Stereochemistry of 16-Membered Azo- and Azoxycrown Ethers. Structures of Their Sandwich Potassium Iodide Complexes

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Abstract. 16-Membered dibenzoazo- and dibenzoazoxycrown ethers have been synthesized. The Z and E isomers of the azocrown compound have been separated and the geometry of the –N=N– and —N(O)=N— groups determined. Potassium iodide complexes of the azo- and azoxycrown ethers were obtained and their structures were determined by the X-ray method. The crystal of the azocrown ether complex is triclinic, space group P$\bar{1}$, $a = 21.071(5)$, $b = 12.112(4)$, $c = 8.757(2)$ Å; $\alpha = 81.28(2)$, $\beta = 84.66(2)$, $\gamma = 107.49(2)°$. The azoxycrown ether complex is monoclinic, space group C2/c, $a = 15.648(3)$, $b = 19.597(4)$, $c = 14.651(3)$ Å; $\beta = 111.30(3)$.
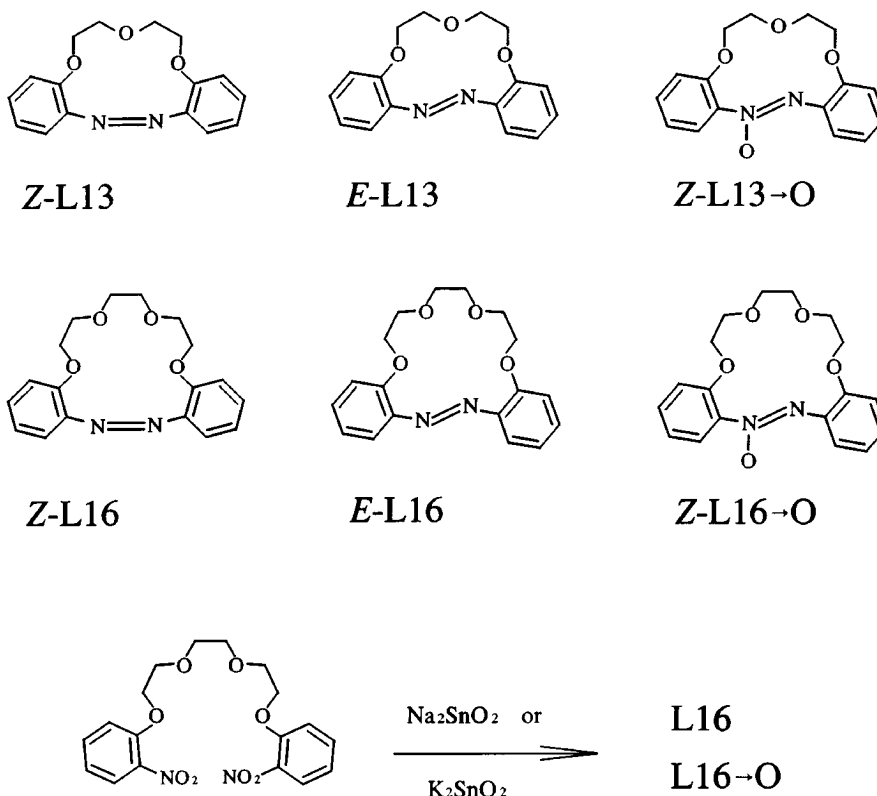
1. Introduction

Reversible $Z \rightleftarrows E$ isomerization of azo compounds could be useful in constructing molecular switches or memory devices [1]. Molecules possessing the —N=N— group attached to crown ether moiety combine unique functionalities of both molecular sites. Reviews on the physicochemical behavior of crown ethers with an azo group inside or outside the macrocycle have been published [1b,2].

Individual isomers of azo- and azoxycrown ethers (see formulas) are characterized only in few cases. Thus, both Z and E forms of 13-membered azocrown ether L13 have been separated [3]. On interaction with sodium iodide L13 forms a solid complex of formula [Na(L13)$_2$]$^+$·I$^-$ with E geometry of the coordinated ligand. In a monolayer, isomerization of the bis(tetramethylbutyl) derivative of Z-L13 was observed upon interaction with a sodium salt, which led to a complex with the E-isomer [4]. In the case of the azoxycrown ether L13 → O the aromatic residues

are oriented *trans* (isomer *Z*) around the —N=N(O)— moiety in both the free state [5] and in its NaI complex [3].

Shiga reported [6] the first synthesis of 16-membered azocrown ether L16 and described its $Z \rightleftarrows E$ isomerization in solution upon illumination. He found also that this crown ether extracts sodium and potassium salts into benzene; the respective values of log K_{ex} are 2.7(7) for K^+ and 4.1(7) for Na^+. The stability constants for the 1 : 1 complexes in acetonitrile are: log K_{ML} = 3.15 and 3.69 for potassium and sodium, respectively.

We have synthesized compounds L16 and L16 $\rightarrow$ O by a method similar to that already described for 13-membered azo- and azoxycrown ethers [7]. The aim of our work was to describe the stereochemistry of both the free and complexed 16-membered azo- and azoxycrown ethers.

Z-L13	*E*-L13	*Z*-L13→O

Z-L16	*E*-L16	*Z*-L16→O

$$\text{NO}_2 \quad \text{NO}_2 \xrightarrow[\text{K}_2\text{SnO}_2]{\text{Na}_2\text{SnO}_2 \quad \text{or}} \begin{array}{l} \text{L16} \\ \text{L16}\rightarrow\text{O} \end{array}$$

2. Experimental

2.1. GENERAL

All materials and solvents were of analytical reagent grade. ^{1}H-NMR were recorded immediately after dissolution of the individual isomers on a Varian (200 MHz) instrument. LC was performed on a HPLC Merck-Hitachi instrument equipped with

a L-4250 UV-VIS detector, a L-6200A Intelligent Pump and a D-2500 Chromato-Integrator using a SUPELCOSIL 2C-CN (grain diameter 5 μm) column (15 cm × 4.6 mm). Separations were performed in a linear gradient from a chloroform – heptane (3 : 2) mixture to pure chloroform after 17 min; flow rate = 1 mL/min. The UV-VIS λ_{max} were determined directly during HPLC separation. TLC was performed on aluminium sheets covered with Silica gel 60 F_{254} (Merck) in a methylene chloride/acetone (10 : 1 v/v) solvent system. Preparative TLC was performed on silica gel on glass plates (Merck) in methylene chloride/acetone (7 : 1 v/v). The m.p. are uncorrected.

