs. 1a-d). Nevertheless there are some peculiarities to be underlined.

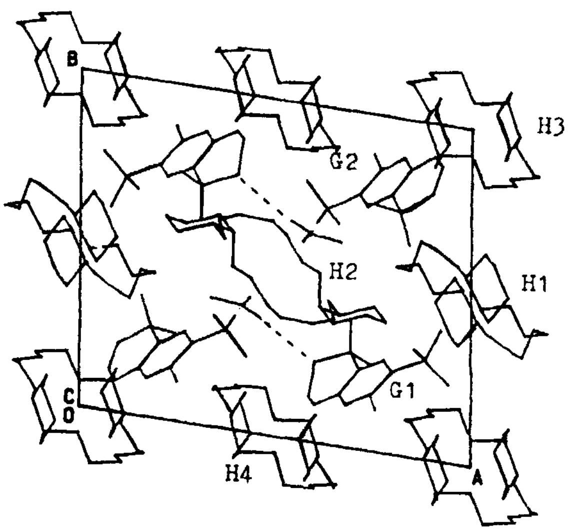

Figure 4 Packing of the complexes I in the unit cell on the plane xy.

Table 4 Bond angles (°)

Hypothiazide molecules *Atoms*	*N=1*	*N=2*
N(1GN) -S(1GN) -C(2GN)	106.6(5)	106.6(4)
O(2GN) -S(1GN) -C(2GN)	106.0(5)	105.7(5)
O(2GN) -S(1GN)-N(1GN)	107.3(4)	108.0(4)
O(1GN) -S(1GN) -C(2GN)	108.3(5)	108.3(5)
O(1GN) -S(1GN)-N(1GN)	108.5(5)	109.5(5)
O(1GN) -S(1GN)-O(2GN)	119.5(5)	118.2(5)
N(2GN) -S(2GN) -C(6GN)	103.2(4)	103.2(5)
O(4GN) -S(2GN) -C(6GN)	107.5(4)	109.6(5)
O(4GN) -S(2GN)-N(2GN)	107.7(5)	103.4(6)
O(3GN) -S(2GN) -C(6GN)	108.9(5)	109.4(5)
O(3GN) -S(2GN)-N(2GN)	109.4(5)	110.7(6)
O(3GN) -S(2GN)-O(4GN)	119.0(5)	119.3(6)
S(2GN) -N(2GN) -C(7GN)	113.5(7)	125.4(9)
C(5GN) -N(3GN) -C(7GN)	122.5(9)	121.9(9)
C(2GN) -C(1GN) -C(6GN)	124.5(9)	123.2(9)
S(1GN) -C(2GN) -C(1GN)	122.8(8)	122.8(7)
C(1GN) -C(2GN) -C(3GN)	117.4(9)	116.7(8)
S(1GN) -C(2GN) -C(3GN)	119.8(7)	120.5(7)
Cl(1N) -C(3GN) -C(2GN)	121.0(8)	120.6(7)
C(2GN) -C(3GN) -C(4GN)	120(1)	119.8(9)
Cl(1N) -C(3GN) -C(4GN)	119.1(8)	119.5(8)
C(3GN) -C(4GN) -C(5GN)	123(1)	123.1(9)
N(3GN) -C(5GN) -C(4GN)	120.7(9)	121.0(8)
C(4GN) -C(5GN) -C(6GN)	116.9(9)	116.3(9)
N(3GN) -C(5GN) -C(6GN)	122.4(9)	122.6(9)
C(1GN) -C(6GN) -C(5GN)	118.3(8)	120.6(9)
S(2GN) -C(6GN) -C(5GN)	119.3(7)	118.9(7)
S(2GN) -C(6GN) -C(1GN)	122.4(7)	120.4(7)
N(2GN) -C(7GN) -N(3GN)	110.9(8)	121(1)

