Structure of Dibenzocrown Ethers and their H-Bonded Adducts. 1. [1.5]Dibenzo-18-Crown-6 and Biphenyl-20-Crown-6: Complexes with Amidosulfuric Acid

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Abstract

The interaction of the amidosulfuric acid NH_3SO_3 with 15 distal and proximal dibenzocrown ethers, including diphenyloxide, diphenylsulfide and biphenyl ones leads to the stable (1:1) complexes only in the case of [2.4]- and [1.5]dibenzo-18-crown-6 and biphenyl-20-crown-6. According to the data of the X-ray analysis, in the two last adducts the amidosulfuric acid coordinates to hexadentate crown ethers in a zwitterion form through a near-ideal 'tripod' arrangement to alternate crown oxygen atoms. The conformations of crown molecules are different in complexes and in initial macrocyclic ligands.

Introduction

Since their discovery by Pedersen [1] an excellent ability of crown ethers to yield the well-defined and stable complexes with metal cations attracts the persistent interest. This property finds the potential applications in catalysis, solvent extraction, isotope separation and materials science [2–5]. So far it is now also proven the crown ethers' ability to complex well with more complicated compounds containing ammonium and alkylammonium ions [6, 7].

Study of crown ethers' complexes with zwitterions is very important for the creation of new complexones for separation of chiral aminoacids and the development of molecular receptors for single peptide units in the problems of peptide recognition. For instance, some efforts have been already successful here using both classic 18-crown-6 and its aromatic chiral derivatives [8].

More simple molecules could be useful to simulate this type of macrocyclic receptor interactions and among them amidosulfuric acid might stand ahead. It is in the first turn connected with its ability to be transformed into the zwitterionic form: $H_2NSO_3H \leftrightarrow NH_3^+NSO_3^-$.

Earlier we [9] and others [10] have unambiguously demonstrated the near-ideal tripod-like coordination geometry afforded for amidosulfuric acid zwitterion by 18- and 20-member crown ethers (18-crown-6, *cis*-dicyclohexano-18-crown-6, benzo-18-crown-6,18,19-benzo-1, 16-diaza-4,7,10,13-tetraoxacycloicosa-17,20-dione) in their (1:1) adducts. Smaller crown ethers such as 15-crown-5 and 12-crown-4 provide a less optimal geometry for the amidosulfuric acid zwitterion accommodation. In these cases the zwitterions themselves form the centrosymmetric dimers or more developed linear associates and provide only two or one of three available hydrogen atoms for the interaction with the crown ethers [11].

Our further interest lays in the synthesis and structure of the dibenzocrown ethers (**A–E**) and their derivatives, and the influence of these crown ethers composition, structure (relative position of aromatic units) and macrocycle size on their ability to form a 'host-guest' complexes with a different H-bond donors, and also the adducts' stoichiometry, the mode of hydrogen bonding and possible π–π interactions in these systems.

Comparing symmetric (distal, **A**) and asymmetric (proximal, **B**) dibenzocrown ethers it may be seen, that diphenyloxide and diphenylsulfide macrocycles (**D, E**)

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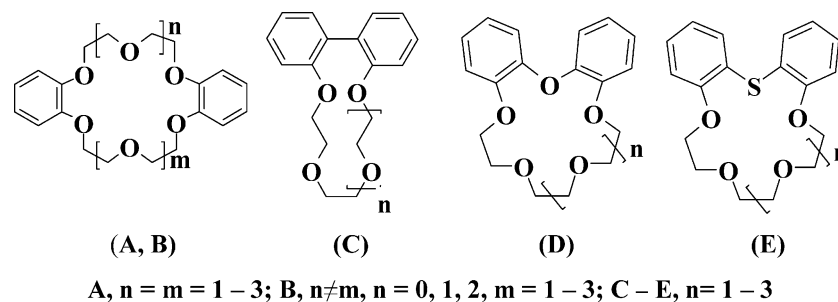A, n = m = 1 – 3; B, n≠m, n = 0, 1, 2, m = 1 – 3; C – E, n= 1 – 3

Chart 1.

represent that extreme case, when the 'bridge' between benzene rings is minimal (the oxygen or sulfur atoms) and in biphenyl analogs (**C**) benzene cycles are maximally approached (Chart 1). It is obvious also that the quantity of less basic oxygen atoms (so-called 'aromatic' oxygen atoms bound with benzene rings) varies depending on the topology and composition of these dibenzocrown ethers. For example, in the series of discussed crown ethers (Chart 1) quantity of the oxygen atoms of such type is maximal (4) in macrocycles **A** and **B** and minimal (2) in biphenyl (**C**) and diphenylsulfide (**E**) macrocycles.

This study was focused on the investigation of the effect of dibenzocrown ethers (**A–E**) composition and structure on formation of complexes with the amidosulfuric acid, and on the basis of X-ray structure analysis to discuss the conformational variations of these macrocycles after complexation and the structural peculiarities of obtained complexes.

We have improved the obtaining of crown ethers (**A, B**) [12] and have developed convenient ways of crown ethers' (**C, D**) [13] and (**E**) [14] synthesis, which allowed to exclude the column chromatography under the isolation of these macrocycles (purity > 99%).

The interaction of the crown ethers **A–E** with amidosulfuric acid was carried out in the boiling aqueous isopropanol and the host-guest complexes (1:1) with 70–91% yields were obtained only for [1.5]dibenzo-18-crown-6 (**D**, **1**), biphenyl-20-crown-6 (**C**, **2**) and [2.4]dibenzo-18-crown-6 (**B**, **3**).

These results show the considerable distinction of the dibenzocrown ethers A–E from aliphatic, cycloaliphatic and monobenzocrown ethers, for which the complexes with amidosulfuric acid in all the cases have been isolated easily [9, 10].

