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Characterization of Small Azocrown Ether Stereoisomers

by E. Luboch[1*], E. Wagner-Wysiecka[1], V.Ch. Kravtsov[2] and V. Kessler[3]

[1]*Department of Chemical Technology, Technical University, 80-952 Gdańsk, Poland*
[2]*Institute of Applied Physics, Academy of Sciences of Moldova, Kishinev, Republic of Moldova*
[3]*Swedish University for Agricultural Sciences, Chemistry Department, Uppsala, Sweden*

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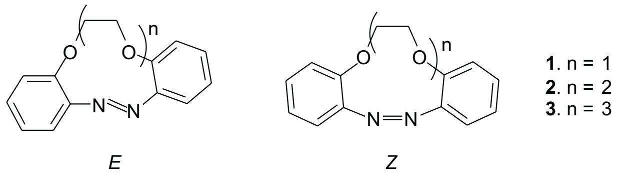
The stable *E*- and *Z*-isomers of 10-membered azocrown ether have been isolated and studied by X-ray, ^{1}H NMR and UV-Vis methods. Their structures in a solid state indicate the stretched conformation for *trans*-isomer and unstressed for *cis*-isomer. The concerted effect of azo-group π-conjugation with benzene residue and steric strain of molecular conformation results in the observed stability of isomers.

Key words: azocompounds, macrocycles, stereoisomers, X-ray structures, conformation, ^{1}H NMR, UV-Vis, complexation

Reversible $Z \rightleftarrows E$ isomerization of azobenzenes and their analogs is utilized in photo- or redox-active molecular switches and for storage of images [1]. Similarly to azobenzenes, azocrown ethers also isomerize. Azocrown ethers of different size of macrocycle were studied. The most exhaustively were studied 13- and 16-membered azocrown ethers [2–7]. For these compounds in solutions and in a solid state preferred formation of cation complexes was found for *trans* isomers [8–11]. Lately, the smaller sized azo- and azoxycrown ethers of expected higher stability of *cis* isomers is subject of our studies [12,13]. However, the structural information for small azocrown isomers is absent.

Recently the X-ray structure of *E* isomer of 10-membered azoxycrown compound [12] and structures of *Z* and *E* isomers of its bis(4-phenyl) derivative [13] were reported by us. The present paper deals with the X-ray diffraction studies of *Z* and *E* stereoisomers of 10-membered azocrown ether (*Z*-**1** and *E*-**1**) and to their spectroscopic properties.



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[*] Author for correspondence.

EXPERIMENTAL

Synthesis: Isolation of 10-membered azocrown compound from reduction products of 1,2-bis(2-nitrophenoxy)ethane was described in our previous paper [13]. The isolated *E*-**1** compound was isomerized in solution and both isomers were separated by preparative TLC in methylene chloride. Isomer *cis* was crystallized from heptane doped with tracer amount of methylene chloride. The eluate containing isomer *trans* was evaporated, dissolved in methanol and the last solvent was exhaustively removed to form a film, from which the desired compound slowly crystallizes.

Stereoisomers of 13-membered azocrown **2** and 16-membered azocrown **3** were obtained as described [9,10].

Isomerization: The *E*-**1** compound in a solution in methylene chloride (10 mg in 10 mL) was left for three weeks at room temperature under room light. ^{1}H NMR spectrum of the mixture of isomers was recorded immediately after the solvent was removed. On this basis the abundance of isomers was assessed as equal 70% and 30% for *cis* and *trans* components, respectively.

X-ray crystal structure determination: A red needle shaped monocrystal of $0.05 \times 0.10 \times 0.55$ mm size of *E*-**1** and an orange prism habits monocrystal of $0.25 \times 0.30 \times 0.60$ mm size of *Z*-**1** were used. Data were collected on a Siemens SMART CCD diffractometer (monochromatic Mo-K$_\alpha$ radiation, $\lambda = 0.7107$ Å, φ and ω scan modes). The structures were solved by direct methods using the SHELX97 program package [14]. The non-H atoms were refined with anisotropic displacement parameters. The remaining hydrogen atoms were placed in calculated positions and were refined as riding on the corresponding carbon atom with $U(H) = 1.2U_{eqv}$ of attached atom for *trans* and individual isotropic displacement parameters for *cis* isomer, respectively. The significant crystal data and experimental details on data collection together with structure refinement are summarized in Table 1. Selected geometric parameters and torsion angles for both structures are given in Table 2 and 3, respectively.

