

## Twelve-Membered Crown Ethers: Crystal Structures of Benzo-12-crown-4 and Naphtho-12-crown-4

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(Received: 1 October 1992; in final form: 3 February 1993)

**Abstract.** The crystal structures of two 12-membered crown ethers, benzo-12-crown-4 (**1**) and naphtho-12-crown-4 (**2**), have been determined by X-ray analysis. Both structures are molecular. Compound **1** is monoclinic,  $P2_1/b$ ,  $a = 8.466(3)$ ,  $b = 8.019(3)$ ,  $c = 33.590(10)$  Å,  $\gamma = 90.99(3)^\circ$ . The unit cell contains two crystallographically independent molecules of **1** with similar conformations. Compound **2** is also monoclinic,  $P2_1/a$ ,  $a = 24.148(8)$ ,  $b = 14.535(4)$ ,  $c = 7.987(5)$  Å,  $\gamma = 102.87(2)^\circ$ . Two independent molecules in the unit cell have significantly different conformations.

**Key words.** 12-membered crown ethers, crystal structure, conformation peculiarities, X-ray analysis, CH $\cdots$ O contacts.

**Supplementary data** relating to this publication have been deposited with the British Library as Supplementary Publication No. SUP 82145 (19 pages).

### 1. Introduction

Twelve-membered crown ethers have been extensively studied by X-ray crystallography. After Groth's paper [1] dealing with the structure and conformation of 12-crown-4 at  $-150^\circ\text{C}$  further publications devoted to the X-ray analysis of 12-crown-4 derivatives (dibenzo-12-crown-4 [2], *cis-syn-cis* and *cis-anti-cis* isomers of dicyclohexano-12-crown-4 [3]) have appeared.

However no data in the literature have been found on the structure of free benzo-12-crown-4. The conclusions on its molecular and conformational peculiarities were based on computational approaches [4] or on data obtained from the structural investigations of its complexes [5, 6]. Simultaneously, substituted benzo-12-crown-4 derivatives (acetylbenzo-12-crown-4, diphenylacetylbenzo-12-crown-4) have been described [7, 8]. Interest in these compounds is stimulated by their biological activity and the necessity to understand the mechanism of metal ion–crown ether interactions in systems with a small endocyclic cavity. The latter is characterized by the increased rigidity of the heteroatomic framework caused by a small number of atoms in the ring and by the planarity of the condensed aromatic residues [9].

Discussions on the conformational changes of benzo-12-crown-4 in the process of complexation were, to a certain extent, speculative in character [4, 7] because the conformation of the free ether was unknown.

This prompted us to undertake X-ray studies of the free benzo-12-crown-4 and the related naphtho-12-crown-4.

## 2. Experimental

### 2.1. SYNTHESIS OF COMPOUND 1 (BENZO-12-CROWN-4)

A solution of 4.6 g (0.2 mole) of lithium hydroxide and 8.0 g (0.2 mole) of sodium hydroxide in 20 mL of water was added to a solution of 11.0 g (0.1 mole) of catechol in 200 mL of isoamyl alcohol. The mixture was heated to boiling and 18.7 g (0.1 mole) of 1,2-bis(2-chloroethoxy)ethane were added. Boiling was continued for 12 h. The mixture was cooled to 20° and filtered. The filtrate was evaporated, the residue dissolved in benzene and washed with 10% sodium hydroxide solution. The separated organic layer was evaporated and the residue was distilled *in vacuo*. The fraction boiling at 145–150°C (0.5 mm Hg) was collected. Yield 5.6 g (25%). To obtain crystals suitable for X-ray analysis the product was dissolved in a diethyl ether–hexane (1:1) mixture and allowed to evaporate spontaneously. Colourless transparent crystals melting at 53–54° were obtained. This compound is soluble in benzene, chloroform, ethanol and acetone.

### 2.2. SYNTHESIS OF COMPOUND 2 (NAPHTHO-12-CROWN-4)

1,2-Bis(2-chloroethoxy)ethane (46.8 g, 0.25 mole) was added dropwise to a mixture of 40 g (0.25 mole) of 2,3-dihydroxynaphthalene and 22 g (0.52 mole) of LiOH·H<sub>2</sub>O in 500 mL of *n*-butanol, heated to boiling and stirred under argon. The reaction was continued for 5 days. The mixture was then acidified and evaporated. The residue was mixed with water and extracted with CHCl<sub>3</sub>. The organic layer was dried with MgSO<sub>4</sub> and evaporated. The product, initially purified by extraction with hot *n*-heptane, was placed on a silica gel column. The product was eluted with CH<sub>2</sub>Cl<sub>2</sub> and crystallized from *n*-heptane. Yield: 12 g (17.5%) of naphtho-12-crown-4, m.p. 102–103°C (lit. 102–103°C [10]).