2.2. SYNTHESES OF AZOCROWN AND AZOXYCROWN ETHERS

16-Membered Azo and Azoxycrown Compounds

Reduction of 1,8-bis(2-nitrophenoxy)-3,6-dioxaoctane with sodium stannite: 20 mL water was added dropwise to a mixture of 1,8-bis(2-nitrophenoxy)-3,6-dioxaoctane [8] (1.96g; 5 mmol), stannous chloride dihydrate (4.89g), sodium hydroxide (5 g) and 25 mL acetone. The mixture was gently boiled and vigorously stirred for 2 h. The organic layer was diluted with toluene (20 mL), the solid removed by filtration and the organic layer washed with water. The solvents were evaporated under reduced pressure and the residue chromatographed on a short silica gel column using methylene chloride to remove mainly polymers. The crude product (900 mg) was rechromatographed using an acetonitrile–toluene (1 : 1 v/v) mixture. The first brownish fraction was discarded and the second red fraction containing both isomers of the azocrown ether and the azoxycrown ether was freed from solvents (650 mg).

Isolation of the E-azocrown Ether

The above residue (650 mg) was extracted with boiling heptane. The yield of the oily E isomer was 525 mg (32%). For $C_{18}H_{20}O_4N_2$ (328.36) MS, found m/z = 328. HPLC, λ_{max} = 338 and 430 nm (solvent composition chloroform/heptane 77 : 23 v/v); t_R = 7.04 min. TLC, R_f = 0.1. ^{1}H NMR (200 MHz), CDCl$_3$, δ (ppm) registered immediately after dissolution of a sample: 3.73 (4H, s); 3.92–3.99 (4H, m); 4.24–4.31 (4H, m); 7.00–7.10 (4H, m); 7.31–7.40 (2H, m); 7.66 (2H, dd, J = 1.75 Hz, J = 8.38 Hz). The oily product crystallized from heptane upon seeding with a small amount of its potassium iodide complex or with azoxycompound Z-L16 → O. Yield 400 mg (24%); m.p. 60–61°.

Isolation of the Z-azocrown Ether

The above oily E-isomer (525 mg) was covered with a small amount of *iso*-butyl acetate. Crystallization of the Z isomer proceeds slowly (accordingly to the isomerization). The product was collected and washed with ethyl ether. Yield

400 mg (24%) of the Z-L16 melting at 120–121°. MS, for $C_{18}H_{20}O_4N_2$ (328.36), found m/z = 328. TLC, R_f = 0.33. HPLC, λ_{max} = 312 nm (solvent composition chloroform/heptane 70 : 30 v/v); t_R = 4.38 min. ^{1}H NMR (200 MHz), (CDCl$_3$, δ [ppm]) registered immediately after dissolution: 3.81 (4H, s); 3.90–4.08 (8H, m); 6.78–6.85 (6H, m); 7.06–7.17 (2H, m).

Azoxycrown Ether

Z-L16 → O detected in the reaction mixture was isolated from the respective fraction by preparative TLC. The colorless compound was eluted from the plates with acetone and crystallized from ethanol at low temperature. Yield ∼5%; m.p. 92–93°. This compound was obtained more easily by oxidation of the azocrown ether.

Reduction of 1,8-bis(2-nitrophenoxy)-3,6-dioxaoctane with Potassium Stannite

The reduction with the use of equivalent amount of potassium stannite proceeds similarly. By a similar procedure the macrocyclic products were obtained in comparable yields.

Synthesis of Azoxycrown Ether Z-L16 → O by Oxidation of Azocrown Ether

Z-L16 (350 mg; 1.1 mmol) was heated at 75° in a mixture of acetic acid (3 mL) and 30% hydrogen peroxide (2 mL) for 1 h. The mixture was evaporated under reduced pressure, the residue was dissolved in chloroform and washed with water. The crude product was chromatographed on a silica gel column using chloroform as an eluent to obtain 300 mg of the desired product. It was crystallized from ethyl ether. Yield 190 mg (50%). M.p. 91–93°. For $C_{18}H_{20}O_5N_2$ (344.36) MS found m/z = 344. TLC, R_f = 0.51. HPLC, λ_{max} = 308 and 448 nm (solvent composition chloroform/heptane 85 : 15 v/v); t_R = 10.52 min. ^{1}H NMR (200 MHz), (CDCl$_3$, δ [ppm]): 3.69 (4H, s); 3.88–3.98 (4H, m); 4.22–4.31 (4H, m); 6.99–7.12 (4H, m); 7.30 (1H, dt, J$_1$ = 1.6 Hz, J$_2$ = 8.1 Hz); 7.42 (1H, dt, J$_1$ = 1.6 Hz, J$_2$ = 8.5 Hz); 7.65 (1H, dd, J$_1$ = 1.6 Hz, J$_2$ = 7.7 Hz); 7.75 (1H, dd, J$_1$ = 1.6 Hz, J$_2$ = 8.2 Hz).

2.3. Syntheses of complexes

Synthesis of the Solvate of the Potassium Iodide Complex of E-L16

A mixture of azocrown ether L16 (both Z or E isomers could be used; 164 mg; 0.5 mmol), potassium iodide (83 mg; 0.5 mmol), 2-propanol (10 mL) and methanol (5 mL) was boiled until dissolution. The solvent was removed and the residue was crystallized from acetone containing a small amount of 2-propanol to afford an orange product. Yield 200 mg (90%). M.p. 198–199°. ^{1}H NMR, CDCl$_3$, δ (ppm): 1.21 (6H, d, J = 6.14 Hz); 1.65 (1H, s); 3.79–3.95 (24 + 1H, m); 6.79 (4H, d, J = 8.06); 7.02–7.09 (4H, m); 7.21–7.25 (4H, m); 7.33–7.41 (4H, m).