Unfortunately we failed in growing the single crystals of the crown ether **3** complex with amidosulfuric acid (**3·NH₃SO₃**) from different solvents. We succeeded in growing the suitable for the X-ray analysis crystals of the adducts of macrocycles **1** and **2** from methanol and methanol–ethyl acetate solutions respectively and the compositions of these crystals are **1·NH₃SO₃·MeOH** and **2·NH₃SO₃**.

That is the reason why in the scope of this study we restrict ourselves to the discussion about crystal structures of the dibenzocrown ethers **1** and **2** and their complexes with amidosulfuric acid.

Experimental

Synthesis

The thin layer chromatographic control of the substances purity was performed on the Silufol UV-254 plates. Mass-spectrum analysis was realized on the Varian MATT–112 instrument using 70 eV ionization radiation, and a temperature of 220 °C. ^{1}H NMR spectra were recorded on Varian WXP-300 instrument with frequency ratio 299.95 MHz in deuterochloroform.

Synthesis of *1*

The solution of 2,2′-dihydroxydiphenyloxide (11.0 g, 0.054 mol), tetraethyleneglycol ditozylate (27.1 g, 0.054 mol) and NaOH (6.7 g, 0.12 mol) in dry 1,4-dioxane (100 mL) was stirred while boiling during 20 h. The mixture was cooled, acidified by concentrated HCl up to pH 3–4, the solid was filtered off, washed with cold 1,4-dioxane (2 × 10 mL), treated the filtrate with activated charcoal and the solvent was evaporated under the
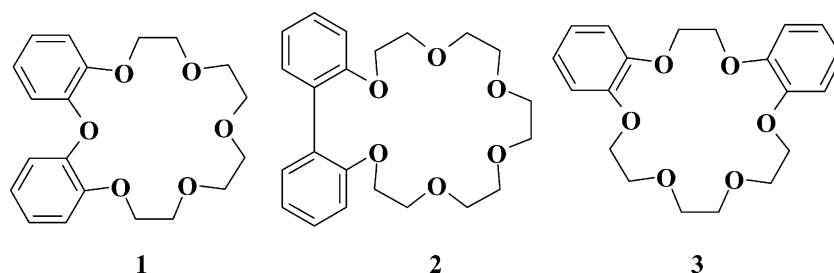

1   **2**   **3**

Chart 2.

lowered pressure. The residue was dissolved in 60 mL of $CHCl_3$, washed with the 5% water solution of NaOH (2×20 mL), water (2×20 mL) and dried over Na_2SO_4. After evaporating the residue was extracted by boiling n-heptane (10×200 mL) and cooled (5–10 °C), the united extracts were filtered off. The solid was washed with n-heptane (2×5 mL) and crystallized from the aqueous acetone. The yield of **1** is 4.7 g (24%). The crystals of **1** and **2** suitable for the X-ray analysis were obtained by the crystallization from the dry ethyl acetate. The crystals **1** M.P. 68–69 °C (205 mg, 76% yield) are colorless, transparent and soluble in methanol, ethanol, acetone, chloroform, benzene and dimethylsulfoxide. ^{1}H NMR, δ: 7.08–6.95 (4H, q, Ar–H), 6.88–6.82 (2H, q, Ar–H), 6.75–6.73 (2H, d, Ar–H), 4.18–4.07 (4H, m, CH_2), 3.73–3.67 (4H, m, CH_2), 3.58–3.45 (8H, m, CH_2). Mass-spectrum, m/z (I%): 360 (67.2), 213 (8.5), 184 (13.4), 128 (15.6), 121 (100.0), 120 (90.4), 119 (18.8), 115 (11.0), 109 (16.6), 108 (49.5), 107 (10.1), 94 (27.0), 92 (22.8), 91 (39.0), 81 (12.2), 80 (16.7), 77 (17.3), 73 (16.5), 65 (16.9), 64 (12.6), 52 (20.6), 51 (10.1), 45 (69.2), 43 (60.0). TLC: R_f – 0.30 (eluent: acetone–hexane 3:7). Found, %: C, 66.65; H, 6.97 for $C_{20}H_{24}O_6$. Calculated, %: C, 66.79; H, 6.92.

Synthesis of 2
It was obtained similarly to **1** from 2,2′–dihydroxybiphenyl (11.2 g, 0.06 mol), pentaethyleneglycol ditozylate (33.3 g, 0.061 mol) and KOH (7.3 g, 0.13 mol). After the treatment (see above) the residue was extracted by the boiling n-heptane (10×200 mL). The united extracts were cooled up to 5 °C, the solid was filtered, washed with n-heptane (2×5 mL) and crystallized from n-hexane. The yield of **2** is 8.6 g (37%). The crystals **2** M.P. 64–65 °C (119 mg, 84% yield) are colorless, transparent and soluble in methanol, acetone, chloroform, benzene, dimethylsulfoxide. ^{1}H NMR, δ: 7.32–7.24 (2H, t, Ar-H), 7.12–7.02 (4H, q, Ar–H), 6.99–6.92 (2H, t, Ar-H), 4.15–3.98 (4H, m, CH_2), 3.67–3.60 (4H, m, CH_2), 3.58–3.40 (12H, m, CH_2). Mass-spectrum, m/z (I%): 388 (93.7), 256 (10.8), 213 (16.0), 212 (61.8), 197 (23.3), 181 (13.5), 169 (29.2), 168 (25.7), 141 (12.1), 139 (26.2), 132 (49.4), 131 (12.7), 128 (13.7), 115 (16.4), 89 (19.1), 73 (20.6), 71 (14.7), 45 (82.7). TLC: R_f–0.67 (eluent: ethyl acetate). Found, %: C, 67.92; H, 7.32 for $C_{22}H_{28}O_6$. Calculated, %: C, 68.02; H, 7.27.

Synthesis of 3
The crown ether **3** was obtained similarly described in [12].

