23. V. L. Heasley, C. L. Frye, R. T. Core, and P. S. Wilday, J. Org. Chem., 2342 (1968).
24. V. L. Heasley and S. K. Taylor, J. Org. Chem., 34, 2779 (1969).
25. M. Sykes, Reaction Mechanisms in Organic Chemistry [Russian translation], Khimiya, Moscow (1977).
26. K. Blaha, O. Cervinka, and J. Kovar, Principles of Stereochemistry and Conformational Analysis [Russian translation], Khimiya, Moscow (1974).
27. A. I. Kitaigorodskii, Mixed Crystals [in Russian], Nauka, Moscow (1983).

CRYSTAL AND MOLECULAR STRUCTURE OF THE 1:2 COMPLEX OF THE CIS-ANTI-CIS-DIASTEREOISOMER OF DICYCLOHEXANO-18-CROWN-6 WITH 4-ACETYLAMINOBENZENESULFONAMIDE

Yu. A. Simonov, E. V. Ganin, M. S. Fonar', A. A. Dvorkin, and S. A. Kotlyar

UDC 548.737:547.898:547.541.521

The crystal structure of the 1:2 complex of the cis-anti-cis-diastereoisomer of dicyclohexano-18-crown-6 with 4-acetylaminobenzenesulfonamide has been determined by x-ray structural analysis. A complex of the "host—guest" type is formed, with the production of H-bonds between the proton-donor groups of the guest molecules and the O atoms of the oxyethylene ring of the crown ether. The N—H...O distances lie in the range 2.94-2.97 Å. The crown ether is centrosymmetric, and its conformation is described as an alternation of six gauche C—C bonds, ten trans C—O bonds, and two gauche C—O bonds.

The present authors [1] previously detected the selective formation of a crystalline complex of the "host—guest" type by 4-aminobenzenesulfonamide with one of the sterically nonequivalent cis-diastereoisomers of dicyclohexano-18-crown-6 (DCH-18-C-6), namely the cis-anti-cis-form, with a "guest—host" ratio of 2:1. An x-ray structural study of this material showed that with allowance for the H-bonds the structure is pseudopolymeric. Each of the two molecules of 4-aminobenzenesulfonamide is coordinated in two neighboring molecules of the crown ether through the H_2N groups of its amine and sulfonamide fragments, forming a double bridge of the "head—tail" type. The conformation of DCH-18-C-6 is characterized by six gauche rotamers with respect to the C—C bonds and ten trans rotamers with respect to the C—O bonds. Two of the C—O bonds in the centrosymmetric DCH-18-C-6 (the cis-anti-cis-diastereoisomer) are in the gauche conformation. The angular fragment (two gauche$^{\pm}$-gauche$^{\pm}$-bonds) are in the "catechol" part of the crown ether. A similar conformation for this diastereoisomer was also found in the compounds with maleic anhydride and 2,4-dinitroaniline [2, 3].

The study of complex formation by the cis-diastereoisomers of DCH-18-C-6 with 4-acetylaminobenzenesulfonamide, in which one of the functional groups (the amino group) is blocked by an acetyl substituent, revealed the corresponding ability of the "guest" molecule to take part in the selective formation of a crystalline complex with the cis-anti-cis-diastereoisomer of DCH-18-C-6. An interesting characteristic of 4-acetylaminobenzenesulfonamide is that its selectivity is greater than that of 4-aminobenzenesulfonamide; it does not form a crystalline complex with either the cis-syn-cis-diastereoisomer of DCH-18-C-6 or the sterically unhindered 18-crown-6.

The present paper gives the results of an x-ray structural study of the molecular and crystal structure of a new complex of the cis-anti-cis-diastereoisomer DCH-18-C-6.2(4-CH_3-

---

Institute of Applied Physics, Academy of Sciences of the Moldavian SSR. All-Union Scientific-Research and Design Institute of Monomers. Translated from Zhurnal Strukturnoi Khimii, Vol. 31, No. 4, pp. 106-110, July-August, 1990. Original article submitted March 14, 1988.

0022-4766/90/3104-0617$12.50

TABLE 1. Coordinates of the Basis Atoms ($\times 10^4$)

