Synthesis and structure of 13- and 26-membered crown ethers, derivatives of resorcinol

E. Luboch,[a] M. S. Fonar',[b] Yu. A. Simonov,[b] V. K. Bel'sky,[c] and J. Biernat[a]*

[a]*Department of Chemical Technology, Technical University of Gdansk, 11/12 ul. Narutowicza, 80952 Gdansk, Poland. Fax: (48 58) 415 821*

[b]*Institute of Applied Physics, Academy of Sciences of Republic Moldova, 5 ul. Academicheskaya, 277028 Kishinev, Republic Moldova. Fax: (042 2) 738 149*

[c]*L. Ya. Karpov Institute of Physical Chemistry, 10 ul. Vorontsovo Pole, 103064 Moscow, Russian Federation. Fax: (095) 975 2450*

13- and 26-Membered crown ethers have been synthesized based on resorcinol and 1,8-dichloro-3,6-dioxaoctane. The products with substituents in the benzene ring have been prepared by alkylation of 13-membered crown ether. Complexing properties of the macrocycles have been studied with the use of ion-selective membrane electrodes. The structures of 13- and 26-membered crown ethers have been established by X-ray structural analysis.

Key words: resorcinol-based crown ethers, crystal structure, intramolecular nonbonded C—H...O contacts.

Currently, along with classic benzo- and dibenzo-crown ethers, which exhibit considerable conformational flexibility in reactions of complex formation with metal cations and neutral organic molecules,[1] macrocycles in which pyrocatechol fragments are replaced by isomeric resorcinol or hydroquinone groups are being intensively studied. Upon complex formation, the behavior of the host (the macrocycle) in this class of compounds may substantially depend on positional isomers of this "building block."

Several works are known in which crown ether derivatives of resorcinol have been described.[2—5] In particular, crown ethers containing five or six oxygen atoms in the cycle were synthesized by template condensation on a cesium matrix.[3] Bis-1,3-phenylene-32-crown-10 was prepared with the use of mono-*O*-benzylresorcinol as a starting compound.[4] A distinguishing feature of the latter compound compared to crown ethers based on *o*-xylene is the formation of numerous intramolecular C—H...O contacts that provide conformational stability to the cycle. In this case, aromatic substituents are virtually perpendicular to the main plane of the macrocycle. A high conformational flexibility of the 32-membered cycle results in its rearrangement upon formation of inclusion compounds with such bulky cations as $[Pt(bipy)(NH_3)_2]^{2+}$ (where bipy is 2,2'-bipyridyl) and dications containing the bipyridine fragment, for example, with 1,1'-ethylene-2,2'-bipyridinium (Diquat) or 1,1'-dimethyl-4,4'-bipyridinium (Paraquat) ions.[4]

Previously, we studied crown ethers that are derivatives of pyrocatechol and pyrocatechol with substituents in the aromatic ring. It has been demonstrated[6,7] that in most cases, alkylation of these crown ethers enhances their ionophore properties. This effect is determined by an increase in their lipophilicity and by a change in selectivity; we followed the manifestation of this effect using benzo-12-crown-4 as an example.[6,7]

A membrane electrode containing benzo-12-crown-4 and *o*-nitrophenyl octyl ether as a plasticizer exhibits higher selectivity toward potassium ions compared to sodium ions ($\log K_{Na,K} = 0.8$). However, alkyl derivatives of benzo-12-crown-4 exhibit selectivity toward sodium ions, and the values of $\log K_{Na,K}$ for these compounds are in the range from -0.9 to -1.0. An increase in the length of alkyl radicals at position 4 of the benzene ring does not cause further changes in selectivity; for these compounds, the limiting value of $\log K_{Na,K}$ remains equal to -1.0.

With the aim of searching other selective ionophores, we attempted to increase the size of the cavity of the macrocycle by using the resorcinol fragment instead of the pyrocatechol fragment. We synthesized 13- and 26-membered crown ethers according to Scheme 1. For 13-membered crown ether, alkylation at the benzene ring was carried out.