Synthesis of 1·NH₃SO₃ and 1·NH₃SO₃·MeOH
One gram (0.0028 mol) of **1** was dissolved in 10 mL of boiling isopropanol and while stirring added the solution of 0.41 g (0.0042 mol) amidosulfuric acid in 3 mL of distilled water. The reaction mixture was boiled during 30 min, and then cooled to 15 °C. The solid was filtered and washed with a small amount of cold isopropanol. The yield of **1·NH₃SO₃** is 0.99 g (77%), M.P. 166–168 °C. Found, %: C, 52.60; H, 6.08; N, 2.99; S, 7.12 for $C_{20}H_{27}NO_9S$. Calculated, %: C, 52.51; H, 5.95; N, 3.06; S, 7.01. Crystals of **1·NH₃SO₃·MeOH** suitable for X-ray analysis formed in methanol by slow evaporation of solvent at room temperature. Colorless and transparent crystals (M.P. 139–141 °C) were selected with the yield 73% (185 mg). Found, %: C, 51.48; H, 6.45; N, 2.79; S, 6.52 for $C_{21}H_{31}NO_{10}S$. Calculated, %: C, 51.52; H, 6.38; N, 2.86; S, 6.55. The crystals of **1·NH₃SO₃·MeOH** are soluble in methylene chloride, dimethylsulfoxide, dimethylformamide, boiling alcohols and weakly in chloroform and ethyl acetate.

Synthesis of 2·NH₃SO₃
The complex was obtained similarly described above for **1·NH₃SO₃**. The yield of **2·NH₃SO₃** is 0.96 g (70%). The crystals, suitable for the X-ray analysis were obtained by the crystallization from the mixture methanol–ethyl acetate 1:1. The **2·NH₂SO₃** crystals are colorless and transparent, M.P. 162–163 °C (56%, 121 mg), the solubility is nearly similar to that for **1·NH₃SO₃**. Found, %: C, 54.31; H, 6.53; N, 2.80; S, 6.54 for $C_{22}H_{31}NO_9S$. Calculated, %: C, 54.42; H, 6.44; N, 2.88; S, 6.60.

Synthesis of 3·NH₃SO₃
The complex was obtained similarly described above. The yield of **3·NH₃SO₃** is 1.15 g (91%), M.P. 192–193 °C. Found, %: C, 52.50; H, 5.95; N, 3.09; S, 6.90 for $C_{20}H_{27}NO_{19}S$. Calculated, %: C, 52.46; H, 5.90; N, 3.06; S, 6.99.

Data collection and structure refinement

The X-ray intensity data for **1** and **2** were collected on a 'Siemens P3/PC' four-circle diffractometer equipped with graphite monochromatic M_o-K_α radiation using $2\theta/\theta$ scan mode. Unit cell parameters were obtained and refined from angular values of 24 reflections (θ range = 5.6–16.2°) accurately well centered on the diffractometer. The intensity of two standard reflections, recorded for every 98 reflections, showed no significant changes. The recorded data were corrected for polarization and Lorentz effects. The X-ray intensity data for **1·NH₃SO₃·MeOH** and **2·NH₃SO₃** were collected on a Bruker CCD diffractometer [15] with graphite monochromatic M_o-K_α radiation. Unit cell parameters were obtained and refined using the whole data set. Frames were integrated and corrected for Lorentz and polarization effects. Cell parameters were obtained by the global refinement of the positions of all collected reflections. Reflections, which were partly measured on previous and subsequent frames, were used to scale these frames on each other. The structure solution and refinement proceeded similarly for all the structures using SHELX-97 program package [16]. Direct methods yielded all non-hydrogen atoms of the asymmetric unit. These atoms were treated aniso-

tropically (full-matrix least squares method on F^2). The disorder was found in three of four structures. In **2** the carbon atoms C11 and C12 were (see below) assumed to be disordered over two orientations. The occupancy factors refined to 0.679(1) for the major component and 0.321(1) for the minor component. In **1·NH₃SO₃·MeOH** one of oxygens of amidosulfuric acid zwitterion was disordered over two orientations O2S and O2SA. The occupancy factors refined to 0.846(1) for the major component and 0.154(1) for the minor component. Methanol molecule resides around an inversion center and was treated with the 50% occupancy. In **2·NH₃SO₃** the fragment of the oxyethylene chain restricted by the atoms O4B···C12B (see below) was disordered over two orientations with the occupancy factors 0.657(1) and 0.343(1) for major and minor components correspondingly, while in one of two crystallographically independent amidosulfuric acids moieties defined by S2 atom the oxygens of sulfonate group also occupy two positions with the occupancy factors equal 0.618(1) and 0.382(1) correspondingly. All the disordered fragments were treated anisotropically. C-bound hydrogen atoms were placed in calculated positions with their isotropic displacement parameters riding on those of the parent atoms, while the N-bound and O-bound (methanol molecule) H-atoms were found from differential Fourier maps at an intermediate stage of the refinement and were treated isotropically. The X-ray data and details of the refinement for crown ethers **1** and **2**, and adducts **1·NH₃SO₃·MeOH** and **2·NH₃SO₃** are given in Table 1.

Results and discussion

Interaction of dibenzocrown ethers with amidosulfuric acid

Under interaction of amidosulfuric acid in boiling aqueous isopropanol with symmetric (distal, **A**) and asymmetric (proximal, **B**) dibenzocrown ethers containing from 6 to 10 oxygen atoms, only in case of proximal [2.4]-dibenzo-18-crown-6 (**3**) the corresponding complex (1:1) was separated from reaction mixture. It is significant that the similar result was observed for the diphenyloxide isomer of macrocycle **3** – [1.5]dibenzo-18-crown-6 (**1**) and their hexadentate analog – biphenyl-20-crown-6 (**2**).

Interestingly that in studied conditions the complexes both of the distal isomer of crown ether **3** – [3.3]dibenzo-18-crown-6 and the diphenylsulfide analog of [1.6]dibenzo-21-crown-7 (respectively **E** and **C**, $n = 3$), in macrocycle of which there are six oxygen atoms, were not separated too.