Synthesis of the Potassium Iodide Complex of Z-L16 → O

A single crystal of the potassium iodide complex of azoxycrown ether was found in a mixture of complexes obtained in acetone/2-propanol from a mixture of the azo and azoxycrown ethers. The complex loses solvent at ∼130° and melts at 170–175°. Its composition is $C_{39}H_{48}IKN_4O_{10.32}$ (according to X-ray studies). ^{1}H NMR (200 MHz), (CDCl$_3$, δ [ppm]); ligand: 3.78 (8H, s); 3.79–3.83 (4H, m); 3.84–3.88 (4H, m); 3.98–4.03 (4H, m); 4.21–4.25 (4H, m); 6.86 (2H, d, J = 9.5 Hz); 6.87–7.14 (6H, m); 7.28 (2H, dt, J_1 = 9 Hz, J_2 = 1.8 Hz); 7.41–7.57 (6H, m). The chemical shifts for 2-propanol are: 1.21 (6H, d, J = 6.1 Hz); 1.63 (1H, broad s); 4.00 (1H, sept, J = 6.1); intensities of the signals were assumed to correspond to a complex not having L16 as contamination.

A complex, without azocrown as an admixture, was prepared using pure azoxycrown ether Z-L16 → O (0.5 mmol) and potassium iodide (0.5 mmol). A yellowish product which does not contain solvent was obtained. Yield 80%. M.p. 175–176°C. ^{1}H NMR (200 MHz), (CDCl$_3$, δ [ppm]); ligand: 3.78 (4H, s); 3.79–3.83 (2H, m); 3.84–3.88 (2H, m); 3.98–4.03 (2H, m); 4.21–4.25 (2H, m); 6.86 (1H, d, J = 9.5 Hz; 6.87–7.14 (3H, m); 7.28 (1H, dt, J_1 = 9 Hz, J_2 = 1.8 Hz); 7.41–7.57 (3H, m).

2.4. LIBERATION OF *E*-L16 AND *Z*-L16 → O FROM KI COMPLEXES

A sample of the *E*-L16 potassium iodide complex solvate was dissolved in carbon tetrachloride and washed three times with 10^{-3} M hydrochloric acid and water. The organic layer was separated and the solvent was removed under reduced pressure. The residue was crystallized from heptane. M.p. 60°. By NMR spectra and HPLC this compound is identical with isomer *E*.

The azoxycrown ether was liberated from its KI complex in a similar way. M.p. 91–93°. The compound is identical with the *Z*-L16 → O used for the synthesis of the complex.

2.5. X-RAY STUDIES

2.5.1. *Azocrown Ether Complex* [K(*E*-L16)$_2$·I·(CH$_3$)$_2$CHOH]

The complex predominantly forms crystal twins. A single triclinic crystal (0.02 × 0.10 × 0.70 mm) suitable for X-ray studies was selected among very small samples. The parameters of the elementary cell were refined by the least squares method based on 24 reflections collected on a DAR-UMB diffractometer by θ-angle setting in the range of 11.1–23.4° (Table I). The experimental data were obtained on the same diffractometer by the $\omega - \theta/2\theta$ scanning method. The structure was solved by the heavy atom method. Analysis of the Patterson function determined the location of the iodine atom. Two consequent Fourier map calculations localized all the non-hydrogen atoms. It was also found that the crystal entrapped solvating

Table I. Summary of crystal data, experimental details and structure refinement for [K(E-L16)$_2$·I·(CH$_3$)$_2$CHOH] and [K(Z-L16 → O)$_2$·I·(CH$_3$)$_2$CHOH]

	[K(E-L16)$_2$·I·(CH$_3$)$_2$CHOH]	[K(Z-L16→O)$_2$·I·(CH$_3$)$_2$CHOH]
Empirical formula	C$_{39}$H$_{48}$IKN$_4$O$_9$	C$_{39}$H$_{48}$IKN$_4$O$_{10.32}$
Formula weight	882.81	953.94
Temperature	293(2) K	293(2) K
Wavelength	1.54180 Å	0.71073 Å
Crystal system	Triclinic	Monoclinic
Space group	P$\bar{1}$	C2/c
Unit cell dimensions	$a = 21.071(5)$ Å	$a = 15.648(3)$ Å
	$b = 12.112(4)$ Å	$b = 19.597(4)$ Å
	$c = 8.757(2)$ Å	$c = 14.651(3)$ Å
	$\alpha = 81.28(2)°$	$\alpha = 90°$
	$\beta = 84.66(2)°$	$\beta = 111.30(3)°$
	$\gamma = 107.49(2)°$	$\gamma = 90°$
Volume Å^3	2084.0(10)	4186(2)
Z	2	4
Density (calculated)	1.407 g·cm^{-3}	1.434 g·cm^{-3}
Absorption coefficient	7.396 mm^{-1}	0.924 mm^{-1}
F(000)	908	1858
Crystal size	0.02 × 0.1 × 0.7 mm	0.2 × 0.2 × 0.4 mm
Theta range for data collection	2.22 − 67.44°	1.74 − 22.47°
Index ranges	−24 ≤ h ≤ 23	0 ≤ h ≤ 16
	−12 ≤ k ≤ 14	0 ≤ k ≤ 20
	0 ≤ l ≤ 9	−15 ≤ l ≤ 14
Reflections collected	1855	1471
Independent reflections	1844 [R(int) = 0.0383]	1409 [R(int) = 0.0171]
Refinement method	Full matrix LSM on F^2	Full matrix LSM on F^2
Data/restraints/parameters	1838/34/440	1404/0/244
Goodness-of-fit on F^2	1.035	1.055
Final R indices [I>2sigma(I)]	R1 = 0.0655	R1 = 0.0374
	wR2 = 0.1694	wR2 = 0.1052
R indices (all data)	R1 = 0.0664	R1 = 0.0381
	wR2 = 0.1725	wR2 = 0.1141
Largest diff. peak and hole	0.515 and −0.555 Å^{-3}	0.577 and −0.251 e.Å^{-3}

2-propanol molecules. Refinement of the structure was done by the least squares method in the anisotropic approach for non-hydrogen atoms.