^{1}H NMR spectra were recorded on Varian instrument (500 MHz) in $CDCl_3$ or in CD_3CN.

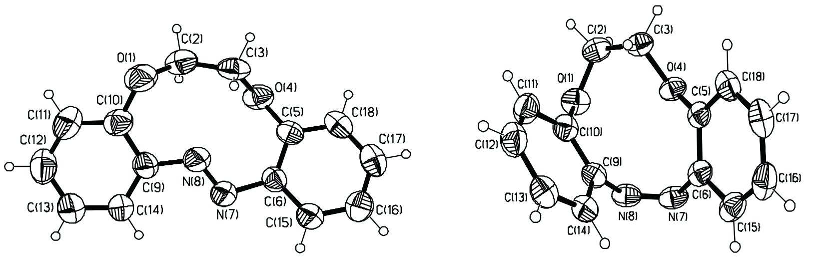
Cation complexation was studied by NMR in acetonitrile: first spectrum was taken of 0.01 mmole of azocrown ether dissolved in 0.7 mL acetonitrile. Then the solution was mixed with 0.5 mmol of solid $MClO_4$ (M = Li or Na) until dissolution and the second spectrum was registered.

UV-Vis spectra in acetonitrile were recorded on a Unicam UV-330 Spectrophotometer in 1 cm quartz cell at 25°C.

RESULTS AND DISCUSSION

The 10-membered azocrown ether was obtained as one of the reductive cyclization products of 1,2-bis(2-nitrophenoxy)-ethane. The small sized azocrown ether is formed rather with low yield. The main isomer formed under the reaction conditions is isomer *trans*, which undergoes in solution spontaneous isomerization giving mixture of isomers in which the *cis* compound predominates (opposite to larger azocrowns). Among studied azocrown ethers the 10-membered azocrown shows the highest stability of *cis* isomer (the extrapolated ambient-temperature time constant being of the order of several years). The stability of the *cis* form in the darkness combined with good isomerization reversibility may be promising for future application of the material in optical data storage [15,16]. Both isomers of **1** were obtained in a crystalline state. Geometry of the azo group in both isomers was determined by ^{1}H NMR and UV-Vis spectroscopy in solution, TLC [13], and by X-ray studies.

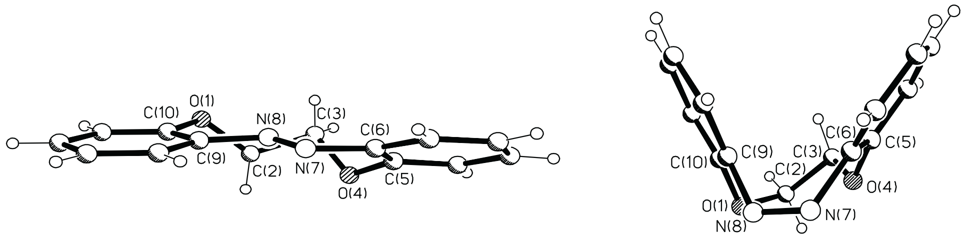
Structure description of isomers of 10-membered azocrown ethers. The displacement ellipsoid plots with the atom-numbering scheme for *trans* and *cis* isomers in the projection on the best plane of heteroatoms are shown in Figure 1.



E-**1** *Z*-**1**

Figure 1. Top view of isomeric 10-membered azocrown ethers. The thermal displacement ellipsoids are given with the 30% and 50% probability for *trans* and *cis*, respectively.

Figure 2 illustrates the conformational difference of these two isomers. The molecule of *trans*-isomer is roughly planar. Root mean squares deviation of fitted atoms from the best plane of the molecule equal 0.289 Å. The divergence of O(1) and O(4) atoms are –0.653(2) and 0.561(2) Å respectively, while deviations of other atoms are in the range from –0.318(3) to 0.304(2) Å. The azo group adopts the *E* geometry with aromatic moieties in the *trans*-positions.