It is quite obvious that obtained results are not able to characterize unambiguously the complexing properties of studied dibenzocrown ethers **A**–**E** with respect to amidosulfuric acid. We assume that reported results just reflect the synthetical (preparative) aspects of this kind

Table 1. Crystallographic data for **1**, **2**, **1·NH₃SO₃·MeOH** and **2·NH₃SO₃**

|	Compound			
	1	**2**	**1·NH₃SO₃·MeOH**	**2·NH₃SO₃**
Composition	$C_{20}H_{24}O_6$	$C_{22}H_{28}O_6$	$C_{21}H_{31}NO_{10}S$	$C_{22}H_{31}NO_9S$
Formula weight	360.39	388.44	473.51	485.54
Space group	$P2_1/c$	$P{-}1$	$P2_1/n$	$P{-}1$
a (Å)	9.715(5)	9.797(6)	8.6587(17)	8.739(2)
b (Å)	9.551(5)	10.062(6)	21.502(4)	13.536(3)
c (Å)	19.88(1)	12.129(8)	12.691(3)	20.833(4)
α (deg)	90	107.73(1)	90	88.67(3)
β (deg)	97.03(5)	108.23(3)	98.57(3)	88.84(3)
γ (deg)	90	93.95(1)	90	89.45(3)
V (Å^3)	1831(3)	1064(1)	2337(1)	2463(1)
Z	4	2	4	4
Dcalc (g cm^{-3})	1.307	1.213	1.346	1.309
μ (mm^{-1})	0.096	0.088	0.191	0.181
$F(000)$	768	416	1004	1032
Reflections collected/unique	3399/3198	3707/3489	22357/5148	24549/10241
	[R(int) = 0.0590]	[R(int) = 0.1239]	[R(int) = 0.0372]	[R(int) = 0.0250]
Reflections with $I > 2\sigma(I)$	2348	2325	3267	7876
Refinement method		Full-matrix least-squares on F^2		
Data/restraints/parameters	3198/0/235	3489/0/272	5148/5/305	10241/13/729
Goodness-of-fit on F^2	0.997	1.024	1.062	1.069
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0616, 0.1704	0.0696, 0.1924	0.0562, 0.1594	0.0478, 0.1323
$R1$, $wR2$ (all data)	0.0907, 0.1806	0.1094, 0.2163	0.0959, 0.1763	0.0618, 0.1403
Largest diff. peak and hole e Å^{-3}	0.295/−0.434	0.253/−0.245	0.375/−0.436	0.319/−0.417
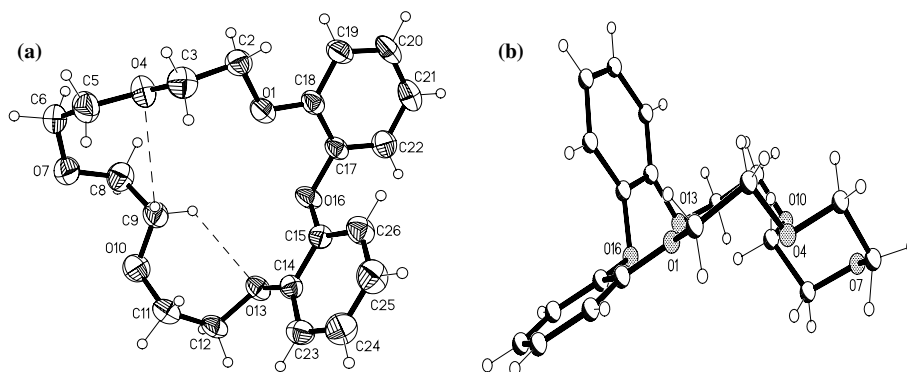
Figure 1. (a) ORTEP drawing of macrocycle **1** with the shortened intramolecular CH⋯O contacts shown by dotted lines and (b) side view of macrocycle **1**.

adducts formation, specified both by the reaction conditions and the influence of these macrocycles composition, topology and structure, and also by electronic and conformational factors (e.g., see the review [17]) determinant an optimal interaction of amidosulfuric acid zwitterion with such crown ethers cavity (see below) *via* tripod-like bifurcated N-H⋯O hydrogen bonds. Exactly to these aspects of dibenzo-crown ethers **A**–**E**; functioning we are going to devote our following publications.

Structure of 1 and 2

Macrocycle **1** has a hearth-like shape. The ORTEP drawing and the side view is shown in Figure 1 a, b. Oxygen atoms O7 and O16 have the maximal deviations

of 0.410(1) and 0.365(1) Å correspondingly from the mean least-square plane through all oxygen atoms. The trans-annular O⋯O distances range from 5.074(4) Å (O1–O10) to 5.979(5) Å (O7–O16). The benzene rings are arranged approximately perpendicular to each other, with the twist angle between their mean planes equal 87.5(1)°. The macrocyclic cavity is filled by the intramolecular shorten interactions C9⋯O4 3.237(4) Å, H9B⋯O4 2.76 Å, angle C9–H9B⋯O4 111°; C9⋯O13 3.163(4) Å, H9A⋯O13 2.53 Å, angle C9–H9A⋯O13 123°; C8⋯O4 2.960(4) Å, H8A⋯O4 2.43 Å, angle C8–H8A⋯O4 114°, that close the 6-member and 7-member intramolecular cycles and although being weak are responsible for the unusual orientation of C_{Ar}–O bonds that become *gauche* instead of favorable *trans* (Table 2). The availability of shortened C–H⋯O contacts in these