Dicyclohexano-18-crown-6 molecules

Atoms	*N=1*	*N=2*	*N=3*	*N=4*
C(N9)- O(N1)- C(N2)	116.4(6)	115.0(8)	112.5(6)	108.7(9)
O(N1)- C(N2)- C(N3)	111.7(9)	123(2)	109.3(8)	111(1)
C(N2)- C(N3)- O(N4)	109.4(9)	129(2)	107.8(9)	109(1)
C(N3)- O(N4)- C(N5)	113.0(8)	115(1)	111.5(9)	114(1)
O(N4)- C(N5)- C(N6)	115(1)	133(2)	112(1)	115(1)
C(N5)- C(N6)- O(N7)	110.8(9)	118(2)	114(1)	109(1)
C(N6)- O(N7)- C(N8)	113.3(8)	113(1)	113.8(8)	117(1)
O(N7)- C(N8)- C(N9)*	106.4(8)	109(1)	108.7(9)	115(1)
O(N7)- C(N8)- C(N04)	111.2(9)	112.5(9)	115.5(9)	123(1)
C(N9)- C(N8)- C(N04)	111.4(9)	112(1)	111.8(9)	108(1)
C(N8)*-C(N9)- O(N1)	110.2(8)	108(1)	107.4(8)	99(1)
C(N8)*-C(N9)- C(N01)	113.3(9)	108(1)	112.2(9)	114(1)
C(N01) -C(N9)- O(N1)	112.8(8)	111(1)	111.2(9)	116(1)
C(N9) -C(N01)- C(N02)	112.7(8)	113(1)	112(1)	109(2)
C(N01) -C(N02)- C(N03)	109.8(9)	110(1)	112(1)	109(2)
C(N02) -C(N03)- C(N04)*	113.9(9)	113(1)	110(1)	115(2)
C(N8) -C(N04)- C(N03)*	111.2(9)	111(1)	112.1(9)	116(2)

In the chain—*H1*—*G1*—*H4*—
|
$OC(CH_3)_2$

the hypothiazide molecule binds host molecules having different symmetry: C_i(*H1*) and D_{3d}(*H4*). The corresponding torsion angles along the heterocyclic frame-

Table 5 Selected Least-Square Planes with Deviations(Å) and Dihedral Angles (°)

Plane 1.	0(11)	-0.26	O(14)	0.23	O(17)	-0.23	O(11)*	0.26
	O(14)*	-0.23	O(17)*	0.23	N1G1	-1.74		
Plane 2.	O(21)	-0.29	O(24)	0.28	O(27)	-0.33	O(21)*	0.29
	O(24)*	-0.28	O(27)*	0.33	N1G2	1.87		
Plane 3.	O(31)	-0.15	O(34)	0.16	O(37)	-0.17	O(31)*	0.15
	O(34)*	0.16	0(37)*	0.17	N2G2	-1.43		
Plane 4.	O(41)	-0.05	O(44)	0.05	O(47)	-0.07	O(41)*	0.05
	O(44)*	0.05	O(47)*	0.07	N3G1	1.75	N2G1	1.01
Plane 5.	C(1G1)	-0.01	C(2G1)	0.03	C(3G1)	-0.03	C(4G1)	0
	C(5G1)	0.02	C(6G1)	-0.02				
Plane 6.	C(1G2)	0.02	C(2G2)	-0.03	C(3G2)	0.03	C(4G2)	-0.01
	C(5G2)	-0.01	C(6G2)	0				

Dihedral angles (deg)

1 – 2	14.4	2 – 3	131.1	4 – 2	131.5
1 – 3	142.1	2 – 6	87.5	4 – 3	2.0
1 – 4	142.0	3 – 6	79.2	4 – 5	78.7
1 – 5	100.1	5 – 6	2.6		

Planes 1 – 4 are through the proper host oxygen atoms.

work are given in Table 6. *H1* is described by C_i-symmetry with the "corner fragments" displaced from the cyclohexane-substituents along the heterocyclic chain at the C15(C15*) atoms. *Gauche*-torsion angles are in the expected range of 60(1) – 71(1)°, anti-torsion angles are rather normal as well, 147.7(7) – 175.2(8)°. Previously the same type of macrocyclic symmetry was found in the *DCH-6B* complexes with 4-methylbenzenesulphamide[2], 2-methylbenzenesulphamide[17], and 4-nitrobenzenesulphamide[18]. It is characterized by the distortion of the macrocycle from the elliptic one as in the complexes of *DCH-6B* with 4-aminobenzenesulpamide[5] and 2,4-dinitroaniline[4]. The 0...0 distance, 5.219(9)Å, between one pair of cyclohexanediolic oxygen atoms, 0(11)...0(11)*, is diminished in comparison with two others which are 0(14)...0(14)*, 5.743(9)Åand 0(17)...0(17)*, 6.003(9)Å. *H3* and *H4* molecules are characterized by pseudo-D_{3d} symmetry. The meaning of the C-C torsion angles are in limits 59(1) – 78(1)°, and C-O torsion angles are in the range 159(1) – 178(1)°. However, the D_{3d} conformation is somewhat distorted here in comparison with that found for *DCH-6B* and *18-crown-6* in their metal complexes. This is manifested in the scattering of trans-annular 0...0 distances which deviate from the equidistant ones. For *H3* and *H4* they are 0(31)...0(31)*, 6.306(9)Å; 0(34)...0(34)*, 5.426(9)Å; 0(37)...0(37)*, 5.270(9)Å; 0(41)...0(41)*, 6.260(9)Å; 0(44)...0(44)*, 5.386(9)Å; 0(47)...0(47)*, 5.336(9)Å. The increased 0...0 distances are between oxygen atoms taking part in host-guest interactions. The *H2* molecule is rather distorted. It is connected with partial atom disorder (see Table 2). This results in the unusual molecular geometry and conformation. Thus, the C-C torsion angles in the independent part of the molecule are 6, 31, and 62°, and the C-O torsion angles are in the interval 124 – 179°, being decreased as well. The limits of coplanarity for O-atoms in