### 2.3. X-RAY DATA COLLECTION, STRUCTURE DETERMINATION AND REFINEMENT FOR COMPOUNDS 1 AND 2

Crystal and experimental parameters are given in Table I. For compounds 1 and 2, data were collected on a DAR-UMB diffractometer by the  $\omega$ - $\theta$ /2 $\theta$  scan technique, using CuK $\alpha$  radiation (graphite monochromator,  $\lambda$  CuK $\alpha$  = 1.54178 Å). Standard selected reflections were monitored every hour to check the intensity variation. The deviations of their intensity were lower than 3%. The intensities were corrected for Lorentz and polarization effects but not for absorption.

Both structures were solved using direct methods in the SHELXTL package [11]. All nonhydrogen atoms were found and refined with anisotropic temperature factors, whereas all hydrogen atoms were found and refined isotropically. The final

Table I. Experimental data for the crystallographic analyses of compounds **1** and **2**

	<b>1</b>	<b>2</b>
Formula	C <sub>12</sub> H <sub>16</sub> O <sub>4</sub>	C <sub>16</sub> H <sub>18</sub> O <sub>4</sub>
Molecular weight	224.26	274.32
Space group	<i>P</i> 2 <sub>1</sub> / <i>b</i>	<i>P</i> 2 <sub>1</sub> / <i>a</i>
<i>a</i> Å	8.466(3)	24.148(8)
<i>b</i> Å	8.019(3)	14.535(4)
<i>c</i> Å	33.590(10)	7.987(5)
$\gamma$	90.99(3)	102.87(2)
<i>V</i> (Å) <sup>3</sup>	2279.8	2732.9
<i>Z</i>	8	8
<i>d</i> <sub>calc</sub> , g cm <sup>-3</sup>	1.307	1.333
Crystal size, mm	0.20 × 0.25 × 0.40	0.25 × 0.30 × 0.60
Diffractometer	DAR-UMB	DAR-UMB
$\mu$ cm <sup>-1</sup> (CuK $\alpha$ )	8.19	7.91
Scan speed deg.min <sup>-1</sup>	8	8
Radiation	CuK $\alpha$	CuK $\alpha$
$\sin \theta/\lambda$ (Å) <sup>-1</sup>	≤ 0.62	≤ 0.63
<i>h</i> range	0:10	0:30
<i>k</i> range	0:9	0:8
<i>l</i> range	0:37	0:8
Scan mode	$\omega$ - $\theta$ /2 $\theta$	$\omega$ - $\theta$ /2 $\theta$
Number of measured reflections	3074	3848
Condition for observed reflection	<i>I</i> > 3 $\sigma$ ( <i>I</i> )	<i>I</i> > 3 $\sigma$ ( <i>I</i> )
Number of reflections used for refinement	2702	3622
Number of refined parameters	321	373
$R = \frac{\sum \Delta }{\sum F_0 }$	0.058	0.057
<i>R</i> <sub>w</sub>	0.065	0.073

*R*-factors for compounds **1** and **2** are given in Table I,  $w = [\sigma(F)]^{-2}$ . The final positional parameters of atoms are given in Table II, the bond lengths and angles are given in Tables III and IV.

### 3. Results and Discussion

Figures 1 and 2 represent the crystal structures of compounds **1** and **2**. The presence of two independent molecules in the unit cell is a specific feature of the compounds. This property probably promotes close packing in the crystal lattice. The possibility of stacking interactions [12] of aromatic fragments in **1** and **2** was considered. This stacking is characterized by: (1) an antiparallel column arrangement of the aromatic rings; and (2) shortened distances between them. Compound **2** exhibits the first characteristic: the reciprocal arrangement of the aromatic residues of independent (a and b) molecules is close to parallel and is described by the dihedral angle

Table II. Fractional atomic coordinates ( $\times 10^4$ ) for compounds **1** and **2**