Table 2. Selected torsion angles in **1**, **1·NH₃SO₃·MeOH**, **2**, **2·NH₃SO₃**

| Angle	**1**	**1·NH₃SO₃·MeOH**	**2**	**(2A)·NH₃SO₃**	**(2B)·NH₃SO₃**
O1–C2–C3–O4	−72.1(3)	65.5(3)	82.2(3)	−61.5(2)	−74.1(4)
C2–C3–O4–C5	−175.8(2)	175.5(2)	175.3(3)	−170.0(2)	−88.5(7)
C3–O4–C5–C6	−175.1(2)	175.7(2)	−171.2(3)	−173.0(2)	178.9(7)
O4–C5–C6–O7	79.1(3)	−70.2(3)	77.7(4)	69.4(3)	−74(1)
C5–C6–O7–C8	−68.1(3)	−177.2(2)	179.7(3)	178.0(2)	−176.0(8)
C6–O7–C8–C9	107.6(3)	−177.4(2)	92.7(5)	−178.1(2)	178.3(9)
O7–C8–C9–O10	72.2(3)	65.2(3)	−75.4(6)	−66.5(3)	62(1)
C8–C9–O10–C11	−179.3(2)	−175.7(2)	150.8(5)	−177.6(2)	171(1)
C9–O10–C11–C12	−85.1(3)	−176.6(2)	177.1(5)	−176.7(2)	154(1)
O10–C11–C12–O13	73.8(3)	−67.0(3)	65.5(8)	68.1(2)	0.3(2)
C11–C12–O13–C14	73.5(2)	−95.0(3)	73.1(7)	168.7(2)	164.4(8)
C12–O13–C14–C15	−157.2(2)	176.9(2)	163.3(5)	−171.2(1)	−174.4(7)
O13–C14–C15–O16	2.6(3)	−5.8(3)	−176.8(2)	−77.7(2)	0.1(8)
C14–C15–O16–C17	−178.9(2)	136.6(2)	−172.3(2)	−168.4(2)	166.0(4)
C15–O16–C17–C18	−95.1(2)	159.3(2)	170.0(2)	152.6(2)	104.8(3)
O16–C17–C18–O1	5.4(3)	−5.8(3)	–	–	–
C17–C18–O1–C2	171.9(2)	177.4(2)	–	–	–
C18–O1–C2–C3	−176.3(2)	177.6(2)	–	–	–
O16–C17–C18–C19	–	–	−2.2(4)	1.7(2)	−1.5(2)
C17–C18–C19–C20	–	–	−66.1(4)	70.0(2)	68.8(2)
C18–C19–C20–O1	–	–	1.0(4)	−2.1(2)	−1.8(3)
C19–C20–O1–C2	–	–	−180.0(2)	121.0(2)	157.2(2)
C20–O1–C2–C3	–	–	−179.0(2)	160.4(2)	−170.8(2)
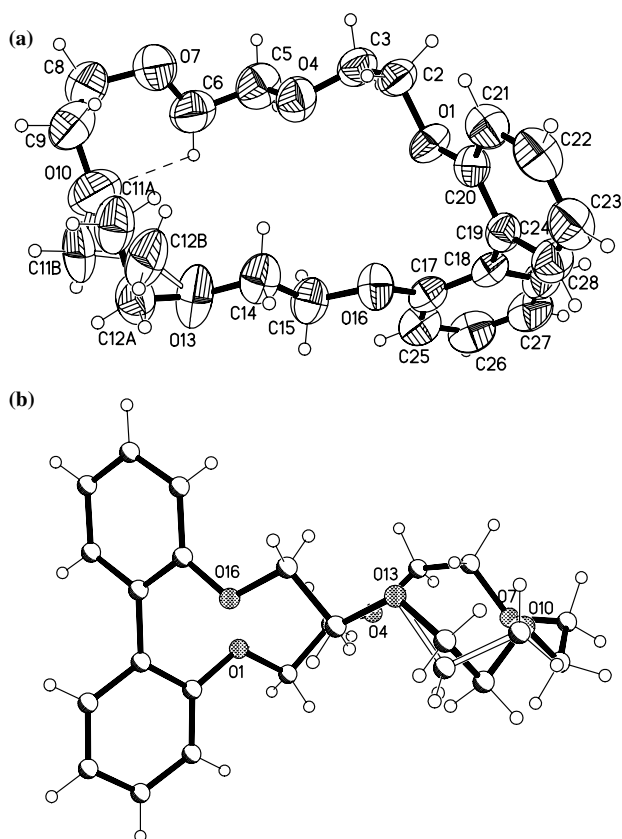
Figure 2. (a) ORTEP drawing of macrocycle **2** with the shorten intramolecular CH···O contacts shown by dotted lines and (b) side view of macrocycle **2**, the disordering fragment is shown by open lines.

crown ethers is a common point and was previously noted [18, A.Y. Nasavenko: Private communication (2002)].

Macrocycle **2** has a boat–like shape. The ORTEP drawing (top) and side view is shown in Figure 2 a, b. Oxygen atoms O1 and O4 have the maximal deviations of 0.455(2) Å and 0.315(2) Å from the mean plane through all oxygens. The cycle is elongated along O1···O10 direction, that is evident from the comparison of trans-annular O···O distances, O1···O16 2.963(3) Å,

O4···O13 4.507(5) Å, O7···O10 2.969(5) Å, O1···O10 6.614(5) Å and O7···O16 6.298(4) Å.

The benzene rings are arranged with the twist angle between their mean planes equal 63.8(1)°. The macro-cyclic cavity is rather strained, it accommodates the intramolecular shorten contact, C6···O10 3.202(6) Å, H6B···O10 2.62 Å, angle C6–H6B···O10 119°; that is responsible for the 6-membered intramolecular cycle closed by this weak CH···O interaction. Two of C–O bonds, O7–C8 and C12–O13, are in energetically unfa-vorable *gauche*–conformation (Table 2).

