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Crystal Structures of Inclusion Compounds of 4-Aminobenzenesulfamidine (Sulfaguanidine) with Two Dicyclohexano-18-crown-6 Isomers

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Abstract. The crystal structures of inclusion compounds of 4-aminobenzenesulfamidine (sulfaguanidine) (L) with two dicyclohexano-18-crown-6 (DCH-6) isomers **A**(*cis-syn-cis*) and **B**(*cis-anti-cis*) have been determined by X-ray methods. The complexes exhibit 1:2 host–guest ratios. In fact the complex of isomer **A** is formulated as $[DCH\text{-}6^{A}.[L]H_2O]L$ (complex **I**), while that of isomer **B** is $DCH\text{-}6^{B}L_2$ (complex **II**).

In the crystals, host and guests are connected by O—H···O and N—H···O bonds.

Key words. Crown ether, dicyclohexano-18-crown-6, crystal structure, 4-aminobenzenesulfamidine.

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1. Introduction

In order to understand chemical and biochemical processes it is important to study neutral molecular complexes of the host–guest type. Macrocyclic molecules with different donor atom species often act as a host [1], the best known being the crown ethers. The structure of host–guest complexes with 18-crown-6 [2–3] has been studied in detail. Conformation and symmetry transformations of the crown ether take place during the formation of the complexes. The crown ether symmetry generally becomes D_{3d} or C_i, depending on the geometry of the guest proton donor groups and on the host–guest ratios. The presence of rigid aromatic systems in the dibenzo-18-crown-6 molecule hinders the formation of stable host–guest complexes. Within the crown ethers a particular place is occupied by dicyclohexano-18-crown-6, (DCH-6), where different molecular complexes can be formed depending on the particular isomers used [4]. The fused six-membered rings introduce additional rigid configurational constraints into the macrocyclic polyether ring [5]

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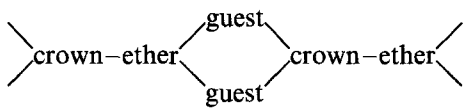
similar to the effect of introducing a benzene ring [6]. On the other hand, there is a possibility in this system of *cis-trans* isomerism at the two bridge bonds [4]. Five isomers are available for DCH-6: **A**, *cis-syn-cis*; **B**. *cis-anti-cis*; **C**. *trans-syn-trans*; **D**. *trans-anti-trans* and **E**. *trans-anti-cis*. During the formation of complexes by some of the five isomers of DCH-6 it is essential to block the ether–oxygen atoms by the cyclohexane groups. In the malononitrile complexes with the **A** and **B** DCH-6 isomers a dependence of the host–guest ratio (1 : 1 for isomer **A** and 2 : 1 for isomer **B** respectively) according to the isomer can be observed [7].

We have already studied [8, 9] the structure of the complexes formed between these two macrocyclic isomer compounds (**A** and **B**) with aminosulfonic acid and with its derivatives. Aminosulfonic acid forms complexes with both isomers with a ratio of 1 : 1. The framework of the crown–ether in both cases has D_{3d}-symmetry due to the ion-dipole interaction between the $^{-}O_3SNH_3^{+}$ zwitter ion and the crown–ether.

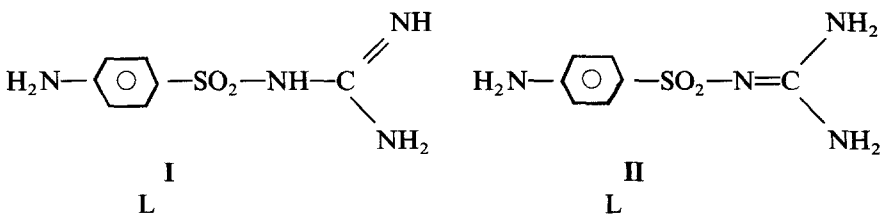
In the isomer **A** complex, aminosulfonic acid is at the distal side with respect to the cyclohexyl groups. 4-Aminobenzenesulfamide, $NH_2PhSO_2NH_2$, forms complexes only with isomer **B** [10]. In this case the guest molecule forms a double bridge of the following kind:



and this structure has a polymeric character.

The blocking of one proton of the *p*-aminogroup in 4-aminobenzenesulphamide, with the consequent formation of the 4-acetylamino-benzenesulphamide, leads to the formation, for the **B** isomer, of the molecular complex guest–crown–ether–guest.

We have studied by X-ray diffraction methods the complexes formed by the **A** and **B** isomers with sulfaguanidine.



Both isomers form stable complexes with a crown–ether/ligand ratio of 1 : 2.

2. Experimental

The crystals of **I** and **II** were grown from solutions of **I** and **II** in acetone. The resulting crystals were large, clear and colourless.

Intensity data were collected on a Philips PW1100 diffractometer using the ω-2θ scan technique. A summary of data collection and crystal data of **I** and **II** are given in Table I.

Table I. Experimental data for the crystallographic analyses of the compounds

Compound	I	II
Formula	$C_{34}H_{58}O_{11}N_8S_2$	$C_{34}H_{56}O_{10}N_8S_2$
m.w.	818.98	800.98
Space group	$P\bar{1}$	$P2_1/n$
a/Å	17.063(3)	15.580(8)
b/Å	11.748(2)	11.962(6)
c/Å	10.451(3)	11.202(6)
α/deg	77.41(1)	90.0
β/deg	98.68(3)	102.83(2)
γ/deg	100.56(2)	90.0
V/Å^3	1996(2)	2036(2)
Z	2	2
d_c/g cm^{-3}	1.356	1.307
Temperature/K	294	294
Crystal size/mm^3	0.20 × 0.65 × 0.72	0.30 × 0.75 × 0.55
Diffractometer	Philips PW1100	Philips PW1100
μ/cm^{-1}(MoK_α)	1.885	1.842
Scan speed/deg min^{-1}	3–9	3–9
Scan width/deg	1.40 + 0.35 tan θ	1.40 + 0.35 tan θ
Radiation	MoK_α	MoK_α
θ-range	3–24	3–23
h-range	−18:15	−16:16
k-range	−9:12	0:12
l-range	0:10	0:12
Scan mode	ω-2 θ	ω-2 θ
N of reflections measured	5532	3153
Condition for observed reflection	$I > 2\sigma(I)$	$I > 2\sigma(I)$
N of reflections used in the refinement	3234	1610
N of refined parameters	333	348
$R = \Sigma\|\Delta F\|/\Sigma\|F_0\|$	0.0334	0.0498
$R_w = [\Sigma w(\Delta F)^2/\Sigma w F_0^2]^{1/2}$	0.0363	0.0536
k, $g(w = k[\sigma^2(F_0) + gF_0^2])$	0.31, 3.38.10^{-3}	0.81, 2.65.10^{-3}