Atom	x	y	z	Atom	x	y	z
O1	4775(4)	9493(2)	—2394(4)	S1A	5353(1)	8299(1)	1206(2)
C2	5804(6)	9346(5)	—3257(7)	N1A	5109(4)	9112(2)	507(5)
C3	6926(6)	9094(4)	—2457(8)	O1A	6210(4)	7747(2)	351(6)
O4	7044(4)	9708(3)	—1700(5)	O2A	5653(4)	8385(3)	2592(5)
C5	8144(6)	9488(6)	—898(10)	O3A	227(3)	7473(3)	3161(4)
C6	8251(7)	10047(6)	17(10)	C1A	3990(4)	8086(3)	1203(6)
O7	7368(4)	10270(3)	1048(5)	C2A	3630(5)	7828(3)	11(6)
C8	7304(5)	9761(4)	2103(7)	C3A	2553(5)	7670(3)	—7(5)
C9	3651(5)	9783(4)	—3073(6)	C4A	1825(4)	7766(3)	1106(5)
C10	3287(6)	9166(4)	—3783(8)	C5A	2191(5)	8019(4)	2313(5)
C11	2067(7)	9510(5)	—4485(9)	C6A	3280(5)	8169(3)	2346(6)
C12	1096(6)	9969(5)	—3514(9)	C7A	29(5)	7442(3)	1952(6)
C13	8501(6)	9412(4)	2851(8)	C8A	—1006(6)	7214(5)	1437(8)
				N2A	728(4)	7596(2)	978(5)

TABLE 2. Bond Lengths (d, Å)

Bond	d	Bond	d	Bond	d	Bond	d
O1—C2	1,42(1)	S1A—N1A	1,598(5)	C8—C9 *	1,50(1)	C4A—C5A	1,40(1)
C2—C3	1,46(1)	S1A—O1A	1,442(5)	C8—C13	1,51(1)	C5A—C6A	1,39(1)
C3—O4	1,41(1)	S1A—O2A	1,429(5)	O1—C9	1,41(1)	C1A—C6A	1,37(1)
O4—C5	1,44(1)	S1A—C1A	1,759(6)	C9—C10	1,51(1)	C4A—N2A	1,42(1)
C5—C6	1,41(1)	C1A—C2A	1,38(1)	C10—C11	1,51(1)	N2A—C7A	1,35(1)
C6—O7	1,40(1)	C2A—C3A	1,38(1)	C11—C12	1,51(1)	C7A—O3A	1,22(1)
O7—C8	1,42(1)	C3A—C4A	1,36(1)	C12—C13 *	1,52(1)	C7A—C8A	1,49(1)

---

*The atoms marked are those related to the basis atom by the center of inversion at the point (0.5; 1; 0).

$CONHC_6H_4SO_2NH_2$) (I). The determination of the structure of this compound makes it possible to establish the characteristic features of the interaction of the component parts of the complex, in which, in contrast to 4-aminobenzenesulfonamide [1], one of the two proton-donor groups is blocked by the $-C(=O)-CH_3$ group, and also to establish the influence of the "guest" molecules on the conformation of the macrocyclic ring.

EXPERIMENTAL

Complex I was synthesized in methanol. 4-Acetylaminobenzenesulfonamide (0.428 g, 0.002 mole) and the cis-anti-cis-diastereoisomer of DCH-18-C-6 (0.744 g, 0.002 mole) were dissolved together in 20 ml of methanol at 64°C, and the solution was left to crystallize at room temperature. The crystals obtained were washed with methanol and dried in air.

The colorless transparent crystals are soluble in ethanol, isopropyl alcohol, acetone, and chloroform; mp = 199-210°C. The IR spectrum (IKS 29 instrument, KBr disks) ν, cm^{-1}: 3320, 3240 (—H); 2940, 2860 (C—H); 1650 (C=O); 1345 (SO_2), 1100 (C—O—C). Chemical analysis: found for the complex, %: N 7.10; S 8.15; calculated, %: N 6.99; S 8.01.

A single crystal with a prismatic habit and linear dimensions 0.2 × 0.3 × 0.3 mm was taken for the x-ray structural study. The crystal is monoclinic, with unit cell parameters a = 11.653(4), b = 18.591(5), c = 9.837(3) Å; γ = 70.67(4)°; symmetry space group $P2_1/b$, Z = 2 with the composition $C_{36}H_{56}N_4O_{12}S_2$, d_{calc} = 1.32 g/cm^3. The experimental material was obtained on a DAR-UMB diffractometer using CuKα radiation. The calculation and refinement were carried out using 2607 reflections with $I \geq 2\sigma(I)$. The structure was determined by direct methods on an SM-4 computer using the set of programs SHELX-SM. The refinement was carried out in the anisotropic approximation for the atoms other than hydrogen, and is the isotropic approximation for the hydrogen atoms. The final R-factor was 0.075.

The values of the coordinates are given in Table 1, and the bond lengths and valence angles in Tables 2 and 3.