Structure of *1·H₃NSO₃·MeOH* and *2·H₃NSO₃*

The ORTEP drawing and the side view for the crown ethers **1** and **2** hydrogen-bonded adducts with the zwitterion of amidosulfuric acid are shown in Figures 3 and 4. The adduct **2·NH₃SO₃** contains two complexes in the asymmetric unit (further we will name the macrocycles as **2A** and **2B** in accord with the numbering schemes in the Figures). They share the same general conformation, but differ from each other slightly in details. The crown ethers in the independent complexes are arranged in such a way that the dihedral angle between the planes through their six oxygen atoms (**2A**/**2B**) is equal 70.0(1)°. The zwitterion form of amidosul-furic acid is convinced by the similar S–O distances and objective localization of three hydrogen atoms in the close proximity and in the tetrahedral arrangement around the nitrogen atom (Table 3). The zwitterion perches above the mean plane defined by the oxygen atoms of the crown ether, with the nitrogen atom at 1.121(2) Å in **1·H₃NSO₃·MeOH**, and 1.009(2) (N1) and 1.290(3) (N2) in **2·H₃NSO₃**. These distances are a bit longer than in the complexes of $NH_3^+SO_3^-$ and NH_4^+ ion with the steric non-hindered 18-crown-6 [6–8]. The anchoring hydrogen bonds between H₃NSO₃ and alter-nate oxygen atoms in the crown ether are indicated by the short N–H···O distances to these three oxygens, as it is a major component of the bifurcated N–H···O hydrogen bonds, while three remaining crown oxygens
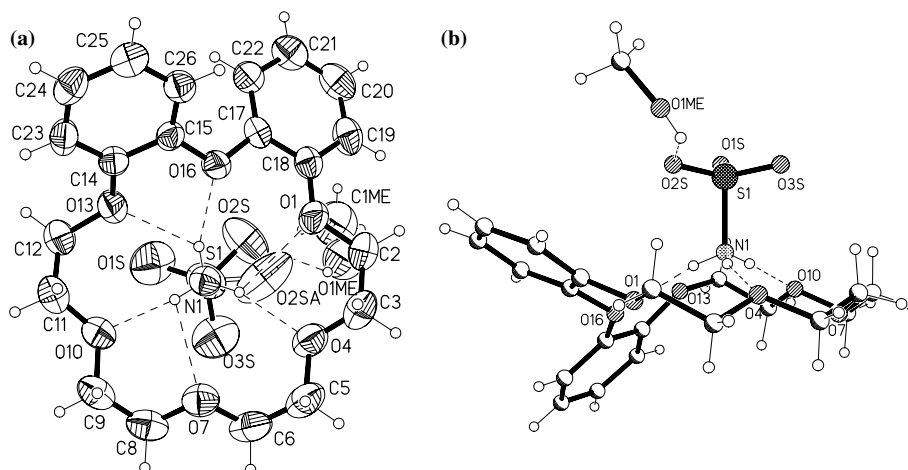

Figure 3. (a) ORTEP drawing (top view) and (b) side view of 1·NH₃SO₃·MeOH with hydrogen bonds shown by dotted lines.

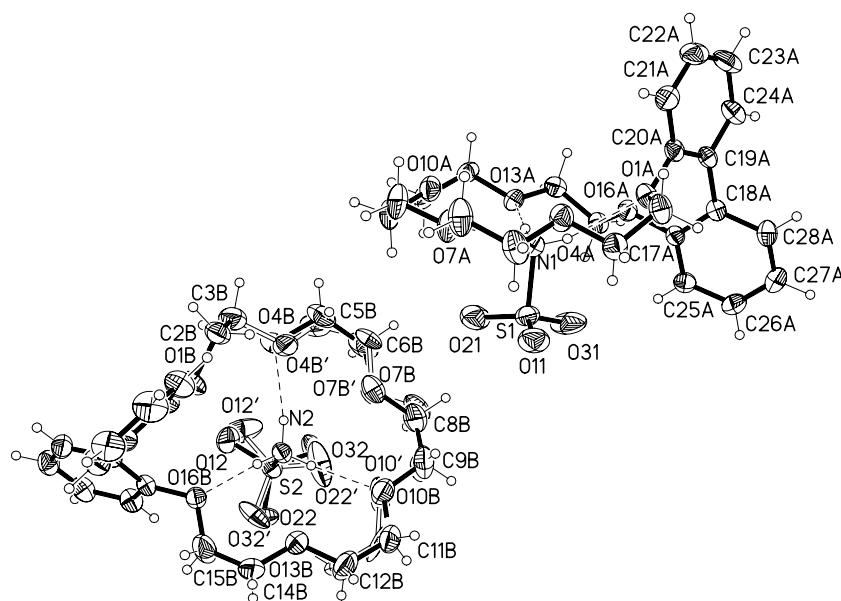*Figure 4*. ORTEP drawing of **2·NH₃SO₃** with hydrogen bonds shown by dotted lines and disordered fragments shown by open lines.

Table 3. Selected bond lengths (Å) and angles (deg) in **(1)·NH₃SO₃·MeOH** and **(2)·NH₃SO₃**

Bond	**1·NH₃SO₃·MeOH**	Bond	**(2A)·NH₃SO₃**	Bond	**(2B)·NH₃SO₃**
S1–O2S	1.400(3)	S1–O31	1.406(2)	S2–O12′	1.37(1)
S1–O3S	1.414(3)	S1–O11	1.412(2)	S2–O32′	1.39(1)
S1–O1S	1.429(3)	S1–O21	1.418(2)	S2–O22′	1.40(1)
S1–O2SA	1.45(3)	S1–N1	1.794(2)	S2–O32	1.401(9)
S1–N1	1.767(2)			S2–O22	1.406(6)
				S2–O12	1.429(6)
				S2–N2	1.782(2)
Angle					
O1S–S1–O2S	113.2(4)	O31–S1–O11	116.9(1)	O12′–S2–O32′	119(1)
O1S–S1–O3S	113.8(2)	O31–S1–O21	115.8(2)	O12′–S2–O22′	115(1)
O2S–S1–O3S	121.3(3)	O11–S1–O21	115.1(1)	O32′–S2–O22′	112(1)
O1S–S1–N1	102.4(1)	O31–S1–N1	101.7(1)	O32–S2–O22	117.6(7)
O2S–S1–N1	101.2(2)	O11–S1–N1	102.3(1)	O32–S2–O12	117.8(6)
O3S–S1–N1	101.0(1)	O21–S1–N1	101.4(1)	O22–S2–O12	112.5(5)
				O32–S2–N2	103.3(5)
				O22–S2–N2	102.3(4)
				O12–S2–N2	99.6(4)

also participate in the minor component of the bifurcated hydrogen bond (Table 4).