Atom	Compound 1				Compound 2			
	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B<sub>eq</sub></i>	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B<sub>eq</sub></i>
O(1A)	9605(2)	70(2)	1564(1)	419(6)	4057(1)	1325(2)	1472(3)	305(6)
C(2A)	9297(4)	-1682(1)	1628(1)	436(10)	3813(1)	2127(2)	1209(4)	300(10)
C(3A)	9854(4)	-2567(4)	1258(1)	437(9)	3178(2)	1758(3)	1044(4)	310(10)
O(4A)	8771(3)	-2287(3)	940(1)	466(7)	2943(1)	1285(2)	2528(3)	315(7)
C(5A)	9505(4)	-1820(5)	574(1)	524(11)	2598(1)	368(3)	2267(4)	345(10)
C(6A)	9855(4)	8(4)	547(1)	477(10)	2922(2)	-369(3)	1923(4)	334(10)
O(7A)	8412(2)	841(3)	452(1)	458(7)	3223(1)	-521(2)	3406(3)	315(7)
C(8A)	8528(4)	2602(4)	463(1)	467(10)	3606(2)	-1128(2)	3134(4)	343(10)
C(9A)	7898(4)	3303(4)	843(1)	416(9)	4141(2)	-654(2)	2243(4)	297(9)
O(10A)	8857(2)	2715(3)	1158(1)	400(6)	4455(1)	75(2)	3298(2)	267(6)
C(11A)	8183(3)	2545(4)	1527(1)	329(8)	4839(1)	776(2)	2473(3)	224(8)
C(12A)	8594(3)	1151(3)	1739(1)	316(8)	4635(1)	1475(2)	1560(4)	237(8)
C(13A)	8012(4)	921(4)	2120(1)	392(9)	5009(1)	2216(2)	850(4)	248(9)
C(14A)	6978(4)	2063(4)	2285(1)	451(10)	5605(1)	2272(2)	991(3)	236(8)
C(15A)	6529(4)	3418(4)	2060(1)	462(10)	5809(1)	1580(2)	1882(4)	240(8)
C(16A)	7135(4)	3680(4)	1681(1)	408(9)	5409(1)	829(2)	2639(4)	249(8)
C(17A)	-	-	-	-	6403(1)	1654(3)	1997(4)	328(10)
C(18A)	-	-	-	-	6779(2)	2375(3)	1244(5)	386(11)
C(19A)	-	-	-	-	6578(2)	3058(3)	314(5)	407(11)
C(20A)	-	-	-	-	6007(2)	3010(2)	195(4)	328(10)
O(1B)	5353(2)	2631(2)	-1555(1)	469(6)	550(1)	5938(2)	1856(3)	346(7)
C(2B)	5649(4)	882(4)	-1598(9)	439(9)	709(1)	5258(2)	2903(4)	352(11)
C(3B)	5148(4)	43(4)	-1223(1)	456(9)	1341(1)	5409(2)	2786(5)	332(10)
O(4B)	6253(3)	411(3)	-915(1)	487(7)	1618(1)	6312(2)	3426(2)	272(6)
C(5B)	5569(4)	832(5)	-543(1)	573(12)	1978(1)	6895(2)	2260(4)	282(9)
C(6B)	5206(4)	2650(5)	-514(1)	578(12)	1669(1)	7417(2)	1099(4)	272(9)
O(7B)	6648(3)	3571(3)	-447(1)	509(7)	1469(1)	8111(2)	2051(3)	283(6)
C(8B)	6503(4)	5310(5)	-477(1)	503(11)	1136(1)	8626(2)	1117(4)	303(9)
C(9B)	7156(4)	5969(4)	-862(1)	449(10)	511(1)	8194(2)	1227(4)	289(9)
O(10B)	6160(2)	5338(3)	-1169(1)	444(6)	371(1)	7375(2)	175(2)	271(6)
C(11B)	6829(3)	5137(4)	-1537(1)	338(8)	-101(1)	6722(2)	700(4)	243(8)
C(12B)	6390(3)	3711(3)	-1744(1)	346(8)	-11(1)	5926(2)	1602(4)	248(8)
C(13B)	6966(4)	3444(4)	-2119(1)	404(9)	-460(1)	5239(2)	2142(4)	278(9)
C(14B)	8016(4)	4580(4)	-2292(1)	454(10)	-1027(1)	5316(2)	1771(4)	250(8)
C(15B)	8497(4)	5967(4)	-2083(1)	442(9)	-1118(1)	6109(2)	858(4)	249(8)
C(16B)	7891(4)	6255(4)	-1707(1)	426(9)	-639(1)	6801(2)	326(4)	264(9)
C(17B)	-	-	-	-	-1681(1)	6166(3)	484(4)	333(10)
C(18B)	-	-	-	-	-2133(1)	5481(3)	1012(5)	380(11)
C(19B)	-	-	-	-	-2048(1)	4716(3)	1934(5)	398(11)
C(20B)	-	-	-	-	-1502(1)	4629(3)	2338(4)	345(10)

$$B_{eq} = \exp[-1/4(B_{11}a^*2h^2 + B_{22}b^*2k^2 + \dots + 2B_{23}b^*c^*kl)]$$

between them ( $3.2^\circ$ , compared to  $61.4^\circ$  in compound **1**). In spite of the parallel arrangement no stacking is present due to the large distances between molecules. The dihedral angles between the mean planes defined by the heteroatoms of the independent crown ether molecules are  $3.6^\circ$  (between **1a** and **1b**) and  $38.2^\circ$  (between **2a** and **2b**). The mutual arrangement of the aromatic and heterocyclic