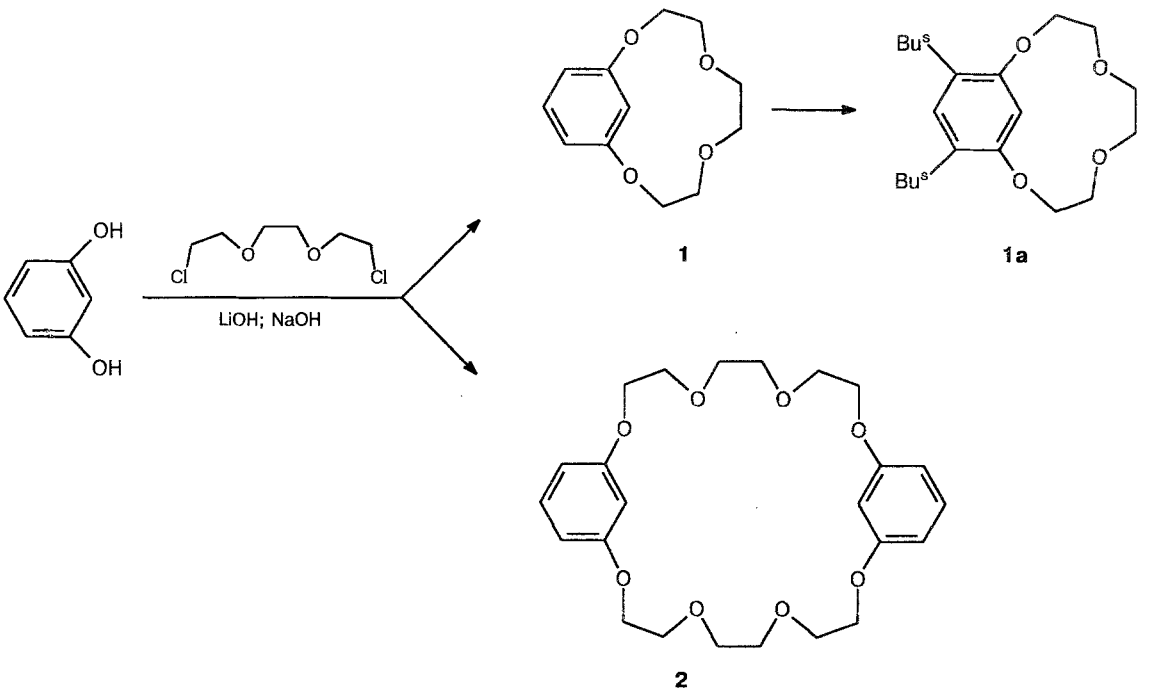
Experimental

^1H NMR spectra were obtained on a Varian spectrometer (60 MHz) in $CDCl_3$. Mass spectra were recorded on an

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 12, pp. 2458—2464, December, 1995.

1066-5285/95/4412-2353 $12.50

Scheme 1



AMD-604 spectrometer. Measurements with membrane electrodes were carried out according to the procedure described previously.[7–9]

X-ray structural study of compounds 1 and 2. The principal X-ray diffraction characteristics of the crystals of **1** and **2** and the details of the experiment and calculations are given in Table 1.

Compound 1. A crystal with dimensions of 0.3×0.3×0.25 mm was used for X-ray structural analysis. X-ray diffraction study was performed on a four-circle RED-4 diffractometer. The unit-cell parameters were obtained by the least-squares refinement of 15 reflections in the angle range $15 < 2\theta < 35°$. A total of 1364 independent reflections with $I > 3\sigma(I)$ were collected using the $\theta/2\theta$ scanning technique to $\sin(\theta/\lambda)_{max} = 0.6$ Å^{-1} (using Mo-Kα radiation with a graphite monochromator) in the ranges of indices $-15 < h < 15$, $-11 < k < 11$, $0 < l < 9$. The structure was solved and refined on an SM-4 computer using the CSD program package.[10] The structure was solved by direct methods. Nonhydrogen atoms were refined anisotropically; hydrogen atoms were located from difference Fourier syntheses and refined isotropically. The refinement converged to $R = 0.055$ with the use of the unit weighting scheme. Atomic coordinates and temperature parameters of nonhydrogen atoms are given in Table 2; geometric parameters of molecules **1A** and **1B** are given in Table 3. Computer graphing was performed using the ORTEP program.

Compound 2. A crystal with dimensions of 0.6×0.4×0.25 mm was used for X-ray structural analysis. X-ray diffraction study was performed on a four-circle Syntex $P\bar{1}$ diffractometer. The unit-cell parameters were determined by the least-squares refinement of 25 reflections in the angle range $18 < 2\theta < 42°$. A total of 2521 independent reflections with $I > 3\sigma(I)$ were collected using the $\theta/2\theta$ scanning technique to $\sin(\theta/\lambda)_{max} = 0.57$ Å^{-1} (using Mo-Kα radiation without a monochromator). The structure was solved by direct methods using the SHELXTL program.[11] Nonhydrogen atoms were refined anisotropically; hydrogen atoms were located from difference Fourier syntheses and refined isotropically. The final atomic coordinates of basis atoms are given in Table 4; geometric parameters of the molecule are listed in Table 5.

Table 1. Crystallographic characteristics of compounds **1** and **2**

Characteristic	**1**	**2**
Molecular formula	$C_{12}H_{16}O_4$	$C_{24}H_{32}O_8$
Sp.gr.	$P\bar{1}$	$P2_1/n$
a/Å	13.631(4)	11.398(1)
b/Å	9.417(5)	16.125(2)
c/Å	8.784(6)	12.895(1)
α/deg	89.71(3)	90
β/deg	86.35(2)	102.48(1)
γ/deg	90.78(2)	90
V/Å^3	1125(2)	2314(1)
d_{calc}/g cm^{-3}	1.324(2)	1.287
μ/cm^{-1}	1.07	0.90
Z	4	4
Radiation	Mo-Kα	Mo-Kα
Diffractometer	RED-4	Syntex $P\bar{1}$
N (number of reflections)	1364	2521
$R(hkl)$	0.055	0.034
R_w	—	0.038

1,3-Phenylene-13-crown-4 (1) and bis(1,3-phenylene)-26-crown-8 (2). A mixture of resorcinol (22 g, 0.2 mol), *n*-butanol (300 mL), sodium hydroxide (8.4 g, 0.21 mol), lithium hydroxide hydrate (8.4 g, 0.2 mol), and 1,8-dichloro-3,6-dioxaoctane (37.4 g, 0.2 mol) was boiled for 3 days. Then the mixture was acidified to pH 3 and evaporated to dryness

Table 2. Atomic coordinates of nonhydrogen atoms ($\times 10^4$) and U_{eq} for compound **1**