Calculations were carried out with SHELX76 system computer programs [11]. Atomic scattering factors for S, O, N, C, H were taken from [12]. For geometrical calculations the program PARST was used [13]. Figures were obtained by using the programs ORTEP [14] and CRYSRULER [15]. The final value of the positional parameters are quoted in Tables IIa and IIb for **I** and **II** respectively.

All non-H atoms were refined anisotropically, H-atoms found from difference electron density maps were included in the refinement as fixed contributions.

3. Discussion

The molecular complex of the *cis-syn-cis* isomer of dicyclohexano-18-crown-6 with sulfaguanidine [DCH—$6^A \cdot L \cdot H_2O$][1] is shown in Figure 1. A fundamental role in its formation is played by the NH···O and OH···O system, shown in Table IV.

Table IIA. Fractional atomic coordinates × 10^4 of **I**

Atom	x/a	y/b	z/c	U_{eq}	Atom	x/a	y/b	z/c	U_{eq}
O(1)	1682(1)	5787(2)	9245(2)	497	O(1A)	10340(1)	909(2)	3899(2)	434
C(2)	1033(2)	6447(3)	8924(3)	468	O(2A)	10879(1)	2223(2)	1956(2)	451
C(3)	1273(2)	7453(3)	7804(3)	450	N(1A)	13796(2)	−748(3)	4194(4)	510
O(4)	1425(1)	7051(2)	6671(2)	445	N(2A)	10179(2)	303(2)	1677(3)	363
C(5)	721(2)	6629(3)	5899(4)	498	N(3A)	9623(2)	−1277(3)	3270(3)	474
C(6)	931(2)	6371(3)	4665(4)	514	N(4A)	9488(2)	−1374(3)	1096(4)	505
O(7)	1280(1)	5319(2)	4975(2)	465	C(1A)	11607(2)	487(3)	3136(3)	357
C(8)	1498(2)	5023(3)	3839(3)	519	C(2A)	11738(2)	−337(3)	4280(4)	412
C(9)	1823(2)	3884(3)	4203(4)	537	C(3A)	12455(2)	−756(3)	4617(4)	413
O(10)	2611(2)	4060(2)	4885(2)	595	C(4A)	13074(2)	−346(3)	3830(4)	393
C(11)	3002(2)	3036(3)	5152(4)	545	C(5A)	12932(2)	460(3)	2660(4)	460
C(12)	2902(2)	2303(3)	6525(4)	490	C(6A)	12214(2)	861(3)	2325(4)	430
O(13)	3182(1)	3057(2)	7463(2)	447	C(7A)	9768(2)	−770(3)	2038(3)	361
C(14)	3156(2)	2446(3)	8811(4)	578	S(B)	4747(1)	7765(1)	7989(1)	435
C(15)	3155(2)	3277(3)	9682(3)	509	O(1B)	5338(1)	7013(2)	8049(3)	537
O(16)	2393(1)	3652(2)	9494(2)	541	O(2B)	5002(2)	9010(2)	7582(3)	599
C(17)	2299(2)	4225(3)	10517(4)	556	N(1B)	3515(3)	6810(4)	13180(4)	743
C(18)	1545(2)	4747(3)	10196(4)	574	N(2B)	3940(2)	7435(2)	7079(3)	424
C(19)	888(2)	6958(4)	10079(4)	633	N(3B)	4107(3)	5460(3)	7157(4)	576
C(20)	1621(3)	7774(4)	10554(4)	654	N(4B)	2908(2)	6074(4)	6461(4)	605
C(21)	1884(2)	8753(3)	9414(4)	666	C(1B)	4459(2)	7530(3)	9577(3)	387
C(22)	2013(2)	8265(3)	8234(4)	550	C(2B)	4185(2)	8401(4)	10012(4)	522
C(23)	3867(2)	3431(3)	4906(4)	608	C(3B)	3892(3)	8162(4)	11219(4)	620
C(24)	4324(2)	2385(4)	5209(4)	736	C(4B)	3852(2)	7045(4)	12015(4)	512
C(25)	4324(2)	1688(3)	6584(4)	668	C(5B)	4145(2)	6180(4)	11581(4)	530
C(26)	3361(2)	1273(3)	6752(4)	608	C(6B)	4443(2)	6411(3)	10383(4)	491
OW(1)	1235(2)	3608(2)	7302(3)	598	C(7B)	3669(2)	6320(3)	6929(3)	402
S(A)	10702(1)	1045(1)	2698(1)	364					