Table III. Bond distances (Å) in compounds **1** and **2**

Bond	Compound <b>1</b>	Compound <b>2</b>
O(1A)—C(2A)	1.440(4)	1.435(4)
C(2A)—C(3A)	1.510(5)	1.513(5)
C(3A)—O(4A)	1.430(4)	1.421(4)
O(4A)—C(5A)	1.423(4)	1.423(4)
C(5A)—C(6A)	1.493(5)	1.487(5)
C(6A)—O(7A)	1.438(4)	1.431(4)
O(7A)—C(8A)	1.414(4)	1.429(4)
C(8A)—C(9A)	1.496(5)	1.503(5)
C(9A)—O(10A)	1.420(4)	1.431(4)
O(10A)—C(11A)	1.371(3)	1.382(3)
C(11A)—C(12A)	1.374(4)	1.427(4)
C(12A)—C(13A)	1.384(4)	1.366(4)
C(13A)—C(14A)	1.393(4)	1.426(4)
C(14A)—C(15A)	1.382(5)	1.409(4)
C(15A)—C(16A)	1.388(5)	1.424(4)
C(16A)—C(11A)	1.382(4)	1.361(4)
C(12A)—O(1A)	1.362(3)	1.367(4)
C(17A)—C(15A)	—	1.417(4)
C(17A)—C(18A)	—	1.364(5)
C(18A)—C(19A)	—	1.410(5)
C(19A)—C(20A)	—	1.371(5)
C(14A)—C(20A)	—	1.425(4)
O(1B)—C(2B)	1.436(4)	1.414(4)
C(2B)—C(3B)	1.488(5)	1.495(5)
C(3B)—O(4B)	1.421(4)	1.427(4)
O(4b)—C(5B)	1.421(4)	1.419(4)
C(5B)—C(6B)	1.498(5)	1.497(4)
C(6B)—O(7B)	1.434(4)	1.427(4)
O(7B)—C(8B)	1.405(4)	1.425(4)
C(8B)—C(9B)	1.497(5)	1.501(4)
C(9B)—O(10B)	1.420(4)	1.434(4)
O(10B)—C(11B)	1.372(3)	1.374(4)
C(11B)—C(12B)	1.384(4)	1.420(4)
C(12B)—C(13B)	1.368(4)	1.368(4)
C(13B)—C(14B)	1.389(4)	1.430(4)
C(14B)—C(15B)	1.371(5)	1.411(4)
C(15B)—C(16B)	1.383(5)	1.424(4)
C(11B)—C(16B)	1.382(4)	1.361(4)
O(1B)—C(12B)	1.377(3)	1.367(4)
C(15B)—C(17B)	—	1.417(4)
C(17B)—C(18B)	—	1.369(5)
C(18B)—C(19B)	—	1.385(5)
C(19B)—C(20B)	—	1.388(5)
C(14B)—C(20B)	—	1.417(4)

rings in **1** and **2** is characterized by the dihedral angles between the planar aromatic fragments and the mean planes of the oxygen atoms of the macrocycle:

	<b>1a</b>	<b>1b</b>	<b>2a</b>	<b>2b</b>
Dihedral angle (deg.)	131.4	130.5	169.1	141.8