Atom	A				B			
	x	y	z	$U_{eq} \cdot 10^3/Å^2$	x	y	z	$U_{eq} \cdot 10^3/Å^2$
O(1)	5847(3)	685(5)	3726(5)	4.8	9158(3)	4322(5)	8803(5)	4.9
C(2)	5468(5)	−519(7)	2920(8)	4.5	9624(5)	5539(7)	8042(7)	4.4
C(3)	5768(5)	−1955(7)	3514(7)	4.0	9319(5)	6924(7)	8742(8)	4.6
O(4)	6330(3)	−2641(4)	2307(5)	4.3	8707(3)	7658(5)	7741(5)	4.7
C(5)	6785(6)	−3916(7)	2754(8)	5.3	8109(7)	8658(9)	8570(11)	7.7
C(6)	7688(5)	−3671(7)	3605(8)	5.0	7337(7)	9128(9)	7740(12)	8.2
O(7)	8413(3)	−2947(5)	2662(5)	4.4	6689(3)	8062(5)	7199(5)	5.1
C(8)	9125(5)	−2301(8)	3523(8)	4.8	6008(6)	7437(8)	8282(8)	5.2
C(9)	9720(5)	−1263(8)	2557(9)	5.5	5434(5)	6325(8)	7497(8)	5.0
O(10)	9144(3)	−214(5)	1854(5)	4.4	6025(3)	5225(5)	6808(5)	4.3
C(11)	8486(5)	500(7)	2833(7)	3.5	6602(5)	4502(6)	7821(7)	3.6
C(12)	7505(5)	182(6)	2770(7)	3.3	7584(5)	4849(6)	7791(7)	3.5
C(13)	6840(5)	928(7)	3693(7)	3.7	8168(5)	4106(7)	8753(7)	3.9
C(14)	7139(6)	1996(7)	4658(7)	4.4	7771(6)	3038(7)	9721(8)	4.4
C(15)	8134(6)	2276(7)	4696(7)	4.5	6780(6)	2721(7)	9730(8)	4.6
C(16)	8836(5)	1542(7)	3793(8)	4.2	6173(5)	3460(7)	8786(7)	4.0

Table 3. Bond lengths and bond angles in compound **1**

Parameter	A	B
Bond	d/Å	
O(1)—C(2)	1.447(8)	1.443(8)
C(2)—C(3)	1.51(1)	1.49(1)
C(3)—O(4)	1.430(8)	1.431(8)
O(4)—C(5)	1.424(8)	1.42(1)
C(5)—C(6)	1.49(1)	1.39(1)
C(6)—O(7)	1.414(8)	1.43(1)
O(7)—C(8)	1.402(8)	1.407(9)
C(8)—C(9)	1.48(1)	1.49(1)
C(9)—O(10)	1.432(9)	1.433(8)
O(10)—C(11)	1.384(8)	1.404(7)
C(11)—C(12)	1.371(9)	1.371(9)
C(12)—C(13)	1.379(9)	1.390(9)
O(1)—C(13)	1.368(8)	1.366(8)
C(13)—C(14)	1.392(9)	1.395(9)
C(14)—C(15)	1.38(1)	1.37(1)
C(15)—C(16)	1.39(1)	1.39(1)
C(11)—C(16)	1.396(9)	1.391(9)
Angle	φ/deg	
C(2)—O(1)—C(13)	119.5(5)	119.9(5)
O(1)—C(2)—C(3)	114.6(5)	113.3(5)
C(2)—C(3)—O(4)	107.5(5)	109.4(5)
C(3)—O(4)—C(5)	114.1(5)	110.4(5)
O(4)—C(5)—C(5)	113.6(6)	112.1(7)
C(5)—C(6)—O(7)	110.0(6)	116.7(8)
C(6)—O(7)—C(8)	111.5(5)	116.9(6)
O(7)—C(8)—C(9)	109.8(6)	108.2(6)
C(8)—C(9)—O(10)	113.6(6)	114.0(6)
C(9)—O(10)—C(11)	115.4(5)	114.4(5)
O(10)—C(11)—C(12)	117.8(5)	117.5(5)
C(11)—C(12)—C(13)	118.4(6)	118.0(6)
C(12)—C(13)—C(14)	121.8(6)	121.1(6)
C(13)—C(14)—C(15)	118.0(6)	119.3(6)
C(14)—C(15)—C(16)	122.3(7)	120.7(7)
C(15)—C(16)—C(11)	116.7(6)	118.0(6)
O(1)—C(13)—C(12)	123.0(6)	123.7(6)

Table 4. Atomic coordinates of nonhydrogen atoms ($\times 10^4$) and $U_{eq} \times 10^3/Å^2$ for compound **2**

Atom	x	y	z	$U_{eq} \cdot 10^3/Å^2$
O(1)	0920(1)	5908(1)	2949(1)	56(1)
C(2)	0366(2)	6541(1)	2225(2)	51(1)
C(3)	−0823(2)	6734(1)	2474(2)	55(1)
O(4)	−1639(1)	6076(1)	2111(1)	54(1)
C(5)	−2726(2)	6133(1)	2488(2)	58(1)
C(6)	−2635(2)	5744(1)	3554(2)	56(1)
O(7)	−2508(1)	4866(1)	3518(1)	56(1)
C(8)	−1306(2)	4591(1)	3829(2)	54(1)
C(9)	−1341(2)	3681(2)	3999(2)	65(1)
O(10)	−0119(1)	3399(1)	4164(1)	67(1)
C(11)	0161(2)	2637(1)	4622(2)	47(1)
C(12)	1372(2)	2440(1)	4848(2)	46(1)
C(13)	1757(2)	1707(1)	5362(2)	46(1)
O(14)	2976(1)	1592(1)	5596(1)	60(1)
C(15)	3428(2)	0782(1)	5903(2)	59(1)
C(16)	4757(2)	0845(2)	6272(2)	66(1)
O(17)	5278(1)	1078(1)	5416(1)	57(1)
C(18)	6531(2)	1251(1)	5727(2)	55(1)
C(19)	6800(2)	2121(1)	6126(2)	60(1)
O(20)	6479(1)	2722(1)	5297(1)	62(1)
C(21)	5323(2)	3069(1)	5221(2)	60(1)
C(22)	5155(2)	3704(1)	4349(2)	55(1)
O(23)	3967(1)	4018(1)	4245(1)	68(1)
C(24)	3596(2)	4646(1)	3529(2)	48(1)
C(25)	2479(2)	4975(1)	3541(2)	51(1)
C(26)	2026(2)	5619(1)	2860(2)	46(1)
C(27)	2673(2)	5923(1)	2148(2)	53(1)
C(28)	3782(2)	5576(2)	2148(2)	59(1)
C(29)	4263(2)	4942(1)	2825(2)	54(1)
C(30)	0940(2)	1154(1)	5630(2)	59(1)
C(31)	−0263(2)	1358(1)	5368(2)	64(1)
C(32)	−0677(2)	2092(1)	4866(2)	56(1)