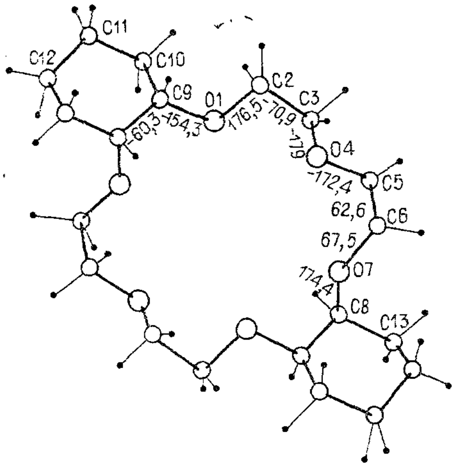

Fig. 1. Three-dimensional structure of the cis-anti-cis-diastereoisomer of DCH-18-C-6 (with the notation for the torsional angles) present in the complex.

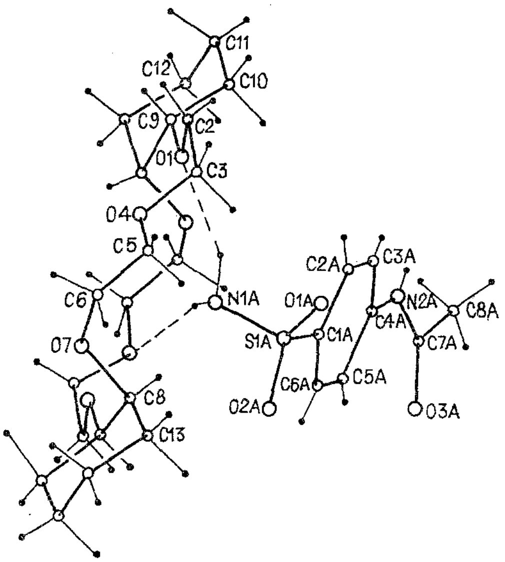

Fig. 2. Three-dimensional structure of the molecular complex of the cis-anti-cis-diastereoisomer DCH-18-C-6.2(4-acetylaminobenzenesulfonamide) (the second 4-acetylaminobenzenesulfonamide molecule is not shown).

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

In the reaction of the crown ether with a metal cation there is a significant change in the conformation of the macrocyclic ring compared with that for the free complexone. The isomers A (cis-syn-cis), B (cis-anti-cis), and C (trans-syn-trans) of DCH-18-C-6 contain gauche$^{\pm}$-gauche$^{\pm}$ angular fragments [4, 5], giving strong trans-annular interactions.

On complex formation with the lead(II) ion, which corresponds topologically to the cavity in the ring, the conformation of DCH-18-C-6 is characterized by a sequence of six gauche rotamers and twelve trans rotamers with respect to the C—C and C—O bonds, respectively. The conformation of the 18-membered ring (neglecting the cyclohexane substituents) has a symmetry close to the D_{3d} symmetry observed for the 18-crown-6 complex.

Figure 1 gives the projection of the centrosymmetric DCH-18-C-6 in structure I on the plane of the ether oxygen atoms. The conformation of the 18-membered ring differs consider-

TABLE 3. Valence Angles (ω, deg)

Angle	ω	Angle	ω
C9—O1—C2	114,1(5)	O1A—S1A—O2A	119,8(3)
O1—C2—C3	110,4(6)	N1A—S1A—O1A	106,6(3)
C2—C3—O4	109,9(6)	N1A—S1A—O2A	106,1(3)
C3—O4—C5	112,0(6)	N1A—S1A—C1A	108,7(3)
O4—C5—C6	115,2(8)	O1A—S1A—C1A	107,6(3)
C5—C6—O7	116,3(8)	O2A—S1A—C1A	107,4(3)
C6—O7—C8	121,6(6)	S1A—C1A—C2A	118,6(4)
O7—C8—C9 *	106,3(5)	C2A—C1A—C6A	119,5(5)
O1—C9—C8 *	109,6(5)	C1A—C2A—C3A	119,0(5)
C10—C9—C8 *	112,3(6)	C2A—C3A—C4A	122,2(5)
C9—C10—C11	110,4(6)	C3A—C4A—C5A	118,8(5)
C10—C11—C12	111,8(7)	C4A—C5A—C6A	119,3(5)
C11—C12—C13 *	109,6(7)	C5A—C6A—C1A	121,0(5)
C12—C13 *—C8 *	110,6(6)	C3A—C4A—N2A	117,8(5)
C13—C8—C9 *	109,7(6)	C4A—N2A—C7A	129,4(5)
N2A—C7A—C8A	114,8(5)	O3A—C7A—C8A	121,8(6)

---

*The atoms marked are those related to the basis atom by the center of inversion at the point (0.5; 1; 0).