Table IIB. Fractional atomic coordinates × 10^4 of **II**

Atom	x/a	y/b	z/c	U_{eq}	Atom	x/a	y/b	z/c	U_{eq}
O(1)	−1997(2)	10400(3)	9138(3)	674	N(2A)	211(2)	11218(4)	6078(3)	603
C(2)	−2517(3)	9404(4)	8945(5)	592	N(3A)	−259(4)	10884(7)	7906(5)	911
C(3)	−2257(3)	8764(4)	7902(5)	600	N(4A)	−317(3)	9517(5)	6480(6)	801
O(4)	−1326(2)	8556(3)	8149(3)	626	S(A)	765(1)	12303(1)	6519(1)	654
C(5)	−988(4)	7948(6)	9226(6)	677	O(1A)	466(2)	12942(3)	7450(4)	891
C(6)	−75(4)	7594(6)	9232(8)	811	O(2A)	808(2)	12905(3)	5424(4)	952
O(7)	474(2)	8528(3)	9473(3)	782	C(1A)	1838(3)	11839(4)	7180(4)	502
C(8)	1365(4)	8221(6)	9448(6)	968	C(2A)	2368(4)	12445(4)	8110(5)	569
C(9)	1923(5)	9187(7)	9643(7)	999	C(3A)	3223(4)	12123(5)	8592(5)	571
C(10)	−3499(3)	9670(6)	8595(6)	754	C(4A)	3564(3)	11170(4)	8174(4)	537
C(11)	−3741(5)	10281(7)	7398(7)	912	C(5A)	3029(4)	10593(5)	7240(5)	611
C(12)	−3481(4)	9640(8)	6397(7)	881	C(6A)	2183(4)	10904(4)	6744(5)	626
C(13)	−2500(4)	9380(6)	6697(5)	742	C(7A)	−117(3)	10557(5)	6833(4)	616
N(1A)	4411(4)	10841(7)	8640(6)	809					

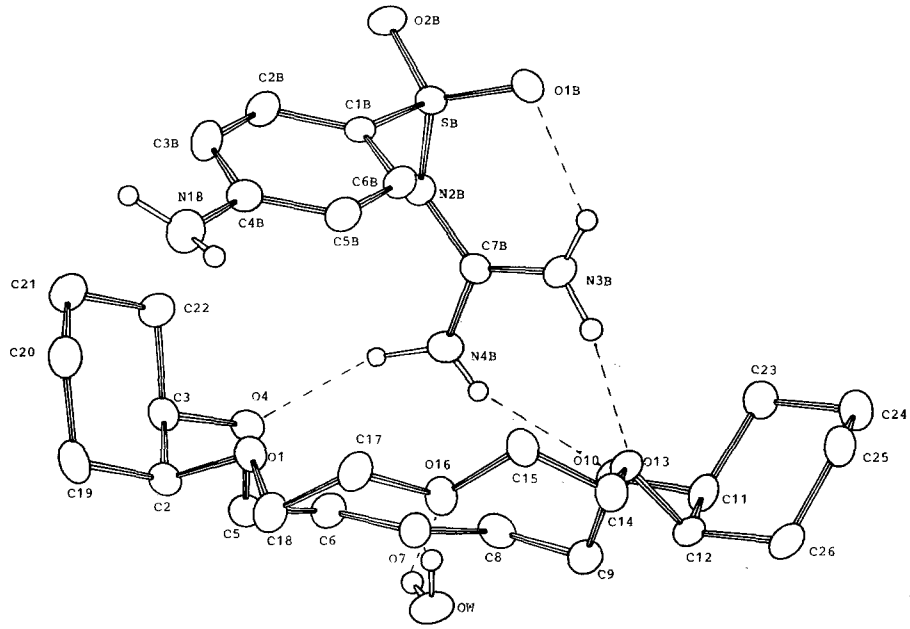


Fig. 1. A view of the molecular structure of **I** with the atomic numbering scheme. H atoms are omitted. Hydrogen bonds are represented by dashed lines. Only the complexed ligand is shown.

In this structure sulfaguanidine is on the side of the crown ring that is proximal to the *syn*-cyclohexyl groups.

In this case, the aminogroup H_2N—Ph in the L molecule does not take part in the interaction with the crown–ether. The L ligand is in the tautomeric form L^{II} with a formal double bond between the C(7) and N(2) atoms. The terminal aminogroups are bound by three H atoms with the ether oxygen atoms in DCH—6 with the parameters indicated in Table IV.

The geometrical parameters of these hydrogen bonds in the molecular complex are similar to the NH—O interactions in crown–ether complexes [10, 16–19]. The sulfaguanidine molecule conformation is stabilized by the intramolecular hydrogen bond N(3B)—H···O1B. The other side of the crown ether is occupied by a water molecule, forming two hydrogen bonds O(W)—H···O(7) = 1.91(4) and O(W)—H···O(16) = 1.88(6) Å.

These two bonds are similar to those present in the complex [DCH—$6^A \cdot H_3O$][ClO_4] [20] and in the complex formed by $HgCl_2$ with hydrated DCH—6^A [21] but the fundamental difference is that these bonds $H_3O^+(H_2O)$ are arranged in a proximal position with respect to the cyclohexyl groups.

A proximal position is also occupied by potassium in the DCH—$6^A \cdot K \cdot$ 2-nitrophenoxide [22] and [DCH—$6^A \cdot K$][$(CN)_2Au$] [23] crystal structures. The guest symmetry in fact influences the configuration and the conformational parameters of the macrocycle. During the formation of the complexes with the metal [22–23] or with the cation (H_3O^+) [18] the distance between the crown ether oxygen atoms is practically equivalent. In the case of transannular bridge formation

O···H—O—H···O, as found in this structure, the cavity in the macrocycle is subjected to a substantial electrical alteration, i.e. the cavity tends to elongate in the direction of the cyclohexyl substituents.

The crown ether conformation in the complex is substantially different (Table III) from that found for the free macrocycle in [24, 25]. In fact the arrangement of the macrocycle O—C—C—O fragments is *gauche*$^+$, *gauche*$^+$, *gauche*$^-$, *gauche*$^-$, *gauche*$^+$, *gauche*$^-$.