under reduced pressure. Water was added to the dry residue, and the products were extracted with chloroform. Organic components were separated by column chromatography on

Table 5. Bond lengths and bond angles in compound **2**

Bond	*d*/Å	Bond	*d*/Å
O(1)—C(2)	1.434(3)	O(1)—C(26)	1.372(3)
C(2)—C(3)	1.490(3)	C(3)—O(4)	1.423(3)
O(4)—C(5)	1.429(3)	C(5)—C(6)	1.495(3)
C(6)—O(7)	1.424(3)	O(7)—C(8)	1.413(2)
C(8)—C(9)	1.486(3)	C(9)—O(10)	1.438(3)
O(10)—C(11)	1.370(3)	C(11)—C(12)	1.385(3)
C(11)—C(32)	1.383(3)	C(12)—C(13)	1.380(3)
C(13)—O(14)	1.370(3)	C(13)—C(30)	1.387(3)
O(14)—C(15)	1.428(3)	C(15)—C(16)	1.489(3)
C(16)—O(17)	1.413(3)	O(17)—C(18)	1.425(2)
C(18)—C(19)	1.503(3)	C(19)—O(20)	1.430(3)
O(20)—C(21)	1.415(3)	C(21)—C(22)	1.503(3)
C(22)—O(23)	1.425(3)	O(23)—C(24)	1.374(3)
C(24)—C(25)	1.382(3)	C(24)—C(29)	1.388(3)
C(25)—C(26)	1.385(3)	C(26)—C(27)	1.385(3)
C(27)—C(28)	1.383(3)	C(28)—C(29)	1.379(3)
C(30)—C(31)	1.379(3)	C(31)—C(32)	1.383(3)
Angle	**ω/deg**	**Angle**	**ω/deg**
C(2)—O(1)—C(26)	118.1(2)	O(1)—C(2)—C(3)	107.6(2)
C(2)—C(3)—O(4)	109.5(2)	C(3)—O(4)—C(5)	113.2(2)
O(4)—C(5)—C(6)	113.2(2)	C(5)—C(6)—O(7)	112.0(2)
C(6)—O(7)—C(8)	113.6(2)	O(7)—C(8)—C(9)	107.2(2)
C(8)—C(9)—O(10)	106.1(2)	C(9)—O(10)—C(11)	118.3(2)
O(10)—C(11)—C(12)	115.1(2)	O(10)—C(11)—C(32)	124.1(2)
C(12)—C(11)—C(32)	120.9(2)	C(11)—C(12)—C(13)	119.7(2)
C(12)—C(13)—O(14)	115.1(2)	C(12)—C(13)—C(30)	120.7(2)
O(14)—C(13)—C(30)	124.2(2)	C(13)—O(14)—C(15)	118.2(2)
O(14)—C(15)—C(16)	107.9(2)	C(15)—C(16)—O(17)	109.8(2)
C(16)—O(17)—C(18)	113.4(2)	O(17)—C(18)—C(19)	113.4(2)
C(18)—C(19)—O(20)	112.1(2)	C(19)—O(20)—C(21)	113.8(2)
O(20)—C(21)—C(22)	106.7(2)	C(21)—C(22)—O(23)	106.1(2)
C(22)—O(23)—C(24)	118.3(2)	O(23)—C(24)—C(25)	115.2(2)
O(23)—C(24)—C(29)	124.1(2)	C(25)—C(24)—C(29)	120.7(2)
C(24)—C(25)—C(26)	119.9(2)	O(1)—C(26)—C(25)	115.1(2)
O(1)—C(26)—C(27)	124.4(2)	C(25)—C(26)—C(27)	120.5(2)
C(26)—C(27)—C(28)	118.3(2)	C(27)—C(28)—C(29)	122.6(2)
C(24)—C(29)—C(28)	118.1(2)	C(13)—C(30)—C(31)	118.1(2)
C(30)—C(31)—C(32)	122.7(2)	C(11)—C(32)—C(31)	117.9(2)

silica gel. 13-Membered crown ether **1**, m.p. 49—51 °C (from heptane), was obtained in 2.2 % (1 g) yield. ^{1}H NMR, δ: 3.50—3.90 (m, 8 H); 4.28 (t, 4 H, J = 4 Hz); 6.43—6.73 (m, 2 H); 7.13 (t, 1 H, J = 8 Hz); 7.53—7.70 (m, 1 H). Mass spectrum, *m/z*: 224 $[M]^+$. $C_{12}H_{16}O_4$. 26-Membered crown ether **2**, m.p. 90—92 °C, was obtained in 2.9 % (1.3 g) yield. ^{1}H NMR, δ: 3.70—4.27 (m, 24 H); 6.37—6.70 (m, 6 H); 7.12 (t, 2 H, J = 8 Hz). Mass spectrum, *m/z*: 448 $[M]^+$. $C_{24}H_{32}O_8$.