Table IV. Bond angles (deg.) in compounds **1** and **2**

Angle	Compound <b>1</b>	Compound <b>2</b>
C(2A)—O(1A)—C(12A)	116.7(2)	117.8(2)
O(1A)—C(2A)—C(3A)	106.4(3)	106.9(3)
C(2A)—C(3A)—O(4A)	109.6(3)	111.2(3)
C(3A)—O(4A)—C(5A)	114.1(2)	114.6(2)
O(4A)—C(5A)—C(6A)	112.8(3)	114.2(3)
C(5A)—C(6A)—O(7A)	108.3(3)	109.0(3)
C(6A)—O(7A)—C(8A)	114.4(2)	112.9(2)
O(7A)—C(8A)—C(9A)	112.1(3)	113.4(3)
C(8A)—C(9A)—O(10A)	107.6(3)	108.6(3)
C(9A)—O(10A)—C(11A)	117.9(2)	114.9(2)
O(10A)—C(11A)—C(12A)	115.9(3)	119.1(2)
O(1A)—C(12A)—C(11A)	117.7(2)	114.5(2)
C(12A)—C(13A)—C(14A)	120.4(3)	119.6(3)
C(13A)—C(14A)—C(15A)	118.8(3)	120.5(3)
C(14A)—C(15A)—C(16A)	121.0(3)	118.6(3)
C(11A)—C(16A)—C(15A)	118.8(3)	120.2(3)
C(12A)—C(11A)—C(16A)	121.1(3)	120.8(3)
C(11A)—C(12A)—C(13A)	119.5(3)	120.0(3)
C(15A)—C(17A)—C(18A)	—	121.2(3)
C(17A)—C(18A)—C(19A)	—	119.9(3)
C(18A)—C(19A)—C(20A)	—	120.0(3)
C(14A)—C(20A)—C(19A)	—	121.1(3)
C(14A)—C(15A)—C(17A)	—	119.2(3)
C(15A)—C(14A)—C(20A)	—	118.3(3)
C(2B)—O(1B)—C(12B)	116.6(2)	120.1(2)
O(1B)—C(2B)—C(3B)	107.6(3)	106.7(3)
C(2B)—C(3B)—O(4B)	109.9(3)	111.5(3)
C(3B)—O(4B)—C(5B)	114.8(2)	114.4(2)
O(4B)—C(5B)—C(6B)	112.2(3)	113.7(2)
C(5B)—C(6B)—O(7B)	108.9(3)	108.2(2)
C(6B)—O(7B)—C(8B)	114.5(3)	114.2(2)
O(7B)—C(8B)—C(9B)	112.0(3)	112.4(3)
C(8B)—C(9B)—O(10B)	106.7(3)	110.1(2)
C(9B)—O(10B)—C(11B)	116.9(2)	113.6(2)
O(10B)—C(11B)—C(12B)	116.4(3)	117.6(2)
C(11B)—C(12B)—O(1B)	116.6(3)	113.2(2)
C(11B)—C(12B)—C(13B)	119.4(3)	120.9(3)
C(12B)—C(13B)—C(14B)	120.4(3)	119.6(3)
C(13B)—C(14B)—C(15B)	119.7(3)	119.5(3)
C(14B)—C(15B)—C(16B)	119.8(3)	118.9(3)
C(11B)—C(16B)—C(15B)	120.4(3)	120.9(3)
C(15B)—C(17B)—C(18B)	—	120.6(3)
C(17B)—C(18B)—C(19B)	—	120.6(3)
C(18B)—C(19B)—C(20B)	—	120.6(3)
C(14B)—C(20B)—C(19B)	—	119.8(3)
C(14B)—C(15B)—C(17B)	—	119.0(3)
C(15B)—C(14B)—C(20B)	—	119.2(3)

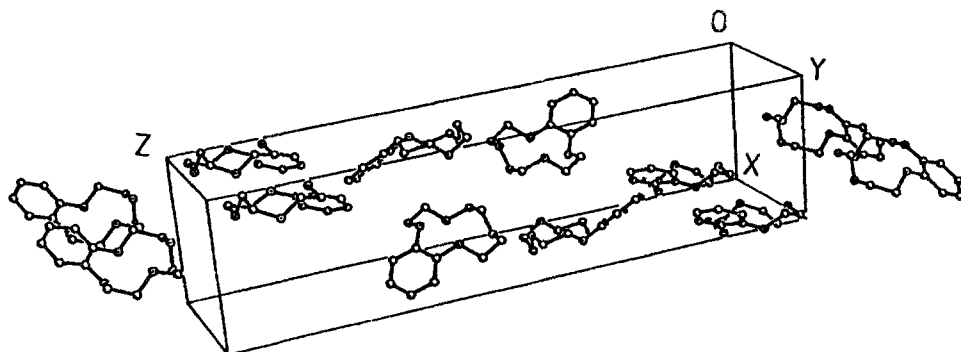


Fig. 1. The crystal packing of compound 1.