It is possible to present the idealized symmetry of isomer **A** as C_2 or C_s [4]. In our case a quasi-planar symmetry is observed. The 'angular' fragments are found in the catechol part of the macrocycle. Interatomic distances in the crown ether (Table III) are normal and the C—O, C—C, and C—C (cyclohexyl) distances remain between the limits found in the literature. The cyclohexyl groups show a chair conformation. In the structure (Figure 2) the ribbon of the single molecular complexes are bound by means of the second sulfaguanidine molecule (Table IV). All three aminogroups of the ligand take part in the formation of H-bonds.

The *cis-anti-cis*-dicyclohexano-18-crown-6 isomer complex with sulfaguanidine [DCH—6^B · L_2]$^{(2)}$. The centrosymmetrical molecular complex which is formed in the case of the *cis-anti-cis* isomer is shown in Figure 3. Its formation, just as in the

Table III. Interatomic distances (Å) and angles (deg) in complex **I**

Atoms	R(Å)	Atoms	R(Å)
O(1)—C(2)	1.423(4)	O(10)—C(11)	1.435(5)
C(2)—C(3)	1.517(4)	C(11)—C(12)	1.520(5)
C(3)—O(4)	1.441(5)	C(12)—O(13)	1.433(4)
O(4)—C(5)	1.416(4)	O(13)—C(14)	1.438(4)
C(5)—C(6)	1.494(6)	C(14)—C(15)	1.473(6)
C(6)—O(7)	1.423(4)	C(15)—O(16)	1.420(5)
O(7)—C(8)	1.424(5)	O(16)—C(17)	1.424(5)
C(8)—C(9)	1.493(6)	C(17)—C(18)	1.488(6)
C(9)—O(10)	1.427(4)	C(18)—O(1)	1.404(4)
C(2)—C(19)	1.530(6)	C(11)—C(23)	1.508(6)
C(19)—C(20)	1.520(5)	C(23)—C(24)	1.524(6)
C(20)—C(21)	1.523(5)	C(24)—C(25)	1.506(6)
C(21)—C(22)	1.528(6)	C(25)—C(26)	1.503(6)
C(22)—C(3)	1.510(5)	C(26)—C(12)	1.516(5)
S(A)—O(1A)	1.446(3)	S(B)—O(1B)	1.444(3)
S(A)—O(2A)	1.434(2)	S(B)—O(2B)	1.435(2)
S(A)—N(2A)	1.590(3)	S(B)—N(2B)	1.587(3)
S(A)—C(1A)	1.747(4)	S(B)—C(1B)	1.752(4)
C(1A)—C(2A)	1.382(5)	C(1B)—C(2B)	1.384(6)
C(2A)—C(3A)	1.370(6)	C(2B)—C(3B)	1.380(7)
C(3A)—C(4A)	1.388(5)	C(3B)—C(4B)	1.388(6)
C(4A)—C(5A)	1.393(5)	C(4B)—C(5B)	1.395(7)
C(5A)—C(6A)	1.363(6)	C(5B)—C(6B)	1.376(6)
C(6A)—C(1A)	1.386(5)	C(6B)—C(1B)	1.397(5)
N(1A)—C(4A)	1.371(5)	N(1B)—C(4B)	1.377(6)
C(7A)—N(2A)	1.332(4)	C(7B)—N(2B)	1.342(5)
C(7A)—N(3A)	1.335(5)	C(7B)—N(3B)	1.324(6)
C(7A)—N(4A)	1.319(5)	C(7B)—N(4B)	1.320(5)

Table III. (continued)