4,6-Di-*sec*-butyl-1,3-phenylene-13-crown-4 (1a). A mixture of 1,3-phenylene-13-crown-4 (0.34 g, 1.5 mmol), polyphosphoric acid (2 mL), and *sec*-butanol (0.37 g, 5 mmol) was heated for 4 h at 70 °C. The mixture obtained was diluted with water, the product was extracted with dichloromethane followed by separation of an organic product by column chromatography on silica gel. Oily di-*sec*-butyl-1,3-phenylene-13-crown-4 (**1a**) was obtained in 70 % yield. ^{1}H NMR, δ: 0.83 (t, 6 H, J = 7 Hz); 1.18 (d, 6 H, J = 7 Hz); 1.53 (q, 4 H, J = 7 Hz); 3.05 (m, 2 H, J = 7 Hz); 3.67—4.05 (m, 8 H); 4.20—4.45 (m, 4 H); 6.94 (s, 1 H); 7.60 (s, 1 H).

Results and Discussion

13- and 26-Membered crown ethers based on resorcinol were prepared (see Scheme 1) according to a procedure analogous to that reported previously by Pedersen.[12] LiOH was added to the reaction medium in an attempt to enhance the yield of small (13-membered) macrocycle. It is known[13] that the presence of Li^+ cations in the reaction favors formation of small, in particular, 12-membered crown ethers. Along with 13-membered macrocycle **1**, 26-membered dimer **2** was also obtained (see Scheme 1). Note that we failed to isolate 13-membered crown ether in the absence of LiOH in the reaction mixture. An analogous effect was observed previously,[5] when the presence of NaOH or KOH in the medium did not afford small, 10- and 13-membered macrocycles based on resorcinol.

Table 6. Characteristics of electrodes in the presence of crown ethers **1** and **1a**

Compound	$\log K_{BuNH_3^+, X}$													
	Na	K	Rb	Cs	Li	Ca	Mg	Ba	Sr	H	NH_4^+	G*	Ala**	Ag
***	−2.39	−1.58	−1.47	−0.61	−2.89	−3.73	−4.40	−3.51	−3.72	−1.92	−2.37	−0.52	−0.72	0.67
1	−2.40	−1.27	−1.31	−0.59	−2.91	−3.75	−4.17	−3.28	−3.63	−2.11	−2.02	−0.22	−0.16	0.58
1a	−2.69	−1.55	−1.47	−0.67	−2.49	−3.80	−4.09	−3.66	−3.77	−1.95	−2.06	−0.03	−0.23	0.35

* G is guanidine hydrochloride. ** Ala is alanine methyl ester hydrochloride *** Without crown ether.

Crown ether **1** is substantially more difficult to alkylate (see Scheme 1) than benzocrown ethers. Virtually no desired product is formed upon alkylation with tertiary alcohols in the presence of polyphosphoric acid. We obtained the best results when the secondary butyl alcohol was used. The yield of 4,6-disubstituted derivative **1a** (see Scheme 1) was 70 %.

The properties of compounds presented in Scheme 1 as ion carriers in membrane electrodes were studied according to the procedure described previously.[6] Membranes contained *o*-phenyl octyl ether, bis(2-ethylhexyl) sebacate, and tris(2-ethylhexyl) phosphate as plasticizers. In all cases, the ionophore properties of plasticizers dominate over those of crown ethers.

The results obtained for electrodes with compounds **1** and **1a** and *o*-nitrophenyl octyl ether as a plasticizer are given in Table 6. Note that compound **2** (see Scheme 1) crystallizes in membranes; therefore, we did not measure its potentiometric characteristics.

The properties of electrodes were slightly modified after introduction of crown ethers. An introduction of alkyl substituents into the resorcinol fragment did not cause a substantial change in the selectivity as it was observed for derivatives of benzo-12-crown-4. The data in Table 6 demonstrate that membranes containing crown ethers **1** and **1a** are most sensitive toward ammonium ions.

An analysis of molecular structures of compounds **1** and **2** demonstrated their differences from the corresponding analogs based on pyrocatechol.

Compound 1. The asymmetric unit of the triclinic unit cell consists of two crystallographically independent molecules (**A** and **B**) of 1,3-phenylene-13-crown-4. No contacts shorter than the sum of the van der Waals radii are observed between these molecules. The atomic numbering scheme in the cycle (Fig. 1, *a*,*b*) was chosen in such a way as to obtain the best agreement between the values of the torsion angles about the macrocyclic nuclei of these molecules. In the molecules, the dihedral angles between the aromatic fragments and the planes through the heteroatoms of crown ethers are 35.5° and 37.2° for molecules **A** and **B**, respectively. Being similar, conformations of two molecules are unusual. These conformations are described by the following sequences of torsion angles: *g*+*g*−(−118)*tg*−*g*−*ttg*+*g*+*g*−*ttc* and *g*+*g*−(−109)*ttg*+*g*+*tg*+*g*+*g*−*ttc* for molecules **A** and **B**, respectively. These conformations, which are identical in the number of *trans* and *gauche* torsion angles, differ in the order in which these angles alternate and in the location of corner fragments in the cycle. All three C—C