The small size of the crystal limited the number of collected reflections (1855) leading to a poor data/parameter ratio. To decrease the number of parameters the aromatic residues were refined as rigid moieties of ideal geometry (C—C = 1.39 Å; C—C—C angle = 120°). The OH hydrogen atom of the solvating 2-propanol was found on a differential Fourier map; the hydrogen atoms of solvent CH$_3$ groups were refined assuming their trigonal pyramidal geometry by rotations around the C—CH$_3$ bond. The residual hydrogens were placed in calculated positions and were refined as constrained to bonding atoms. The potassium cation is coordinated by two ligands. During the refinement it was found that the —N=N— group of one of the crystallographically independent E-L16 ligands (denoted as **b**) is disordered.

It occupies two positions with the same probability. Similar disorder was found for the NaI complex with E-L16 [9]. Calculations were performed using SHELXS86 [10] and SHELX93 [11] packages. The final R-factor equals 0.0655. Crystal data, details of the data collection and refinement procedures are shown in Table I. Atomic coordinates and the equivalent isotropic temperature factors are shown in Table II.

Azoxycrown Ether Complex [K(Z-L16 → O)$_2$·I·(CH$_3$)$_2$CHOH]

For X-ray studies a yellowish crystal (0.2 × 0.2 × 0.4 mm) of a prismatic shape was selected. The parameters of the monoclinic cell were refined by the least squares method based on 25 reflections fitting the θ range = 14.1–21.3°. The experimental data were obtained applying the $\theta/2\theta$ scanning method on a CAD-4 (Enraff-Nonius) diffractometer. 1471 reflections were collected (Table I). The structure was solved by the heavy atom method (SHELX86 package [10]). Potassium and iodine atoms are located on a two-fold crystallographic axis. K$^+$ is surrounded by two equivalent L16 → O ligands resulting in formation of a sandwich structure. Refinement was performed in the anisotropic approach for non-hydrogen atoms. During the refinement a molecule of 2-propanol filling the vacancy formed by bulky complex cations was found. The solvent molecule occupies a position close to a two-fold axis and is disordered. In the model of disorder found during refinement the central carbon atom (C1pr) is located on the two-fold axis. The other atoms of the molecule are equally distributed between two positions in accordance with two-fold symmetry. No close contacts between the solvent and other atoms in the structure were detected. The solvent molecule and the hydrogen atoms were refined in the isotropic approach. It was also found that the position for the oxygen atoms of the azoxy group was not fully occupied. Refinement of the occupational factor by the least squares method shows 67% occupancy for this position. It was assumed that the complex [K(E-L16)$_2$·I·(CH$_3$)$_2$CHOH] cocrystallizes with [K(Z-L16 → O)$_2$·I·(CH$_3$)$_2$CHOH]. Crystallographic, experimental and refinement data for the structure and the final R factor are given in Table I. Table III shows data on coordinates and equivalent isotropic displacement parameters.

Geometric parameters for [K(E-L16)$_2$·I·(CH$_3$)$_2$CHOH] and [K(Z-L16 → O)$_2$ ·I·(CH$_3$)$_2$CHOH] are collected in Table IV.

3. Description of Structures

3.1. [K(E-L16)$_2$·I·(CH$_3$)$_2$CHOH]

The structure of [K(E-L16)$_2$·I·(CH$_3$)$_2$CHOH] is ionic and consists of complex cations of the formula [K(E-L16)$_2$]$^+$, I$^-$ anions and solvating molecules of 2-propanol in a 1 : 1 : 1 ratio. The iodide anions and the solvating alcohol molecules are associated by OH$\cdots$I$^-$ hydrogen bonds: O(1pr)$\cdots$I(1) = 3.69(3); H(1pr)$\cdots$I(1) = 3.1(2); H(1pr)$\cdots$O(1pr) = 0.82 Å and O(1pr)—H(1pr)$\cdots$I(1) angle = 128°.

Table II. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for [K(E-L16)$_2 \cdot$I$\cdot$(CH$_3$)$_2$CHOH]. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x	y	z	U(eq)
I(1)	3736(1)	2261(2)	1058(2)	67(1)
K(1)	3022(2)	5840(4)	5240(4)	45(1)
O(1a)	2130(6)	4281(14)	7879(14)	64(4)
C(2a)	1973(10)	3059(17)	7886(23)	65(6)
C(3a)	2622(11)	2854(19)	7463(20)	73(7)
O(4a)	2881(7)	3369(12)	5880(13)	58(4)
C(5a)	3499(10)	3217(21)	5344(19)	78(8)
C(6a)	4041(10)	3815(17)	6187(23)	70(7)
O(7a)	4149(6)	5050(12)	6032(12)	52(3)
C(8a)	4488(9)	5611(19)	7181(20)	63(7)
C(9a)	4565(9)	6885(19)	6967(22)	63(6)
O(10a)	3912(6)	6974(11)	7249(13)	48(3)
C(11a)	3937(7)	8113(12)	7331(14)	50(6)
C(21a)	4509(6)	9088(17)	6828(15)	79(8)
C(22a)	4488(10)	10207(13)	6956(18)	97(9)
C(23a)	3894(13)	10350(13)	7587(18)	132(14)
C(24a)	3322(10)	9375(19)	8091(16)	97(10)
C(12a)	3343(6)	8256(15)	7962(14)	57(6)
N(13a)	2708(10)	7417(20)	8628(20)	82(7)
N(14a)	2546(8)	6513(17)	8153(17)	59(5)
C(15a)	1888(7)	5712(14)	9011(16)	73(8)
C(16a)	1656(7)	4561(16)	8762(14)	59(6)
C(17a)	1026(8)	3818(13)	9495(19)	85(8)
C(18a)	628(6)	4226(20)	10477(18)	119(12)
C(19a)	860(10)	5377(22)	10726(18)	108(11)
C(20a)	1489(11)	6120(14)	9993(20)	119(11)
O(1b)	2824(9)	8054(16)	3920(19)	90(5)
C(2b)	3433(13)	8941(26)	3141(33)	119(11)
C(3b)	3783(19)	8459(30)	2016(34)	176(20)
O(4b)	4035(8)	7707(16)	3000(16)	88(5)
C(5b)	4430(15)	7131(28)	2220(43)	175(17)
C(6b)	4103(10)	6169(23)	1483(27)	90(8)
O(7b)	3512(7)	5410(12)	2368(13)	63(4)
C(8b)	3038(11)	4968(22)	1393(22)	90(9)
C(9b)	2417(10)	4090(19)	2304(22)	68(6)
O(10b)	2118(6)	4635(12)	3333(14)	64(4)
C(11b)	1491(7)	3987(19)	4117(18)	71(7)
C(21b)	1191(11)	2789(19)	4159(20)	91(8)
C(22b)	550(12)	2210(15)	4985(24)	138(15)
C(23b)	210(7)	2828(25)	5768(22)	166(21)
C(24b)	510(11)	4025(25)	5727(20)	137(15)
C(12b)	1151(11)	4604(14)	4901(22)	80(8)
N(13b)	1184(16)	5751(27)	5039(40)	70(11)
N(14b)	1782(12)	6366(22)	4990(23)	18(6)
N(13#)	1629(17)	5806(27)	4903(38)	60(10)
N(14#)	1303(18)	6392(28)	5441(42)	85(12)
C(15b)	1745(12)	7549(14)	5315(21)	85(8)
C(16b)	2349(9)	8423(22)	4672(17)	75(8)
C(17b)	2454(10)	9572(18)	4899(22)	101(10)
C(18b)	1956(15)	9847(17)	5769(26)	124(13)
C(19b)	1352(12)	8973(28)	6411(20)	137(16)
C(20b)	1247(9)	7824(23)	6184(19)	135(15)
O(1pr)	1889(13)	1356(19)	1373(25)	131(7)
C(1pr)	1443(15)	170(25)	1651(36)	141(14)
C(2pr)	1669(20)	−715(38)	929(48)	227(26)
C(3pr)	777(14)	252(27)	1201(38)	153(16)