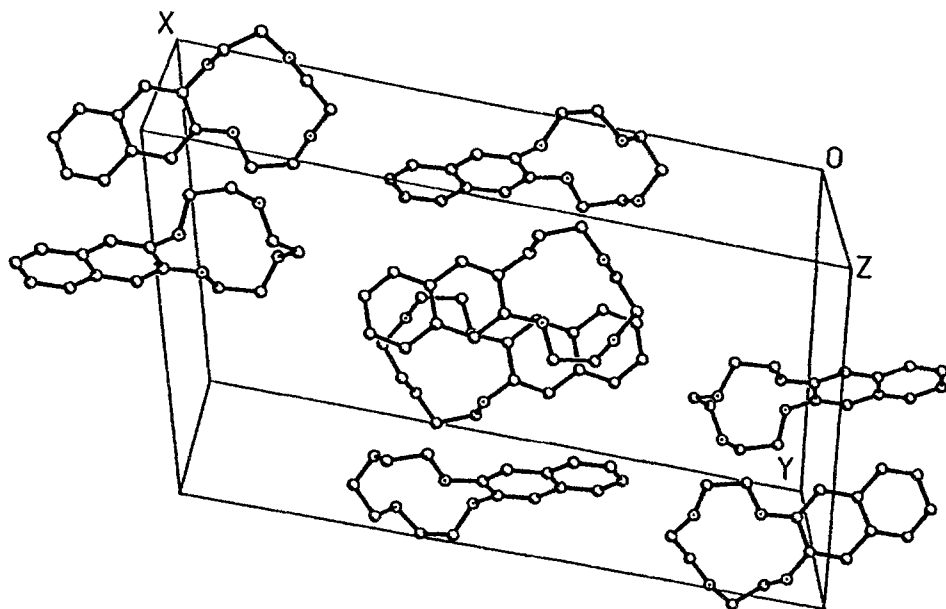


Fig. 2. The crystal packing of compound 2.

The entire conformation of the molecules may be described as half-chair, with the **2a** and **2b** molecules being flatter than **1a** and **1b**; in both structures the pyrocatechol fragment is essentially planar (in **1a** the deviations from the aromatic system plane for atoms O(1) and O(10) are  $-0.029$  and  $0.047$  Å; in **1b**  $-0.041$  and  $0.028$  Å; in **2a**  $0.038$  and  $-0.093$  Å and in **2b**  $-0.018$  and  $0.020$  Å).

It is known, that the *gauche* conformation of C—C bonds and the *trans* conformation of C—O bonds is energetically convenient for the polyoxyethylene chain. This is also true for 18-crown-6 and related 18-membered crown ethers which, under interaction with alkali and alkaline-earth cations as well as with ammonium or hydroxonium cations, adopt a conformation close to  $D_{3d}$  symmetry [13]. In the

free 18-crown-6 molecule [14] two C—O bonds transform from the *trans* to the *gauche* conformation and one of the hydrogen atoms of the two methylene fragments enters the cavity. In [4], two most energetically favoured conformations of benzo-12-crown-4 and acetylbenzo-12-crown-4 were proposed on the basis of conformational approaches. The conformation proposed for acetylbenzo-12-crown-4 [4] is close to that obtained from X-ray data. When describing the crown ether conformation our main concern was turned to:

- the configuration of the bond close to the pyrocatechol fragment;
- the number, the character and the arrangement along the heterocyclic framework of the corner fragments (the location of two *gauche* bonds of the same (pseudo corner) or opposite ('genuine' corner) signs [15]).

The aromatic moiety fused to the heterocyclic framework of the crown ether increases its rigidity and determines the conformation of the part of the ring bound directly to the condensed rings. In crown ethers with 18 or more atoms the pyrocatechol fragment has, as a rule, a *trans-cis-trans* conformation [16–18]. A decrease of the number of atoms in the ring (15–12 membered rings) causes strain in the unsaturated part of the macroring and the conformation of the corresponding fragment may be described as *trans-cis-trans* (dibenzo-12-crown-4 (119°; 2; 155°) [2], benzo-15-crown-5 in the complex with aminosulfuric acid (–158; –1; 132°) [19]), as well as *trans-cis-gauche* (dibenzo-15-crown-5 derivative of 1,4-naphthoquinone (–168; 6.1; –41.6°; –178.8; –8.8; 44.6°) [10]). Figures 3 and 4 present the general view of the independent molecules of **1** and **2**. In both molecules of compound **1** (**1a** and **1b**) the pyrocatechol fragment has a *trans-cis-trans* conformation with a deviation of the *trans* torsion angles from the ideal value of 180° (to 139.4–141.2°) (Table V). A similar conformation of the above fragment