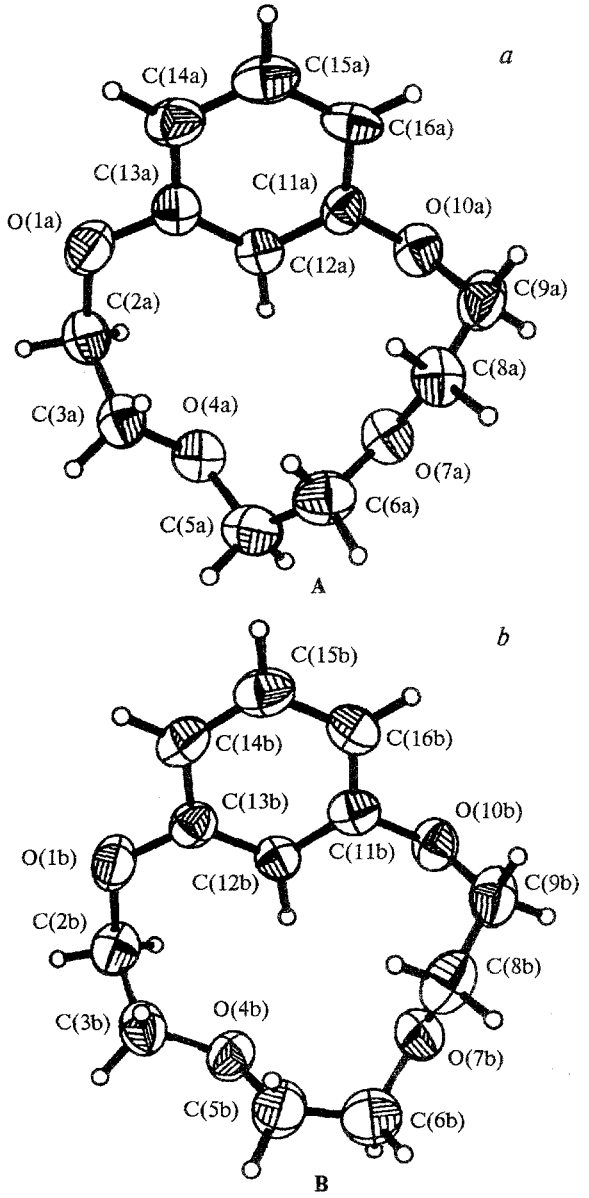


Fig. 1. Structure of independent molecules **A** (*a*) and **B** (*b*) of crown ether **1**.

Table 7. Torsion angles (τ/deg) in the heterocyclic nucleus of molecules **1** and **2**

Angle	1A	1B	2
C(12)—C(13)—O(1)—C(2)	8.3	11.6	—
C(13)—O(1)—C(2)—C(3)	63.8	66.7	—
C(26)—O(1)—C(2)—C(3)	—	—	179.1
O(1)—C(2)—C(3)—O(4)	−118.0	−108.8	−73.7
C(2)—C(3)—O(4)—C(5)	171.4	157.5	169.0
C(3)—O(4)—C(5)—C(6)	−77.3	−164.7	−86.3
O(4)—C(5)—C(6)—O(7)	−62.6	56.1	−67.6
C(5)—C(6)—O(7)—C(8)	160.9	75.3	97.6
C(6)—O(7)—C(8)—C(9)	−165.7	−177.9	166.8
O(7)—C(8)—C(9)—O(10)	55.5	59.2	171.9
C(8)—C(9)—O(10)—C(11)	51.7	57.2	162.4
C(9)—O(10)—C(11)—C(12)	−107.3	−102.4	174.2
O(10)—C(11)—C(12)—C(13)	−177.3	−178.0	—
O(10)—C(11)—C(12)—O(13)	—	—	176.5
C(11)—C(12)—C(13)—O(1)	−179.5	178.2	—
C(11)—C(12)—C(13)—O(14)	—	—	176.8
C(12)—C(13)—O(14)—C(15)	—	—	166.0
C(13)—O(14)—C(15)—C(16)	—	—	171.4
O(14)—C(15)—C(16)—O(17)	—	—	−65.2
C(15)—C(16)—O(17)—C(18)	—	—	172.8
C(16)—O(17)—C(18)—C(19)	—	—	−84.0
O(17)—C(18)—C(19)—O(20)	—	—	−68.9
C(18)—C(19)—O(20)—C(21)	—	—	95.1
C(19)—O(20)—C(21)—C(22)	—	—	177.8
O(20)—C(21)—C(22)—O(23)	—	—	177.1
C(21)—C(22)—O(23)—C(24)	—	—	176.8
C(22)—O(23)—C(24)—C(25)	—	—	174.1
O(23)—C(24)—C(25)—C(26)	—	—	179.2
C(24)—C(25)—C(26)—O(1)	—	—	179.0
C(2)—O(1)—C(26)—C(25)	—	—	176.4

bonds adopt a favorable *gauche* configuration (Table 7, see Fig. 1, *a,b*). The values of these torsion angles are in the range 55.5—118.0°. Of eight C—O bonds, three bonds have a favorable *trans* configuration with torsion angles in the range 157.5—177.9°, four bonds are described by *gauche* torsion angles (51.7—107.3°), and one O(1)—C(13) bond adopts a *cis* configuration. In both molecules, the C(8)...C(11) fragment is described by a series of three *gauche* torsion angles: *g+g+g−*.

Conformations of heterocycles are stabilized through intramolecular CH...O contacts with the participation of the hydrogen atom of the resorcinol fragment directed inward. The parameters of the corresponding CH...O interactions are given in Table 8. An introduction of the resorcinol fragment determines the difference in distances between the oxygen atoms. The distances between the neighboring oxygen atoms in the cycle are 2.818—3.434 and 2.852—3.348 Å in molecules **A** and **B**, respectively. The O(1)...O(10) distance between oxygen atoms of the resorcinol fragment is 4.773 Å and 4.803 Å for **A** and **B**, respectively. It is a normal value for oxygen atoms involved in this fragment.[4] Heterocycle **B** is more flattened compared to **A**. The heteroatoms are coplanar within ±0.22 Å and ±0.50 Å in **B** and **A**, respectively.