For disordered azo group.

Table III. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for [K(Z-L16→O)$_2$·I·(CH$_3$)$_2$CHOH]. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	x	y	z	U(eq)
I	5000	6022(1)	7500	88(1)
K	5000	2727(1)	7500	49(1)
O(2)	4347(6)	808(4)	4957(6)	80
O(1)	3170(3)	2172(3)	6481(4)	69(1)
C(2)	2401(5)	2588(5)	6472(6)	77(2)
C(3)	2590(6)	3279(5)	6229(7)	90(3)
O(4)	3352(3)	3556(3)	6987(4)	68(1)
C(5)	3581(6)	4236(4)	6805(6)	80(3)
C(6)	3920(6)	4291(4)	5969(6)	76(2)
O(7)	4637(4)	3806(2)	6132(4)	68(1)
C(8)	4886(6)	3734(4)	5291(6)	75(2)
C(9)	5681(6)	3261(4)	5530(6)	70(2)
O(10)	5407(3)	2592(3)	5730(4)	63(1)
C(11)	5988(5)	2069(4)	5761(5)	54(2)
C(12)	5696(5)	1411(5)	5724(5)	65(2)
N(13)	4800(5)	1196(4)	5696(6)	84(2)
N(14)	4544(4)	1449(3)	6299(5)	65(2)
C(15)	3720(6)	1085(5)	6367(5)	69(2)
C(16)	3078(5)	1491(5)	6555(5)	62(2)
C(17)	2363(5)	1185(5)	6762(5)	75(3)
C(18)	2301(7)	492(7)	6795(7)	95(3)
C(19)	2932(9)	96(5)	6617(8)	106(3)
C(20)	3640(8)	388(6)	6396(7)	99(3)
C(21)	6879(6)	2165(5)	5798(6)	76(2)
C(22)	7438(6)	1639(7)	5787(7)	91(3)
C(23)	7117(8)	986(7)	5708(7)	100(3)
C(24)	6244(7)	862(4)	5668(7)	84(3)
O(1pr)	−801(27)	3145(20)	7082(27)	179(12)
C(1pr)	0	3294(30)	7500	350(26)
C(2pr)	445(22)	2805(14)	6986(23)	291(12)
C(3pr)	183(20)	4026(14)	7335(25)	312(15)

Two macrocyclic molecules form with potassium a complex sandwich cation. The potassium coordination number is 10; four oxygens and one nitrogen atom from each E-L16 ligand form bonds with the metal cation (Figure 1). The average distances are: K–O = 2.88(13); K–N = 2.97(2) Å for ligand **a**. As mentioned above, the azo group in ligand **b** is disordered resulting in equal probability of potassium coordination to one of two nitrogen atoms (Figure 1, solid and broken lines). The K—N distances equal 2.89(2) and 2.97(4) Å, respectively. The average K—O distance is 2.873(10) Å.

The torsion angle C—N=N—C = 177° for **a** and 175° for ligand **b** indicate *trans* orientation of the substituents. For this group the average distances are: C(12)—N(13) = 1.41, C(15)—N(14) = 1.51 and N(14)—N(13) = 1.23 Å. An angular [12]

Table IV.   Selected interatomic distances, valence and torsion angles for [K(*E*-L16)₂·I·(CH₃)₂CHOH] and [K(*Z*-L16→O)₂·I·(CH₃)₂CHOH]