In the both complexes the crown ethers molecules strictly change their shapes in comparison with the initial ligands. In the adduct **1·H₃NSO₃·MeOH** the macrocycle adopts approximately perfect crown-like conformation approaching D₃d symmetry with all C–C–O–C torsion angles, except C12–O13, being *trans* (the corresponding values are in the range 136.6–177.6°), and all O–C–C–O angles being *gauche,* except those that belong to the benzene units and being *cis* (Table 2). In **2·NH₃SO₃** the conformation of **2A** crown molecule is very close to the common crown-like shape, with all C–O angles being *trans*- and all Csp³–Csp³ bonds being *gauche*. The conformation of **2B** molecule is quite

distorted due to the disorder of the fragment of oxyethylene loop. The complex formation influences the mutual arrangement of benzene rings in the macrocycle **1** – the interfacial angle between the aromatic units in **1·NH₃SO₃·MeOH** is decreased up to 63.4(1)° in comparison with 87.5(1)° in **1** itself but is only slightly increased up to 65.9(2)° and 69.7(2)° in two independent formula units in **2·NH₃SO₃** in comparison with 63.8(1)° in **2** itself.

The molecular packing in **1·NH₃SO₃·MeOH** is dictated by the availability of methanol molecule which fulfills the bridging function and combines the complexes related by the two-fold screw axis in the chain (Figure 5) *via* the O–H···O(S) hydrogen bonds as H-donor (Table 4) and *via* C_Ar–H···O interactions

Table 4. Hydrogen bonds in **1·NH₃SO₃·MeOH** and **2·NH₃SO₃**

D–H···A	d(H···A), Å	d(D···A), Å	∠(DHA), deg
1·NH₃SO₃·MeOH			
N1–H1···O1	2.51(3)	3.047(3)	120(2)
N1–H1···O4	2.04(2)	2.888(3)	164(3)
N1–H2···O7	2.56(3)	3.001(3)	112(2)
N1–H2···O10	2.00(2)	2.865(3)	173(3)
N1–H3···O13	2.28(2)	2.900(3)	128(2)
N1–H3···O16	2.18(2)	3.002(3)	158(3)
O1ME–H1OM···O2S	2.25	2.766(6)	122
O1ME–H1OM···O2SA	1.70	2.39(3)	141
2·NH₃SO₃			
N1–H3···O1A	2.33(2)	3.176(2)	164(2)
N1–H2···O4A	2.65(2)	3.094(2)	113(2)
N1–H2···O7A	2.01(2)	2.873(2)	167(2)
N1–H1···O10A	2.59(2)	3.047(2)	114(2)
N1–H1···O13A	1.98(2)	2.848(2)	170(2)
N1–H3···O16A	2.80(2)	3.211(2)	111(2)
N2–H13···O4B	2.10(2)	2.954(8)	170(2)
N2–H13···O4B′	2.08(2)	2.93(2)	167(2)
N2–H13···O7B	2.53(2)	2.982(5)	114(2)
N2–H13···O7B′	2.43(2)	2.847(8)	110(2)
N2–H12···O10B	2.06(2)	2.93(1)	175(3)
N2–H12···O13B	2.56(3)	2.992(2)	112(2)
N2–H11···O16B	2.02(2)	2.898(2)	170(2)

C23···O1ME(1.5−x, 0.5+y, 0.5−z) 3.481(3) Å, H23···O1ME(1.5−x, 0.5+y, 0.5−z) 2.57 Å, angle C23–H23···O1ME(1.5−x, 0.5+y, 0.5−z) 166° as H-acceptor.

The molecular packing of **2·NH₃SO₃** exhibits some interesting features. Both of independent complexes formed by the crown molecule **2A** or **2B** formulate the similar pseudo-chains (Figure 6a), where the macrocycles are arranged in such a way, that one of the benzene units is displayed approximately perpendicular to the plane of six oxygens of the related by the inversion center macrocycle (the dihedral angle is 119.5°), while the interfacial distance between the related by inversion benzene rings is equal 3.228 Å, however without overlapping typical for π–π stacking interactions.

There may be distinguished zones of lower polarity formed by the zipper-like chains of benzene rings and zones of higher polarity formed by the negative poles of zwitterion dipoles (Figure 6b). The zones of lower polarity are inside these double chains, while zwitterions are oriented by the negative –SO₃⁻ ends outside, in the voids between these chains.

Conclusions

Under interaction of amidosulfuric acid in boiling aqueous isopropanol with symmetric (distal, **A**) and asymmetric (proximal, **B**) dibenzocrown ethers containing from 6 to 10 oxygen atoms, and their biphenyl (**C**), diphenyloxide (**D**) and diphenylsulfide (**E**) analogs containing from 5 to 7 oxygen atoms (15 macrocycles in all), only in the cases of proximal hexadentate [1.5]dibenzo-18-crown-6 (**1**), [2.4]-dibenzo-18-crown-6 (**3**) and biphenyl-20-crown-6 (**2**) the corresponding complexes (1:1) were separated. These results show the considerable distinction of the dibenzocrown ethers from aliphatic, cycloaliphatic and monobenzocrown ethers, for which the complexes with amidosulfuric acid in all the cases have been isolated easily. The proposition that obtained results just reflect the synthetical (preparative) aspects of this kind adducts formation, specified both by the reaction conditions and the optimal interaction of amidosulfuric acid zwitterion with cavity of macrocycles under consideration *via* tripod-like bifurcated N–H···O hydrogen bonds was made.