Table 8. Characteristics of C—H...O interactions in compounds **1** and **2**

Compound	Atoms	$R_{D...A}$	$R_{H...A}$	α(D—H...A)
		/Å		/deg
1A	O(4)..C(12)	3.127(7)	2.37	130
	O(7)..C(12)	3.211(7)	2.70	112
1B	O(4)..C(12)	3.037(4)	2.28	125
	O(7)..C(12)	3.329(8)	2.74	113
2	O(4)..C(8)	3.228(5)	2.75	112
	O(1)..C(8)	3.671(5)	2.87	142
	O(17)..C(21)	3.222(6)	2.64	119
	O(14)..C(21)	3.691(5)	2.81	152

Compound 2. Compound **2** has C_2 pseudosymmetry (Fig. 2). However, the distortion from the symmetry manifests itself in dihedral angles between the mean plane through heteroatoms of crown ether and the planes of the aromatic rings. For the aromatic fragment C(11)...C(32), this angle is 3.1°; for the C(24)...C(29) fragment, the corresponding angle is 29.4°. The angle between aromatic substituents in the molecule is 28.9°.

The conformation of the molecule is described by the following series of torsion angles: *tg−ttg−g−g+ttttttttg−tg−g−g+tttttt*. Along with the O(1)...O(4) and O(14)...O(17) fragments, which are characterized by a sequence of torsion angles *tg+t*, the cycle contains fragments with unusual conformations. First, in compound **2**, as well as in **1**, there are two fragments, O(4)...O(7) and O(17)...O(20), consisting of three bonds in a *gauche* configuration (*g+g+g−*). As in the case of **1**, these fragments of the macrocycle are stabilized by CH...O interactions (see Table 8). And finally, two fragments of the heterocyclic chain (C(2)...O(20) and O(7)...C(15)) containing aromatic cycles, in which sequences of eight bonds in a *trans* configuration occur, adopt the most unusual conformation. We are not aware of other analogous examples although many crown ethers in the free state adopt a conformation with a sequence of three *trans* torsion angles, for example, 2-hydroxy-1,3-xylenediyl-18-crown-5 [14] and 1,3-xylenediyl-18-crown-5.[15] In the closest analog of **2**, bis-*m*-phenylene-32-crown-10, and its complex [Diquat.BMP32C10],[4] a sequence of only three *trans* bonds is also observed. The conformation closest to that described above is the conformation of the 22-membered macrocycle, which contains two pyrocatechol and one pyridine cycles along with one resorcinol fragment.[16] As a whole, for the compound reported previously,[16] conformations of two independent molecules are described by the following sequences of torsion angles: *tttg−cttg+ttttttg−ttcg+ttt* and *tttg−cttg+tcttctg+ttctttt*. These sequences involve series of six and seven bonds in a *trans* configuration.

Macrocycle **2** has a pronounced elliptic shape elongated along the O(4)...O(17) direction. Shortened

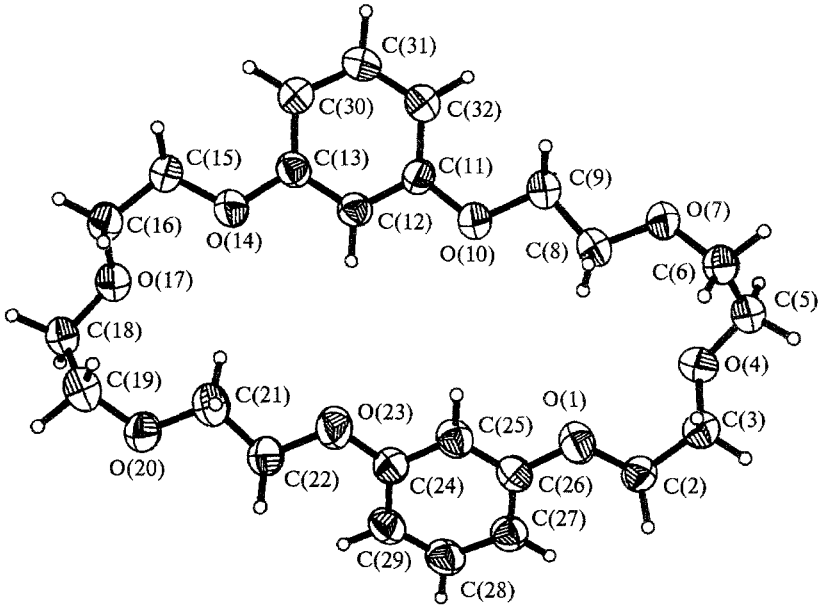


Fig. 2. Structure of the molecule of crown ether **2**.

distances are observed between the following pairs of atoms: O(1)...O(7) 4.457, O(14)...O(20) 4.481, and O(10)...O(23) 4.742 Å. The maximum O...O distance [O(4)...O(17)] is 11.435 Å. This pair of atoms has also the maximum deviation from the plane through heteroatoms of the macrocycle: −0.536 and −0.549 Å for the O(4) and O(17) atoms, respectively, whereas oxygen atoms of two resorcinol fragments are coplanar within ±0.052 Å.

Unlike compound **1**, the conformation of which is stabilized through CH...O contacts with the participation of the hydrogen atom of the resorcinol fragment, the corresponding distances in molecule **2** (C(12)...O(23) and C(25)...O(10)) are larger than 4 Å, and these distances have no effect on the formation of the intramolecular structure.