	K⁺ Complex of *E*-L16		K⁺ Complex of *Z*-L16→O
	Ligand **a**	Ligand **b**	Ligand
K—O(1)	2.859(13)	2.92(2)	2.922(5)
K—O(4)	2.878(14)	2.91(2)	2.902(5)
K—O(7)	2.916(14)	2.81(12)	2.827(5)
K—O(10)	2.881(12)	2.864(12)	2.901(4)
K—N(14)	2.97(2)	2.89(2)	3.009(6)
C(16)—O(1)	1.359(14)	1.37(2)	1.359(8)
O(1)—C(2)	1.42(2)	1.43(2)	1.433(8)
C(2)—C(3)	1.49(2)	1.47(2)	1.460(12)
C(3)—O(4)	1.42(2)	1.41(2)	1.403(9)
O(4)—C(5)	1.42(2)	1.42(2)	1.426(9)
C(5)—C(6)	1.48(2)	1.44(2)	1.505(12)
C(6)—O(7)	1.43(2)	1.38(2)	1.412(8)
O(7)—C(8)	1.43(2)	1.41(2)	1.420(9)
C(8)—C(9)	1.48(2)	1.48(2)	1.467(11)
C(9)—O(10)	1.41(2)	1.40(2)	1.442(8)
O(10)—C(11)	1.379(13)	1.370(14)	1.355(7)
C(12)—N(13)	1.42(2)	1.39(3)	1.448(10)
N(13)—N(14)	1.20(2)	1.25(3)	1.215(8)
N(14)—C(15)	1.49(2)	1.53(2)	1.492(9)
C(16)—O(1)—C(2)	113.8(14)	117(2)	116.4(5)
O(1)—C(2)—C(3)	106(2)	110(3)	107.0(6)
C(2)—C(3)—O(4)	110(2)	102(2)	110.6(7)
C(3)—O(4)—C(5)	115(2)	116(2)	114.0(6)
O(4)—C(5)—C(6)	111(2)	119(2)	114.1(6)
C(5)—C(6)—O(7)	113(2)	113(2)	107.9(6)
C(6)—O(7)—C(8)	116(2)	111(2)	111.8(5)
O(7)—C(8)—C(9)	113(2)	112(2)	109.5(6)
C(8)—C(9)—O(10)	107(2)	109(2)	109.7(6)
C(9)—O(10)—C(11)	111.3(13)	116(2)	117.0(5)
O(10)—C(11)—C(12)	116.1(12)	116(2)	119.8(6)
C(11)—C(12)—N(13)	131(2)	141(2)	126.0(6)
C(12)—N(13)—N(14)	117(2)	108(3)	114.8(7)
N(13)—N(14)—C(15)	111(2)	108(3)	112.3(6)
N(14)—C(15)—C(16)	119(2)	150(2)	116.7(6)
C(15)—C(16)—O(1)	112.2(14)	116(2)	115.8(6)
C(12)—N(13)—O(2)	–	–	115.5(8)
O(2)—N(13)—N(14)	–	–	129.5(8)
O(1)—C(2)—C(3)—O(4)	−69(2)	−73(3)	−66.7(8)
C(2)—C(3)—O(4)—C(5)	−179(2)	−178(2)	179.6(7)
C(3)—O(4)—C(5)—C(6)	−64(2)	−74(4)	−67.3(8)
O(4)—C(5)—C(6)—O(7)	−59(2)	−42(4)	−51.2(8)
C(5)—C(6)—O(7)—C(8)	160(2)	145(3)	168.8(6)
C(6)—O(7)—C(8)—C(9)	−178(2)	176(2)	175.8(6)
O(7)—C(8)—C(9)—O(10)	67(2)	62(2)	64.7(7)
C(8)—C(9)—O(10)—C(11)	170(1)	172(1)	166.7(6)
C(9)—O(10)—C(11)—C(12)	−165(1)	−168(1)	−165.6(6)
O(10)—C(11)—C(12)—N(13)	4(2)	11(3)	−1.2(10)
C(11)—C(12)—N(13)—N(14)	−30(3)	−38(4)	−51.1(10)
C(12)—N(13)—N(14)—C(15)	177(1)	−175(2)	−166.1(6)
N(13)—N(14)—C(15)—C(16)	−172(1)	−155(2)	−143.5(6)
N(14)—C(15)—C(16)—O(1)	8(1)	0(2)	10.9(8)
C(15)—C(16)—O(1)—C(2)	167(1)	175(2)	168.1(6)
C(16)—O(1)—C(2)—C(3)	−157(1)	−162(2)	−171.4(6)

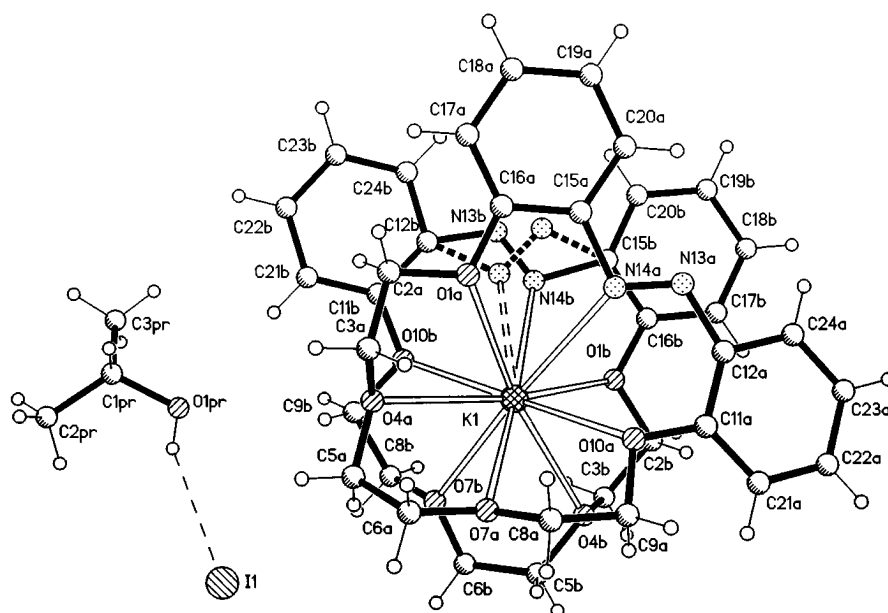*Figure 1.* Structure of [K(*E*-L16)$_2$·I·(CH$_3$)$_2$CHOH]. Broken lines denote the second position of the disordered —N=N— bond.
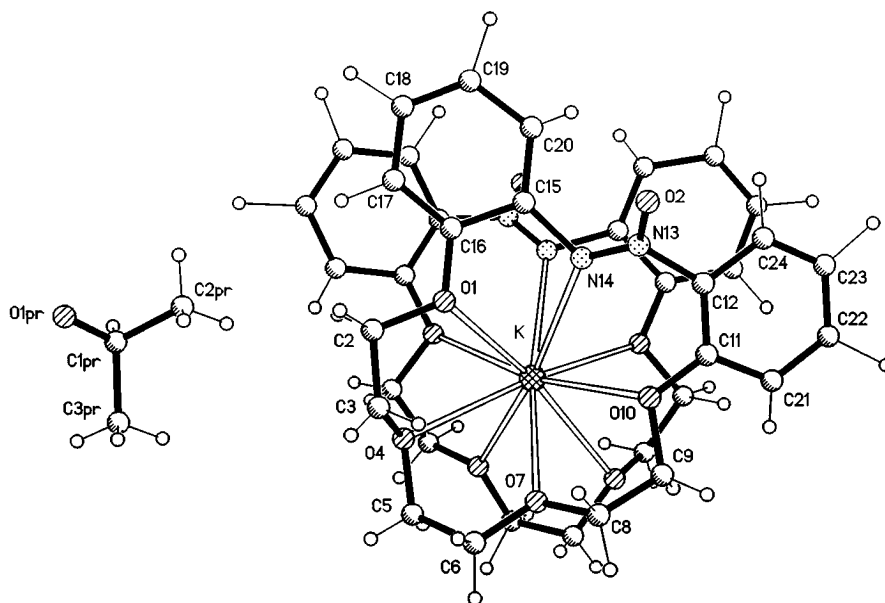