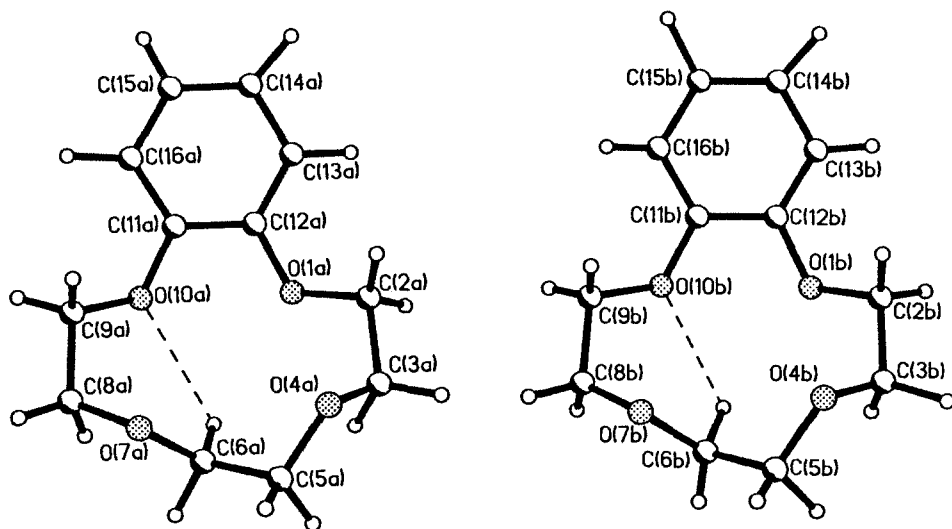


Fig. 3a (left). The structure of molecule **1a** (dotted line denotes intramolecular CH...O contacts).

Fig. 3b (right). The structure of molecule **1b** (dotted line denotes intramolecular CH...O contacts).



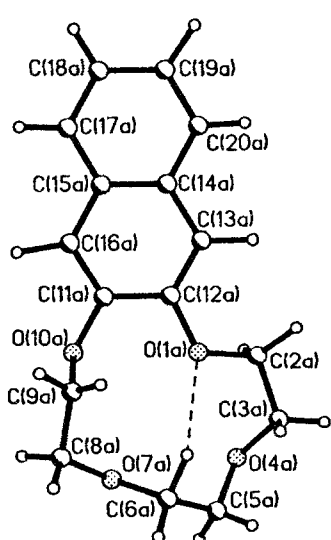


Fig. 4a (left). The structure of molecule 2a (dotted line denotes intramolecular CH...O contacts).

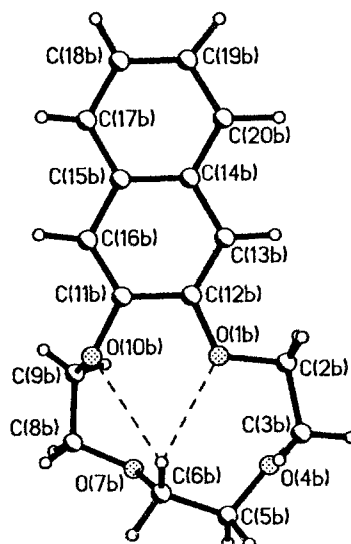


Fig. 4b (right). The structure of molecule 2b (dotted line denotes intramolecular CH...O contacts).

Table V. Torsion angles (deg.) in the crown-ether framework in compounds 1 and 2

Angle	Compound 1	Compound 2
C(12A)—O(1A)—C(2A)—C(3A)	148.6	176.2
O(1A)—C(2A)—C(3A)—O(4A)	-73.7	61.2
C(2A)—C(3A)—O(4A)—C(5A)	133.2	-128.8
C(3A)—O(4A)—C(5A)—C(6A)	-85.9	76.6
O(4A)—C(5A)—C(6A)—O(7A)	-77.9	68.0
C(5A)—C(6A)—O(7A)—C(8A)	173.0	-172.2
C(6A)—O(7A)—C(8A)—C(9A)	-99.9	76.1
O(7A)—C(8A)—C(9A)—O(10A)	63.4	65.2
C(8A)—C(9A)—O(10A)—C(11A)	-151.8	-158.0
C(9A)—O(10A)—C(11A)—C(12A)	139.6	76.3
O(10A)—C(11A)—C(12)—O(1A)	-0.7	-5.8
C(11A)—C(12A)—O(1A)—C(2A)	-141.2	155.4
C(12B)—O(1B)—C(2B)—C(3B)	146.9	174.9
O(1B)—C(2B)—C(3B)—O(4B)	-73.7	63.9
C(2B)—C(3B)—O(4B)—C(5B)	135.6	-121.7
C(3B)—O(4B)—C(5B)—C(6B)	-86.1	82.7
O(4B)—C(5B)—C(6B)—O(7B)	-76.5	69.1
C(5B)—C(6B)—O(7B)—C(8B)	170.3	-176.3
C(6B)—O(7B)—C(8B)—C(9B)	-103.2	93.0
O(7B)—C(8B)—C(9B)—O(10B)	66.8	-76.5
C(8B)—C(9B)—O(10B)—C(11B)	-152.3	153.4
C(9B)—O(10B)—C(11B)—C(12B)	139.5	-99.9
O(10B)—C(11B)—C(12B)—O(1B)	-1.3	1.2
C(11B)—C(12B)—O(1B)—C(2B)	-139.4	172.4

was found in diphenylacetylbenzo-12-crown-4 [8] (the values of the corresponding torsion angles are  $-123; 1.3; 159^\circ$ ) and in the complexes of benzo-12-crown-4 with calcium thiocyanate ( $-118; -3; 138^\circ$ ) [5] and lithium thiocyanate ( $-129.4; 2.1; 137.7^\circ$ ) [6].