Atoms	Angle (deg)	Atoms	Angle (deg)
C(18)—O(1)—C(2)	114.4(3)	C(9)—O(10)—C(11)	113.5(3)
O(1)—C(2)—C(3)	105.5(3)	O(10)—C(11)—C(12)	112.2(3)
C(2)—C(3)—O(4)	112.8(3)	C(11)—C(12)—O(13)	108.2(3)
C(3)—O(4)—C(5)	113.8(3)	C(12)—O(13)—C(14)	113.4(3)
O(4)—C(5)—C(6)	110.1(3)	O(13)—C(14)—C(15)	110.9(3)
C(5)—C(6)—O(7)	109.5(3)	C(14)—C(15)—O(16)	109.8(3)
C(6)—O(7)—C(8)	112.5(3)	C(15)—O(16)—C(17)	111.7(3)
O(7)—C(8)—C(9)	110.4(3)	O(16)—C(17)—C(18)	110.2(3)
C(8)—C(9)—O(10)	109.8(3)	C(17)—C(18)—O(1)	107.9(3)
O(1)—C(2)—C(19)	112.7(3)	O(10)—C(11)—C(23)	108.4(3)
C(19)—C(2)—C(3)	109.0(3)	C(23)—C(11)—C(12)	113.3(3)
C(2)—C(3)—C(22)	111.6(3)	C(11)—C(12)—C(26)	108.9(3)
C(22)—C(3)—O(4)	108.1(3)	C(26)—C(12)—O(13)	112.5(3)
C(2)—C(19)—C(20)	112.2(3)	C(11)—C(23)—C(24)	111.0(3)
C(19)—C(20)—C(21)	110.1(3)	C(23)—C(24)—C(25)	111.0(4)
C(20)—C(21)—C(22)	112.0(3)	C(24)—C(25)—C(26)	110.3(4)
C(21)—C(22)—C(3)	110.8(3)	C(25)—C(26)—C(12)	111.5(3)
N(1A)—C(4A)—C(3A)	120.3(4)	N(1B)—C(4B)—C(3B)	120.2(4)
N(1A)—C(4A)—C(5A)	121.6(4)	N(1B)—C(4B)—C(5B)	121.9(4)
C(6A)—C(1A)—C(2A)	118.2(4)	C(6B)—C(1B)—C(2B)	119.1(4)
C(1A)—C(2A)—C(3A)	121.0(4)	C(1B)—C(2B)—C(3B)	120.4(4)
C(2A)—C(3A)—C(4A)	120.8(4)	C(2B)—C(3B)—C(4B)	121.2(4)
C(3A)—C(4A)—C(5A)	118.1(4)	C(3B)—C(4B)—C(5B)	118.0(4)
C(4A)—C(5A)—C(6A)	120.6(4)	C(4B)—C(5B)—C(6B)	121.3(4)
C(5A)—C(6A)—C(1A)	121.2(4)	C(5B)—C(6B)—C(1B)	120.1(4)
S(A)—C(1A)—C(2A)	121.7(3)	S(B)—C(1B)—C(2B)	121.4(3)
S(A)—C(1A)—C(6A)	120.1(3)	S(B)—C(1B)—C(6B)	119.3(3)
C(1A)—S(A)—O(1A)	107.2(2)	C(1B)—S(B)—O(1B)	107.2(2)
C(1A)—S(A)—O(2A)	107.2(2)	C(1B)—S(B)—O(2B)	107.5(2)
C(1A)—S(A)—N(2A)	106.3(2)	C(1B)—S(B)—N(2B)	104.8(2)
N(2A)—S(A)—O(1A)	113.2(2)	N(2B)—S(B)—O(1B)	113.7(2)
N(2A)—S(A)—O(2A)	105.4(2)	N(2B)—S(B)—O(2B)	106.7(2)
O(1A)—S(A)—O(2A)	117.0(2)	O(1B)—S(B)—O(2B)	116.3(2)
S(A)—N(2A)—C(7A)	123.3(3)	S(B)—N(2B)—C(7B)	121.6(3)
N(2A)—C(7A)—N(3A)	125.2(3)	N(2B)—C(7B)—N(3B)	125.6(4)
N(2A)—C(7A)—N(4A)	116.8(3)	N(2B)—C(7B)—N(4B)	117.1(4)
N(3A)—C(7A)—N(4A)	118.0(4)	N(3B)—C(7B)—N(4B)	117.3(4)
O(1)—C(2)—C(3)—O(4)	58.5(4)	O(10)—C(11)—C(12)—O(13)	−54.9(4)
C(2)—C(3)—O(4)—C(5)	76.7(4)	C(11)—C(12)—O(13)—C(14)	−177.0(3)
C(3)—O(4)—C(5)—C(6)	173.1(3)	C(12)—O(13)—C(14)—C(15)	−159.0(3)
O(4)—C(5)—C(6)—O(7)	73.7(4)	O(13)—C(14)—C(15)—O(16)	73.6(4)
C(5)—C(6)—O(7)—C(8)	−179.8(3)	C(14)—C(15)—O(16)—C(17)	166.2(3)
C(6)—O(7)—C(8)—C(9)	−177.2(3)	C(15)—O(16)—C(17)—C(18)	172.4(3)
O(7)—C(8)—C(9)—O(10)	−74.0(4)	O(16)—C(17)—C(18)—O(1)	−76.9(4)
C(8)—C(9)—O(10)—C(11)	−173.9(3)	C(17)—C(18)—O(1)—C(2)	−174.6(3)
C(9)—O(10)—C(11)—C(12)	−95.2(4)	C(18)—O(1)—C(2)—C(3)	−174.8(3)

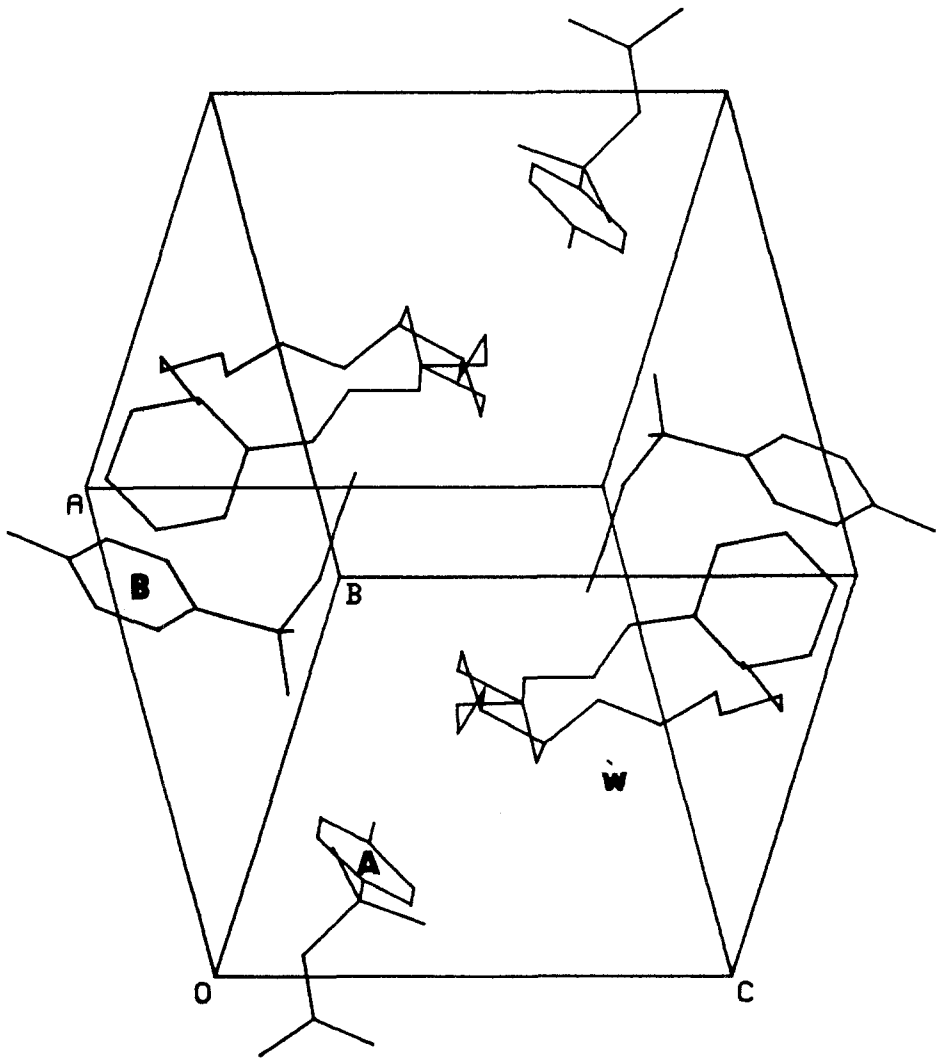


Fig. 2. Representation of the packing of **I** in the unit cell.

preceeding case, takes place thanks to the formation of H-bonds between the amino-groups and the crown ether oxygen atoms.