Figure 2. Structure of [K(*Z*-L16→O)$_2$·I·(CH$_3$)$_2$CHOH].

fragment of the oxyethylene part of both macrocycles was found at C(5a) and C(5b), respectively. The geometric parameters are shown in Table IV. The average distances are: C_{sp^3}—C_{sp^3} = 1.48, C_{sp^2}—O = 1.37 and C_{sp^3}—O = 1.43 Å. The endocyclic angles in the polyoxyethylene chain at C and O atoms are 111 and 114°, respectively.

3.2. [K(Z-L16 → O)$_2$·I·(CH$_3$)$_2$CHOH]

The [K(Z-L16 → O)$_2$·I·(CH$_3$)$_2$CHOH] complex is similar to the former compound being ionic with a sandwich structure of the complex cation (Figure 2). In this case the 2-propanol molecules are not bonded to the anion. The coordination number of the potassium cation is ten, the appropriate oxygen and nitrogen atoms form the apices of the coordination pentagonal antiprism. The K–O and K–N distances are 2.826–2.922 and 3.01 Å, respectively. The K–O distances are close to those found for potassium complexes of benzo- and naphtho-15-crown-5 (2.770–3.006 Å) [13]. The K–N distance is slightly larger than that for K–O, which is in agreement with the larger radius of nitrogen as compared to the oxygen atom. Potassium and iodine ions are located on a two-fold crystallographic axis.

The torsion angles for the C—N(O)=N—C system are −51.1, −166.1 and −143.5° (*gauche-trans-trans*). The lone electron pair of N(14) is directed inside, whereas that of the oxygen atom O(2) is pointing away from the macrocycle cavity. The average distances are: C–N = 1.47, N = N = 1.215 and N–O = 1.291 Å. The distances are close to those found for Z-L13 [14], Z-L13 → O [5] and for the formal dimer of L13 → O [15]. The azoxy group is similar to that found in Z-L13 → O [5].

The dihedral angle between the mean plane of the azoxy group and the mean plane of electron donating atoms [O(1), O(4), O(7), O(10) and N(14)] is 51.9°. The coordinating atoms are not coplanar, the deviations from the mean plane are: O(1) (−0.317), O(4) (0.237), O(7) (−0.088), O(10) (−0.057), N(14) (0.225 Å); the non coordinating N(13) deviates by −0.316 Å. The polyoxyethylene chain is described by five *anti* and one *gauche* conformations of the C—O bonds and by three *gauche* conformations of C—C bonds. At C(5) there is an angular [12] fragment. The benzene rings form a dihedral angle of 14.8°. Their dihedral angles with the N(13)—N(14)—O(2) plane are 51.96 and 54.48°.

4. Discussion

Our synthesis and workup permitted isolation of two isomeric azo compounds E-L16 (m.p. 60–61°) and Z-L16 (m.p. 121–122°) distinguishable by TLC. Based on ^{1}H NMR spectra the E structure was ascribed to the low melting modification. On the same basis the Z structure was assigned to the high melting compound. The NMR spectra of both these isomers (Figure 3) differ from that described by
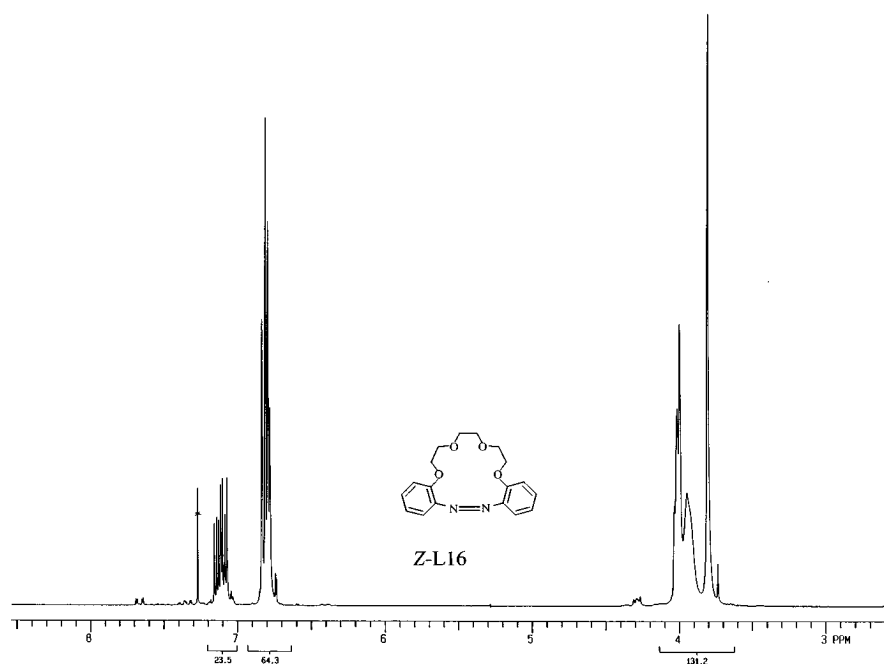
Figure 3a. ^{1}H NMR spectrum of Z-L16.

Shiga et al. for the compound L16 [6]. The m.p. they gave for L16 (67.5–68 °C) corresponds rather to a mixture of both isomers.

Isomers E and Z of L16 are capable of cocrystallizing. The m.p. of the E compound depends on the amount of isomer present in the solid state; it increases with increasing amount of contamination. The KI complexes of E-L16 and Z-L16 → O also cocrystallize.