In both molecules of **2** (**2a** and **2b**) the pyrocatechol fragment has a *trans-cis-gauche* conformation with the *gauche* torsion angle equal to  $+76.3^\circ$  for **2a** and  $-99.9^\circ$  for **2b** (Table V). The same conformation of this fragment was found in acetylbenzo-12-crown-4 ( $163.9; 8.1; -72.7^\circ$ ) [4] and proposed on the basis of conformational calculations for benzo-12-crown-4 [4, 7]. The conformation of the residual polyoxyethylene chain is similar in **1a**, **1b** and **2b**, but very different in **2a**.

Comparing all four structures, first we would like to outline the common features. All four molecules are characterized by two displaced corner fragments in the same manner at atoms C(5) and C(8). The corresponding values of torsion angles are presented in Table V. In these molecules there is a 'genuine' corner at the C(5) atom (torsion *gauche* bonds with the same signs). At the C(8) atom there is a 'pseudo' corner in **1a**, **1b** and **2b** and a 'real' corner in **2a**. Thus, on the whole the conformations of the independent molecules **1a** and **1b** are practically the same; the conformation of **2b** is similar except for the differences in the condensed aromatic residue fragment. In **2a** there are two 'genuine' corner fragments (*gauche* +, *gauche* +). CH...O interactions are found in the rings. They are presented below, as well as in Figures 3 and 4.

	C...O (Å)	H...O (Å)	angle C—H...O (deg.)
<b>1a</b>	3.114	2.51	113
<b>1b</b>	3.173	2.41	121
<b>2a</b>	3.271	2.45	129
<b>2b</b>	3.114	2.48	124
	3.208	2.61	121

In molecules **1a**, **1b** and **2b** the arrangement of donor oxygen atoms is more planar than in **2a**. The first three molecules have oxygen atoms which deviate from the mean plane by  $\pm 0.114$  Å. In molecule **2a** the deviation of oxygen atoms is  $\pm 0.286$  Å. The conformational peculiarities of **1** and **2** are shown by the scattering of *trans*-annular O...O distances in the respective rings: in **1a** and **1b** these are close and lie within the 3.919–4.077 Å (**1a**) and 3.952–4.043 Å (**1b**) limits while the distortions in macrocycles **2a** and **2b** manifest themselves in the shortened O(1)...O(7) distances and in the elongation of the cavity in the direction of O(4)...O(10). The corresponding *trans*-annular O...O distances are in the 3.351–4.436 (**2a**) and 3.435–4.503 Å (**2b**) ranges. The interatomic distances in the macrocycles and in the aromatic moieties are typical for aromatic crown ethers. For molecules **1** the average distances are: for C<sub>(sp<sup>2</sup>)</sub>—O 1.370; C<sub>(sp<sup>3</sup>)</sub>—O 1.427; C<sub>(sp<sup>2</sup>)</sub>—C<sub>(sp<sup>2</sup>)</sub> 1.379; C<sub>(sp<sup>3</sup>)</sub>—C<sub>(sp<sup>3</sup>)</sub> 1.497 Å; in the benzene ring the average C—C distance is equal to 1.382 Å, the endocyclic angles are within the range of 118.8–121.1°. The angles in the polyoxyethylene fragment change from 114.4 to 116.6° at the oxygen atoms and from 106.4 to 112.8° at the carbon atoms. In molecules of **2** the above geometric parameters are close to the values mentioned for molecules of **1** and are as follows: 1.372; 1.426; 1.428; 1.499 Å. Comparison of large (18-membered and larger), intermediate (15-membered) and small (12–13-membered)

macrocycles shows that, during cyclization in the latter, strain is developed with the values of torsion angles along the C—O bonds lying between classic *gauche* and *trans* angles. The torsional strain causes a deformation of valence angles in such small rings.

## Acknowledgements

The authors would like to thank KBN for support with grant No. 205349101.

## Note

<sup>1</sup>In some of the 12-membered condensed crown ethers discussed here, one of the *trans* torsion angles may be close to 120° (within the limits of experimental error). We shall consider it as a *trans* angle.

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