One of the protons of the NH_2 groups of N(3A) takes part in a bifurcated H-bond between the O(4) and O(7) atoms of the ring (Table VI). In this case the H-bond length becomes 3.285(8) and 3.382(8) Å while the H-bond length in N(4A)—H···O(4) is 2.932(7) Å. In the ligand there is an intramolecular bond of the same kind as that already mentioned.

For the crown ether DCH—6^B the arrangement of the O—C—C—O fragments is *gauche*$^{\pm}$. Ten C—O bonds present an *anti*-, while the remaining two C—O bonds present a *gauche*-conformation (Table V).

Table IV. Hydrogen bond systems in **I**.

Donor (D)	Acceptor (A)	R(D···A) Å	R(D—H) Å	R(H···A) Å	D—H···A deg
O(w)	O(16)[1]	2.793(4)	0.94(6)	1.88(6)	164(5)
O(w)	O(7)[1]	2.798(4)	0.92(4)	1.91(4)	162(4)
N(3B)	O(13)[1]	2.948(4)	0.94(5)	2.03(4)	166(4)
N(3B)	O(1B)[1]	2.712(4)	0.89(5)	2.07(4)	129(4)
N(4B)	O(4)[1]	3.017(5)	1.02(5)	2.05(5)	158(4)
N(4B)	O(10)[1]	3.095(6)	0.77(5)	2.39(5)	152(5)
N(1B)	N(1A)[2]	3.202(7)	0.95(6)	2.27(6)	167(4)
N(1A)	O(2B)[3]	3.129(5)	0.80(4)	2.35(4)	165(4)
N(1A)	N(2B)[4]	3.297(5)	0.87(4)	2.46(4)	161(4)
N(3A)	O(1A)[1]	2.804(4)	0.88(6)	2.13(5)	134(5)
N(3A)	O(1A)[5]	3.071(5)	0.88(6)	2.33(6)	142(5)
N(4A)	N(2A)[4]	2.991(4)	0.86(4)	2.13(4)	177(4)

Symmetrical transformation for A

1. $= x, y, z$ 2. $= x-1, 1+y, 1+z$ 3. $= 2-x, 1-y, 1-z$
4. $= 1+x, -1+y, z$ 5. $= 2-x, -y, 1-z$

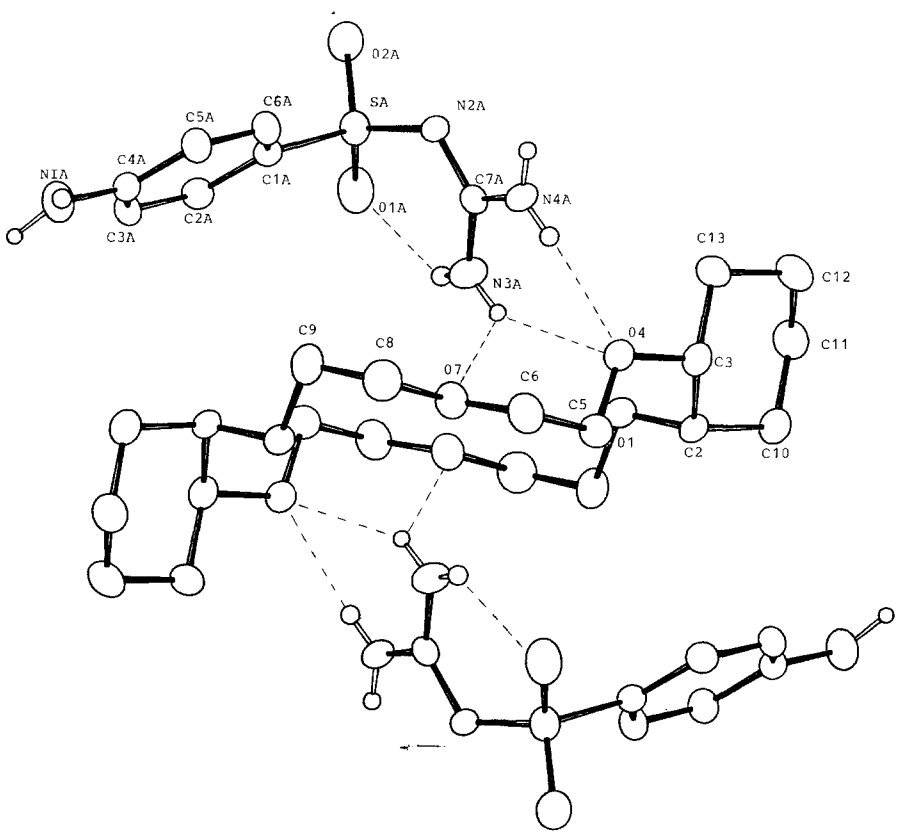


Fig. 3. Structure and numbering scheme of **II**. H atoms are omitted. Hydrogen bonds are represented by dashed lines.