Both Z- and E-L16 isomerize in solution. Their separation was achieved due to differences in solubilities and tendency to crystallization. Both isomers are stable in the solid state. The pure oily E isomer (E-L16) is relatively stable when liberated from the potassium iodide complex. The product crystallizes upon seeding with its KI complex or with Z-L16 → O; m.p. 61°. Its origination from a complex of known stereochemistry and its ^{1}H NMR spectrum allowed us to ascribe it as the E isomer. The Z isomer shows a high tendency to crystallize from solutions (e.g., in ethyl ether or *iso*-butyl acetate) even in the presence of an excess of the E isomer in a mixture.

Both isomers were additionally examined by HPLC. The retention times for Z-L16 and E-L16 are 4.38 and 7.04 min., respectively. The Z isomer has one maximum at $\lambda_{max} = 312$ nm; in the case of the isomer E two maxima are present: at 338 and 430 nm. Both spectra were taken directly during chromatographic
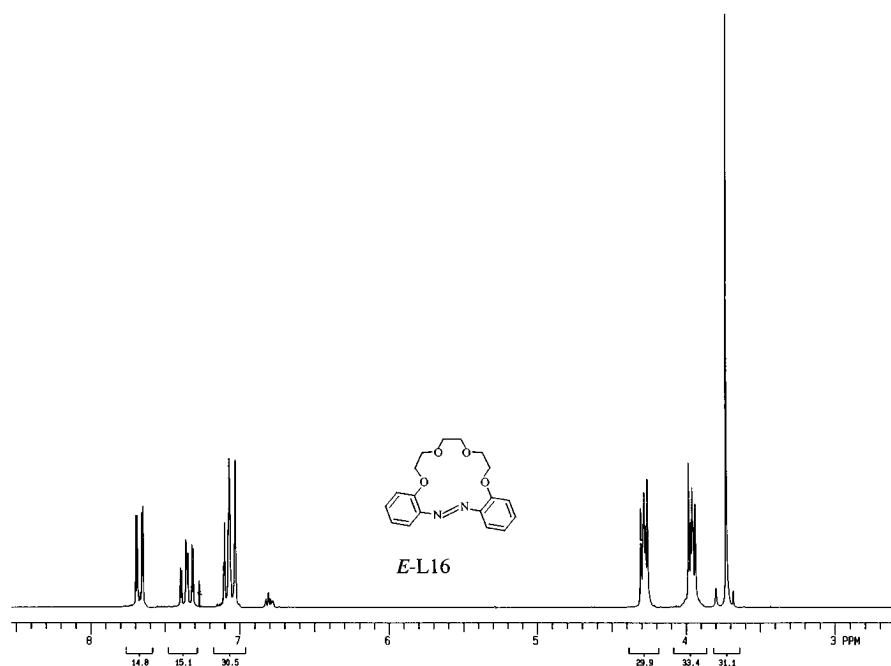
Figure 3b. ^{1}H NMR spectrum of *E*-L16.

separation. The UV-VIS spectra support additionally the stereochemistry ascribed for both compounds.

The stannite reduction of bis(2-nitrophenoxy)-3,6-dioxaoctane under alkaline conditions produces mainly the azocrown ether and small amounts of the azoxy-crown ether. The better synthetic method for the azoxycrown ether is oxidation of the azocrown ether with peracetic acid.

The azoxycrown ether L16 → O has *trans* oriented aromatic residues (isomer *Z*). It follows from its NMR spectrum, which was compared with the spectrum for *Z*-L13 → O of geometry known from X-ray studies [5]. The stereochemistry of the synthetic L16 → O was definitely confirmed by comparing it with a compound (ligand) liberated from its KI complex.

The cavity sizes of crown ethers change systematically with the number of atoms forming the macroring. For classical 15-crown-5 and 18-crown-6 the hole sizes are 1.7–2.2 and 2.6–3.2 Å, respectively [16]. Appropriately, the sodium cation (diameter = 1.90 Å) [17] forms a 1 : 1 complex with the 15-membered crown ether and a sandwich like complex (stoichiometry 1 : 2) with the smaller 12-crown-4. The potassium cation (diameter 2.66 Å) [17] forms a 1 : 1 complex with 18-crown-6 and a 1 : 2 complex with 15-crown-5. The hole diameters of ligands L16 and L16 → O are intermediate as compared to those for 15- and 18-membered crown ethers.

The 13-membered azo- and azoxycrown ethers resemble 12-membered crown ethers by type of formed complexes. The properties of the 16-membered azo- and azoxycrown ethers allow comparison with the 15-membered crown ethers [6a]. Structures of the sodium and potassium complexes also show many similarities. Despite unfavorable stability constants for potassium the azocrown crown ether L16 in membrane ion-selective electrodes shows very high potassium over sodium selectivity. In this respect it again resembles 15-membered benzocrown ethers [18].

5. Conclusions

The geometry for the Z and E isomers of 16-membered azocrown ethers was ascribed. The E form coordinates to potassium cation to form sandwich complexes in the solid state. The azoxycrown ether obtained by reduction of the 1,8-bis(nitrophenoxy)-dioxaoctane or by oxidation of the parent azocrown ether has E geometry in both the free and complexed forms. With regard to the arrangement of the aryl residues the *trans* isomers of the macrocycles are better preorganized to form complexes and within the complexes *trans* —N=N— [6] or —N=N(O)— residues participate in complex formation.

With the exception of the disorder found in the complex cation of the 16-membered azocrown ether there is a close analogy of [K(E-L16)$_2$·I·(CH$_3$)$_2$CHOH] and of [K(Z-L16→O)$_2$·I·(CH$_3$)$_2$CHOH]. They are similar by stoichiometry and ionic structure. In both sandwich complexes the potassium coordination number is 10 and the coordination polyhedron is pentagonal antiprism. Both azo and azoxy groups coordinate potassium by only one nitrogen atom and posses *trans* (in respect to location of the aromatic residues) geometry. The interatomic distances, valence and torsion angles are also very similar. In addition the K–O distances are not essentially different from those found for potassium complexes of crown ethers.

For both complexes $\pi-\pi$ interactions are observed between aromatic residues of ligands within the complex potassium cation.

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