TABLE 4. Geometric Parameters of the Hydrogen Bonds in the Complex

D—H...A	D—H, Å	D...A, Å	H...A, Å	∠D—H...A, deg
N1A—H1 ... O1		2,935	1,95	150
N1A—H1 ... O7 *	1,08	3,130	2,56	112
N1A—H2 ... O4 *		2,973	2,24	149
N1A—H2 ... O7 *	0,82	3,130	2,52	132

D) Proton donor; A) proton acceptors.
*The atoms marked are those related to the basis atom by the center of inversion at the point (0.5; 1; 0).

ably from that observed for the complex [Pb(DCH-18-C-6)(B)$(NO_3)_2$] [6], which is characterized by six gauche rotamers with respect to the C—C bond and ten trans rotamers and two gauche rotamers with respect to the C—O bonds. An angular fragment [7] is formed at the C6 atom. This conformation of the ring on the whole ensures the best conditions for the production of the 2:1 "guest—host" complex. Thus, N—H...O hydrogen bonds are formed with the O1 and O4* atoms of the crown ether (Table 4), and the O7 atom with its lone pair of electrons is oriented in such a way that it is separated to the greatest extent from the interacting parts of the "host" and the "guest." This also ensures the maximum separation of the O7 atom from the oxygen atoms of the sulfonamide group of the "guest."

The six oxygen atoms of the crown ether in compound I are coplanar to within 0.012 Å (the maximum deviation is shown by the O1 and O1* atoms). The cyclohexane substituents have the chair form with an average C—C distance of 1.51 Å and valence angle 110.7°. The average distances in the crown ether are C—C 1.49 and C—O 1.42 Å; the angles are C—C—O 111.3 and C—O—C 115.9°.

The 4-acetylaminobenzenesulfonamide molecules have a planar aromatic ring with average values of the bond lengths C—C 1.38 Å and angle C—C—C 119.7°. The geometry of the sulfonamide group corresponds to published data. The lengths of the bonds S=O, S=N, and S—C are 1.435, 1.598, and 1.759 Å, respectively, and the angles O=S=O = 119.8, N—S—O = 107.4, and C—S—O = 107.5°. The sulfonamide group makes an angle of 92° with the benzene ring. The acetylamino group is practically planar, and makes an angle of 16.8° with the plane of the benzene ring. The C—C, C=O, and N—C distances are 1.49, 1.22, and 1.38 Å, respectively.

The aromatic ring of the "guest" in compound I makes a dihedral angle of 9.6° with the average plane of the heterocavity of the crown ether.

The molecular complexes are joined by a hydrogen bond N2A–H...O3A = 3.005 Å (N2A–H = 0.67, H...O3A = 2.37 Å, angle N2A–H...O3A = 159°). The bond is formed between the basis complex and the complex related to it by the $2_1 \parallel z$ symmetry axis with the symmetry transformation −x; 1.5 − y; −0.5 +z. With allowance for these hydrogen bonds, the compound has a chain structure with chain axis parallel to the z axis.

Thus, the absence of mutual steric and packing restrictions [8] between the molecules of 4-acetylaminobenzenesulfonamide and the cis-anti-cis-diastereoisomer of DCH-18-C-6 apparently explains the selective formation of the crystalline complex, which is also facilitated by the conformational flexibility of dicyclohexano-18-crown-6, revealed, in particular, by the transfer of the angular fragment in the molecule of the crown ether from the "catechol" part to the central part of the cavity. In spite of the fact that 18-crown-6 has C_i symmetry, which assumes that the two sides of the macrocyclic ring are equivalent, a crystalline complex with 4-acetylaminobenzenesulfonamide is not formed, apparently because of the large size of the "guest" molecules, which creates packing noncorrespondence in the crystal on complex formation (Fig. 2).

LITERATURE CITED

1. A. A. Dvorkin, M. S. Fonar', T. I. Malinovskii, et al., Zh. Strukt. Khim., 30, No. 3, 96 (1989).
2. M. S. Fonar', Yu. A. Simonov, A. A. Dvorkin, et al., Dokl. Akad. Nauk SSSR, 301, No. 4, 913 (1988).
3. E. V. Ganin, V. F. Makarov, S. A. Kotlyar, et al., Khim. Geterotsikl. Soedin., No. 9, 1190 (1988).
4. Yu. A. Simonov, N. F. Krasnova, N. A. Tsarenko, et al., Dokl. Akad. Nauk SSSR, 285, No. 4, 892 (1985).
5. N. K. Dalley, D. E. Smith, and S. B. Larson, J. Chem. Soc., Chem. Commun., No. 1, 43 (1975).
6. N. F. Krasnova, Yu. A. Simonov, V. V. Yakshin, and M. B. Korshunov, Kristallografiya, 32, No. 2, 499 (1987).
7. Yu. G. Ganin, Yu. A. Simonov, and T. I. Malinovskii, Izv. Akad. Nauk Moldav. SSR, Ser. Fiz.-Tekh. Mat. Nauk, No. 1, 18 (1985).
8. A. Elbasyouny, H. J. Brugge, K. Deuten, et al., J. Am. Chem. Soc., 105, No. 22, 6568 (1983).