Table V. Interatomic distance (Å) and angles (°) in **II**

Atoms	R(Å)	Atoms	R(Å)
O(1)—C(2)	1.430(6)	S(A)—O(1A)	1.451(5)
C(2)—C(3)	1.524(8)	S(A)—O(2A)	1.437(5)
C(3)—O(4)	1.437(6)	S(A)—N(2A)	1.576(4)
O(4)—C(5)	1.407(7)	S(A)—C(1A)	1.761(4)
C(5)—C(6)	1.483(9)	C(1A)—C(2A)	1.383(7)
C(6)—O(7)	1.396(8)	C(2A)—C(3A)	1.376(7)
O(7)—C(8)	1.442(8)	C(3A)—C(4A)	1.382(8)
C(8)—C(9)	1.433(9)	C(4A)—C(5A)	1.371(7)
O(1)—C(9)*	1.433(8)	C(5A)—C(6A)	1.363(7)
C(2)—C(10)	1.527(7)	C(6A)—C(1A)	1.377(7)
C(10)—C(11)	1.499(10)	N(1A)—C(4A)	1.366(7)
C(11)—C(12)	1.486(12)	C(7A)—N(2A)	1.339(7)
C(12)—C(13)	1.523(9)	C(7A)—N(3A)	1.328(8)
C(3)—C(13)	1.510(8)	C(7A)—N(4A)	1.322(9)
Atoms	**Angles (deg)**	**Atoms**	**Angles (deg)**
C(9)*—O(1)—C(2)	110.7(5)	N(1A)—C(4A)—C(3A)	121.3(5)
O(1)—C(2)—C(3)	107.2(4)	N(1A)—C(4A)—C(5A)	121.3(6)
C(2)—C(3)—O(4)	111.6(4)	C(6A)—C(1A)—C(2A)	118.6(5)
C(3)—C(4)—C(5)	115.1(4)	C(1A)—C(2A)—C(3A)	120.8(5)
O(4)—C(5)—C(6)	109.2(5)	C(2A)—C(3A)—C(4A)	120.6(5)
C(5)—C(6)—O(7)	108.6(5)	C(3A)—C(4A)—C(5A)	117.4(5)
C(6)—O(7)—C(8)	110.2(5)	C(4A)—C(5A)—C(6A)	122.8(6)
O(7)—C(8)—C(9)	110.2(6)	C(5A)—C(6A)—C(1A)	119.7(5)
C(8)—C(9)—O(1)*	110.0(6)	S(A)—C(1A)—C(2A)	120.3(4)
O(1)—C(2)—C(10)	111.5(5)	S(A)—C(1A)—C(6A)	121.1(4)
C(3)—C(2)—C(10)	109.3(5)	C(1A)—S(A)—O(1A)	106.8(2)
C(2)—C(10)—C(11)	111.7(5)	C(1A)—S(A)—O(2A)	107.3(3)
C(10)—C(11)—C(12)	111.6(7)	C(1A)—S(A)—N(2A)	106.0(2)
C(11)—C(12)—C(13)	111.5(6)	N(2A)—S(A)—O(1A)	114.7(3)
C(12)—C(13)—C(3)	109.7(5)	N(2A)—S(A)—O(2A)	105.8(2)
C(2)—C(3)—C(13)	112.6(5)	O(1A)—S(A)—O(2A)	115.6(3)
O(4)—C(3)—C(13)	107.4(4)	S(A)—N(2A)—C(7A)	123.2(4)
		N(2A)—C(7A)—N(3A)	124.2(6)
		N(2A)—C(7A)—N(4A)	117.7(5)
		N(3A)—C(7A)—N(4A)	118.1(6)
O(1)—C(2)—C(3)—O(4)	55.1(5)	C(6)—O(7)—C(8)—C(9)	177.6(6)
C(2)—C(3)—O(4)—C(5)	58.4(6)	O(7)—C(8)—C(9)—O(1)*	66.3(7)
C(3)—O(4)—C(5)—C(6)	168.3(5)	C(2)—O(1)—C(9)*—C(8)*	177.2(5)
O(4)—C(5)—C(6)—O(7)	73.4(6)	C(9)*—O(1)—C(2)—C(3)	−156.7(5)
C(5)—C(6)—O(7)—C(8)	−178.2(5)		

(C(9)*(−x, 2 − y, 2 − z)

The ligand orientation is, relatively to the ring, such that the aminogroup (N(4A) forms a H-bond with the N(2A) atom [−x, 2 − y, 1 − z] (Table VI). In this way it forms a chain along the crystal y-axis. Parallel chains are joined in a framework due to the H-bond N(1A)···O(2A) [1/2 + x, 1/2 + y, 1/2 + z] = 3.008(7) Å (Figure 4).

Interatomic distances within the crown ether have average values for the C—C, C—O, and C—C (cyclohexane) bonds.

Table VI. Hydrogen bond systems in **II**.

Donor (D)	Acceptor (A)	R(D···A) Å	R(D—H) Å	R(H···A) Å	D—H···A deg
N(3A)	O(4)[1]	3.285(8)	0.87(5)	2.51(5)	149(4)
N(3A)	O(1A)[1]	2.803(9)	0.82(5)	2.18(6)	133(5)
N(4A)	O(4)[1]	2.932(7)	0.78(6)	2.17(6)	164(5)
N(4A)	N(2A)[2]	3.037(8)	0.84(6)	2.20(6)	175(5)
N(1A)	O(2A)[3]	3.008(7)	0.93(6)	2.13(6)	158(6)
N(3A)	O(7)[1]	3.382(8)	0.87(5)	2.80(5)	126(4)

Symmetrical transformation for A
$1 = x, y, z$ $2 = -x, 2-y, 1-z$ $3 = 1/2+x, 1/2-y, 1/2+z$