In the complexes **1·H₃NSO₃·MeOH** and **2·H₃NSO₃** the zwitterion form of amidosulfuric acid is convinced by the similar S–O distances and objective localization of three hydrogen atoms in the close proximity and in the tetrahedral arrangement around the nitrogen atom. The anchoring hydrogen bonds between **H₃NSO₃** and alternate oxygen atoms in the crown ether are indicated by the short N–H···O distances to these three oxygen atoms, as it is a major component of the bifurcated N–H···O hydrogen bonds, while three remaining crown oxygens also participate in the minor component of the bifurcated hydrogen bond.

In the both complexes the crown ethers molecules strictly change their shapes in comparison with the initial ligands. At the same time the complex formation influences the mutual arrangement of benzene rings in the macrocycle **1** – the pseudodihedral angle between the
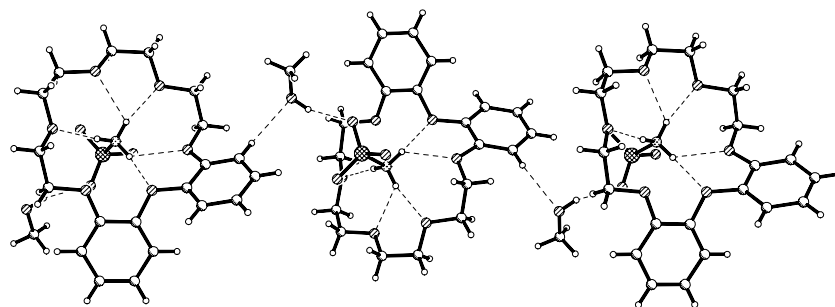

Figure 5. Chain organization in **1·NH₃SO₃·MeOH**.
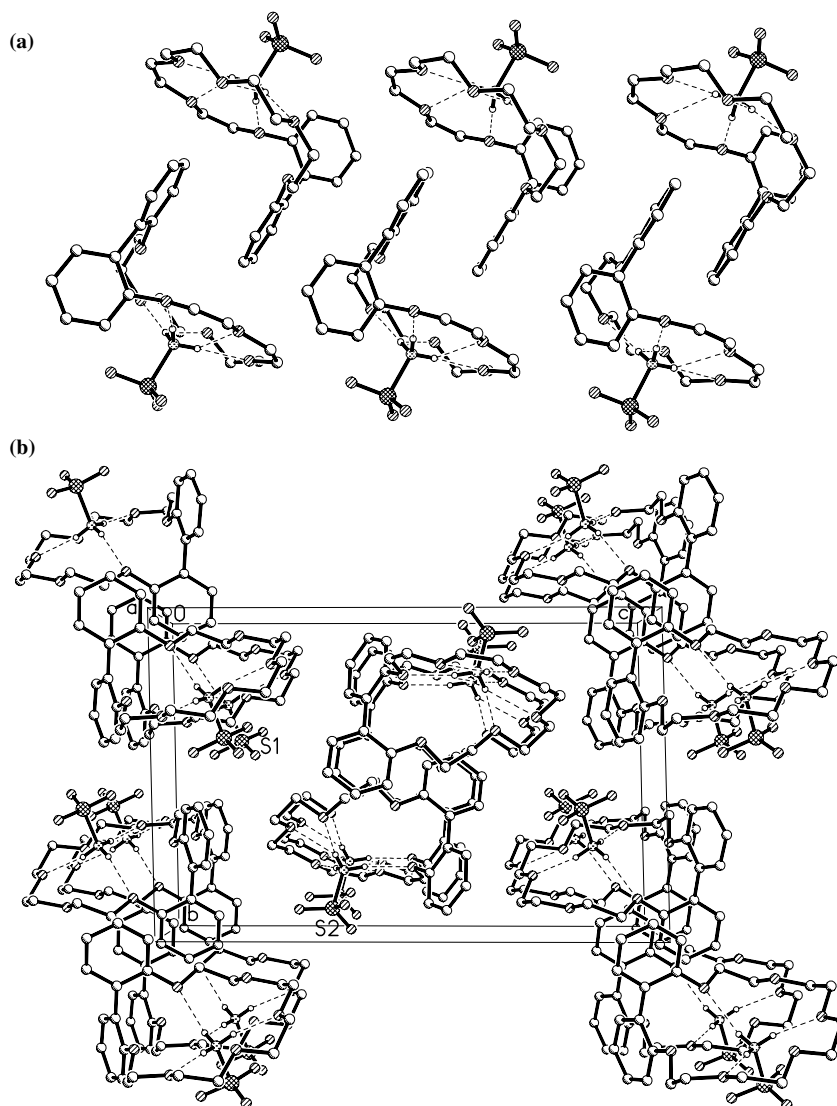
Figure 6. (a) Chain organization in **2·NH₃SO₃**, (b) packing of the chains in the crystal.

aromatic units in **1·NH₃SO₃·MeOH** is decreased more than 24° in comparison with ligand **1** itself but in **2 NH₃SO₃** is only slightly increased into 2–5° in comparison with the initial macrocycle **2** itself.

The molecular packing in **1·NH₃SO₃·MeOH** is dictated by the availability of methanol molecule which fulfills the bridging function and combines the complexes related by the two-fold screw axis in the chain *via* the O–H···O(S) hydrogen bonds as H-donor and *via* C$_{Ar}$–H···O interactions as H-acceptor.

The molecular packing of **2·NH₃SO₃** exhibits some interesting features – complexes form the pseudo-chains, where the macrocycles are arranged in such a way, that one of the benzene units is displayed approximately perpendicular to the plane of six oxygens of the related by the inversion center macrocycle, while the interfacial distance between the related by inversion benzene rings is equal 3.228 Å, however without overlapping typical for π–π stacking interactions.

Supplementary material

Crystallographic data for the structural analysis of four reported compounds have been deposited with the Cambridge Crystallographic Data Center, publication numbers CCDC 235721, CCDC 235722, CCDC 235723, and CCDC 235724. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1233-336-033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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