Table 6 Selected Torsion Angles (deg) in Complex I

Crown ether molecules

Angle, N	N=1	N=2	N=3	N=4
CN9-ON1-CN2-CN3	-170(1)	141(1)	-166(1)	-169(1)
ON1-CN2-CN3-ON4	-67(1)	31(3)	-75(1)	-78(2)
CN2-CN3-ON4-CN5	-171(1)	124(2)	178(1)	172(1)
CN3-ON4-CN5-CN6	-79(1)	-134(3)	173(1)	167(1)
ON4-CN5-CN6-ON7	-70(1)	6(4)	65(1)	68(2)
CN5-CN6-ON7-CN8	164(1)	-131(2)	159(1)	165(2)
CN6-ON7-CN8-CN9	-175(1)	148(1)	-167(1)	-161(1)
ON7-CN8-CN9-ON1	60(1)	62(1)	-59(1)	-64(2)
CN2-ON1-CN9-CN8	148(1)	-179(1)	167(1)	160(1)

Hypothiazide molecules

	N=1	N=2
N2-S2-C6-C5	15(1)	-5(1)
C6-S2-N2-C7	-48(1)	25(1)
C5-N3-C7-N2	-42(1)	21(2)
S2-C6-C5-N3	4(1)	-5(1)
C6-C5-N3-C7	8(2)	-1(1)
N3-C7-N2-S2	63(1)	35(2)

all host molecules are given in Table 5. The *H3* and *H4* molecules are rather flattened in comparison with 18-crown-6 in the same conformation. Geometric host parameters are similar for all molecules except the *H2* molecule (see Tables 3,4).

Guest peculiarities

There are two independent guest molecules (*G1* and *G2*) in (*I*) (Fig. 1ef). The aromatic moieties are rather similar: they are practically flat. The limits of the C-atoms coplanarity are given in Table 5. The average C-C distances are 1.39(1)Å(*G1*) and 1.40(1)Å(*G2*). The endocyclic angles are in the range 116.9(9) – 124.5(9)° for *G1* and 116.3(9) – 123.2(9)° for *G2*. This scattering is connected with the different nature of the substituents in the cycle and is in accordance with[8,19]. The two molecules are essentially distinguished by the heterocycle geometry. In *G1* it is similar to that found for guest in complex *II*. All the bond distances and angles are close to the standard values. In *G2* the bond distance N2-G7=1.265(18)Å is closer to the double bond as are the angles N2-C7-N3, 121(1)°, and S2-N2-C7, 125.4(9)°. We consider the statistical atom disorder as the probable reason of this phenomenon. The increased meanings of the thermal vibration parameters for the atoms in this fragment confirm this supposion (Table 2). Corrections on the thermal vibration lead to bond lengths and angles which are close to those found in *G1*. The conformational guest mobility is characterized by the distortion of a flexible heterocyclic six-membered cycle and described by the torsion angles given in Table 6.

CONCLUSION

1. Inculcation of cyclohexane substituents in the 18-crown-6 molecule reduces its cycle mobility and the ability to fit to the guest molecule. It manifests in the *DCH-6B* impossibility to react simultaneously with the both imino groups of the hypothiazide (as it was in the corresponding complex of 18-crown-6).

2. Conformational host changes are stipulated by the number and nature of NH...O interactions in the process of complex formation.

3. The second guest molecule taking no part by its second imino group in the N...O interactions neither with the host, nor with the solvate (acetone) molecule, appeared to be partially disordered with the distorted geometry of its six-membered heterocycle.

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