Geometry of molecules 1 and 2. Some differences in interatomic distances and bond angles in the molecules under consideration are observed. These differences are associated with the involvement of rigid aromatic fragments in macrocycles. Thus, two types of C—O distances can be mentioned: $C(sp^2)$—O and $C(sp^3)$—O. The average values of these distances (Å) and of the $C(sp^3)$—$C(sp^3)$ and $C(sp^2)$—$C(sp^2)$ interatomic distances are listed below.

Distance	**1** (molecule **A**)	**1** (molecule **B**)	**2**
$C(sp^2)$—O	1.376(8)	1.385(8)	1.372(3)
$C(sp^3)$—O	1.425(8)	1.427(8)	1.425(3)
$C(sp^3)$—$C(sp^3)$	1.49(1)	1.49(1)	1.494(3)
$C(sp^2)$—$C(sp^2)$	1.385(9)	1.385(10)	1.383(3)

Similarly, differences in endocyclic bond angles, the average values (deg) of which are listed below, are observed.

Angle	**1** (molecule **A**)	**1** (molecule **B**)	**2**
$C(sp^3)$—O—$C(sp^2)$	117.5(5)	117.2(5)	118.2(2)
$C(sp^3)$—O—$C(sp^3)$	112.8(5)	113.7(5)	113.5(5)
$C(sp^3)$—$C(sp^3)$—O	111.5(5)	112.3(6)	109.3(2)
$C(sp^2)$—$C(sp^2)$—O	120.4(5)	120.6(6)	115.1(4)
$C(sp^2)$—$C(sp^2)$—$C(sp^2)$	120.0(6)	120.0(6)	120.0(2)

These differences in interatomic distances and bond angles correlate with the data in the literature.[16]

Note once again that it was possible to isolate 13-membered crown ether based on resorcinol from the reaction medium only in the presence of LiOH. Studies of the properties of membrane electrodes are indicative of a low ability of crown ethers based on resorcinol to form complexes with metal cations. This may be caused by the difference in geometry of resorcinol and pyrocatechol fragments. The geometry of the pyrocatechol fragment (the O...O distance and the orientation of the lone electron pairs of oxygen atoms) is optimum for complex formation with metals. In this case, a very stable 5-membered chelate metallocycle is formed in complexes.

Structural studies of compounds **1** and **2** demonstrated that in the case of **1**, lone electron pairs of resorcinol oxygen atoms are oriented outward. In addition, in **1**, as well as in **2**, the hydrogen atom located in position 2 of the resorcinol residue partially or completely blocks the cavity of the macrocycle. Strong transannular C—H...O interactions stabilize a particular conformation of macrocycles **1** and **2** in the form, which is not ready for interaction with metal cations. Apparently, the macrocycle retains this conformation in solution. This fact has a dominant role in the process of complex formation.

The work was supported by Technical University of Gdansk (Project DS No. 946197/003).

References

1. H. M. Colquhoun, E. P. Goodings, J. M. Maud, J. F. Stoddart, D. J. Williams, and J. B. Wolstenholme, *J. Chem. Soc., Chem. Commun.*, 1983, 1140; B. L. Allwood, F. H. Kohnke, A. M. Z. Slawin, J. F. Stoddart, and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1985, 312; H. M. Colquhoun, J. F. Stoddart, and D. J. Williams, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 487.
2. D. N. Rheinhoudt, H. J. den Hertog Jr., and F. Jong, *Tetrahedron Lett.*, 1981, **22**, 2513.
3. B. J. van Keulen, R. M. Kellgg, and O. Pieppers, *J. Chem. Soc., Chem. Commun.*, 1979, 285.
4. B. L. Allwood, H. Shahriari-Zavareh, J. F. Stoddart, and J. Williams, *J. Chem. Soc., Chem. Commun.*, 1987, 1058.
5. Y. Delaviz, J. S. Merola, M. A. G. Berg, and H. W. Gibson, *J. Org. Chem.*, 1995, **60**, 516.
6. E. Luboch, A. Cygan, and J. F. Biernat, *Tetrahedron*, 1990, **46**, 2461.
7. J. Wasilewski and J. F. Biernat, *J. Incl. Phenom.*, 1990, **10**, 109.
8. A. Cygan, E. Luboch, and J. F. Biernat, *J. Incl. Phenom.*, 1988, **6**, 215.
9. E. Luboch, J. F. Biernat, E. Muszalska, and R. Bilewicz, *Supramol. Chem.*, 1996, in press.
10. CSD — *Complex of Programs for Crystal Structure Determination*, L'vov State Univ., Version 2.01.1989.
11. W. Robinson and G. M. Sheldrick, in *Crystallographic Computing-Techniques and New Technologies*, Oxford Univ. Press, Oxford, 1988, 366 pp.
12. C. J. Pedersen, *J. Am. Chem. Soc.*, 1967, **89**, 7017.
13. E. Luboch, A. Cygan, and J. F. Biernat, *15th Intern. Symp. on Macrocyclic Chemistry*, Odessa, 1990, Abstracts, 148; E. Luboch, A. A. Dvorkin, and Yu. A. Simonov, *J. Incl. Phenom.*, in press.
14. C. M. Browne, G. Ferguson, M. A. McKervey, D. L. Mulholland, T. O'Connor, and M. Parvez, *J. Am. Chem. Soc.*, 1985, **107**, 2703.
15. W. J. J. Smeets, A. L. Spek, P. R. Markies, O. S. Akkerman, and F. Bickelhaupt, *Acta Crystallogr.*, 1989, **C45**, 443.
16. E. Weber, H.-J. Kohler, K. Panneerselvam, and K. K. Chacko, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1599.

Received February 7, 1995;
in revised form June 22, 1995