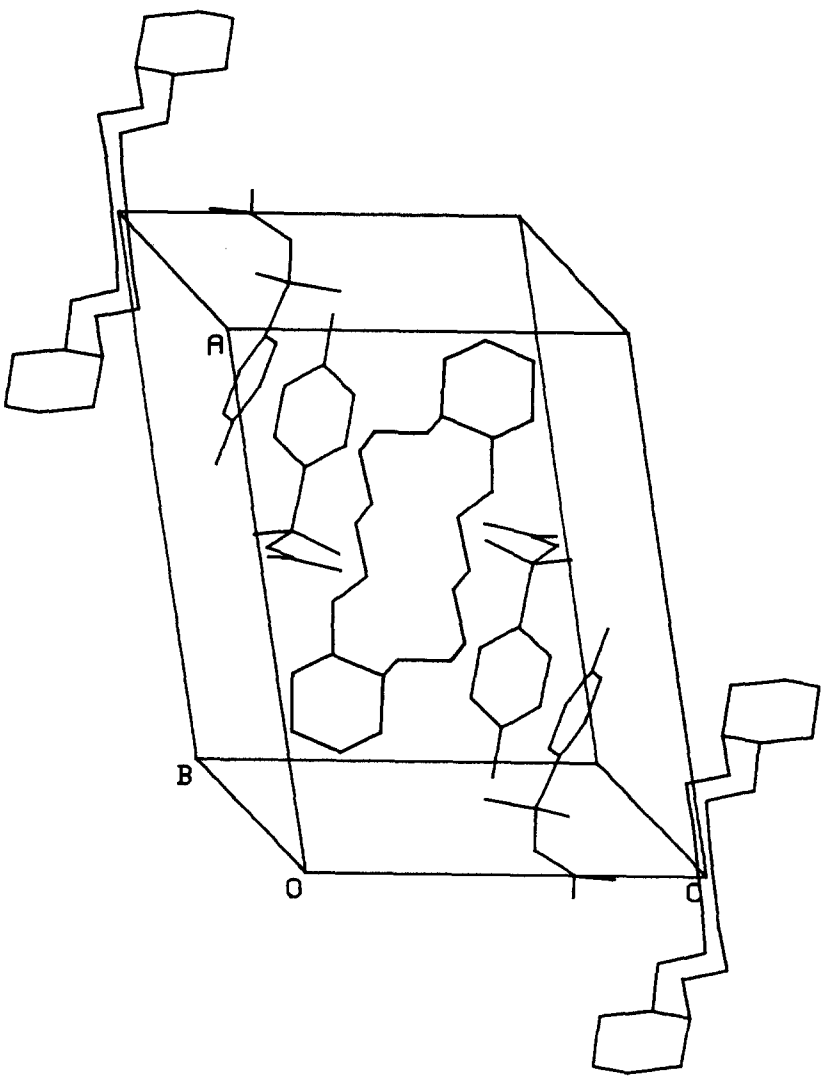


Fig. 4. Representation of the packing diagram for **II**.

The guest structure in **I** and **II** is not essentially different from that found in [26–27]. It is necessary to emphasize that in all structures (two forms of free L [26], $L \cdot H_2O$ [27], PdL_2Cl_2 [27], complexes **I** and **II** (present work)) the coplanar guanidine moiety is fixed to the sulfone group *via* an intramolecular N(3)—H···O(1) bond (numbering corresponds to **I** and **II**) and assumes the tautomeric L^{II} amino form with the following bond lengths:

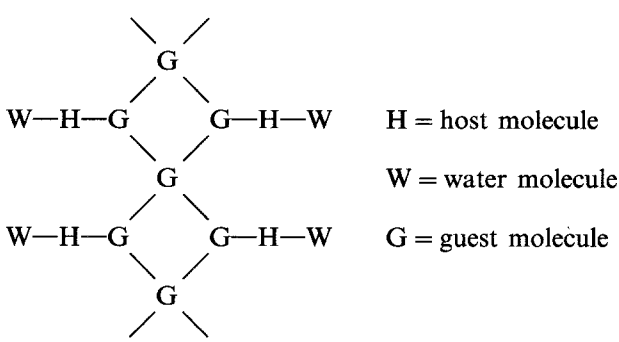
	IL_{free}	IL_{comp}	IIL_{comp}	L_{free}	$L \cdot H_2O$	PdL_2Cl_2
$S—O_{av}$	1.440	1.440	1.444	1.443/ 1.440	1.440	1.456
S—N	1.590	1.587	1.576	1.589/ 1.594	1.586	1.596
$S—C_{ring}$	1.747	1.752	1.761	1.767/ 1.763	1.752	1.763

Angular parameters are given in Table V. The spatial arrangements of the arylamino groups are significantly different for the guest in **I** and **II**. In **I** free and complexed sulfaguanidine molecules have similar conformations with the torsion angles C(6)—C(1)—S—N(2) being 82.0 and 88.1° respectively. This conformation resembles that found in one form of uncomplexed L [N—S—C(1)—C(6) = 94.4°], in $L \cdot H_2O$ and PdL_2Cl_2 [27] and in the majority of $arylSO_2NX, X'$ compounds.

The sulfaguanidine molecule in **II** has an unusual conformation with the torsion angle N—S—C(1)—C(6) being −32.8°. It coincides with the second form of uncomplexed L (angle N—S—C(1)—C(6) = −12.5°). So we confirm the suggestion by A. Kálmán *et al.* [26] about the unhindered rotation of the aryl moieties about the $S—C_{ring}$ bond both in the free and complexed ligands.

In this way both the **A** and **B** isomers of dicyclohexano-18-crown-6 form inclusion compounds with sulfaguanidine in the same host:guest ratio but the character of the complexes are fundamentally different according to the different formation conditions.

For isomer **A** the complex is characterized as [DCH—$6^A \cdot L \cdot H_2O$]. L where only one guest has a direct contact with the crown–ether. The second guest reacts only with the coordinated guest. The structure can be simplified in this way:



For the second DCH—6 isomer a more common situation is observed; guest–host–guest–guest–host–guest··· . The study has shown a substantial influence of the DCH—6 isomeric composition on the formation of the crystal molecular structure in the host–guest type complex.

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