E - **1** *Z* - **1**

Figure 2. Conformations of *trans*- and *cis*-isomers of **1** in side view.

The aromatic residues form dihedral angle 24.8(1)°. The torsion angle around N(7)–N(8) bond equals 174.6(2)° (Table 3). The N(8) atom lone electron pair points inside the macrocycle and that at N(7) atom points outside. The torsion angles around C(6)–N(7) and N(8)–C(9) bonds equal –28.1(3) and –175.4(2)°, respectively. It indicates a slightly different degree of π-conjunction of azo-group with the adjacent benzene rings, manifested also by differences in the corresponding bond lengths: C(6)–N(7) = 1.431(3); N(8)–C(9) = 1.397(3) Å.

The ethylenedioxy group adopts unfavorable conformation described by the following set of torsion angles: sc, -ac, ac, -ac and sc starting from C(10)–O(1) bond. This set differs essentially from usual sequence of torsion angles in O–C–C–O chain for larger macrocyclic crown compounds. The endocyclic bond angles also deviate from common values: the value of C(10)–C(9)–N(8) angle for sp^2-hybridizated C(9) is only 114.0(3)°, while the bond angle on C(2) atom in sp^3- hybridization equals 115.9(2)°. The bond angles on chemically equivalent N(7) and N(8) atoms also differ: the respective values are 110.3(2) and 118.9(2)°. Simultaneously, the geometrical parameters of benzene rings are as expected. The steric strain in *trans*-isomer is obvious and seems that the π-conjunction of azo-group with benzene rings contributes to stabilization of such conformation. The molecule of *cis*-isomer is non-planar and has boat shape (Figure 2). Azo-group possesses *Z*-geometry with aromatic residues in *cis*-position. The dihedral angle between benzene planes equals 66.06(3)°. The overall conformation of the molecule is very close to that found for azoxy-analogs [12,13]. The torsion angles around C(6)–N(7) and N(8)–C(9) bonds equal 67.3(1) and 116.2(1)° and practically exclude the possibility for π-conjunctions of azo group with adjacent aromatic rings. The bond lengths C(6)–N(7) = 1.446(2) and N(8)–C(9) = 1.441(2) Å as well as bond angles on nitrogen atoms 119.9(1) and 120.3(1)° coincide within two standard deviation. In the crystal structures of the relative, larger sized macrocycles the azo group of *Z*-geometry show similar common features and some increasing of one of the torsion angles around C–N bond up to 139.4° in 13-membered azomacrocycle [3] and to 134.2(5) or 129.2(5)° for two crystallographically independent molecules of tribenzo-16-azocrown-6 [5]. It may be considered as a tendency to increase the π-conjunctions of azo group with the attached benzene ring.

Table 1. Crystal data and structure refinement for *E*-**1** and *Z*-**1**.

Compound	*E*-**1**	*Z*-**1**
Empirical formula	$C_{14}H_{12}N_2O_2$	$C_{14}H_{12}N_2O_2$
Formula weight	240.26	240.26
Temperature	293(2) K	293(2) K
Crystal system, space group	monoclinic, $P2_1/c$	orthorhombic, *Pbca*
Unit cell dimensions:		
a, Å	13.935(5)	15.542(1)
b, Å	5.170(2)	8.9032(8)
c, Å	17.212(7)	17.605(2)
β, deg.	99.596(1)	90
V, Å^3	1188.3(8)	2436.1(4)
Z, Calculated density	4, 1.343 g/cm^3	8, 1.310 g/cm^3
Absorption coefficient	0.092 mm^{-1}	0.090 mm^{-1}
Crystal size	0.55×0.10×0.05 mm	0.60×0.30×0.25 mm
θ - range for data collection, deg	1.52 to 27.49°	2.31 to 28.00
Limiting indices	$-17 \leq h \leq 13, -6 \leq k \leq 6,$ $-21 \leq l \leq 22$	$-20 \leq h \leq 12, -11 \leq k \leq 11,$ $-23 \leq l \leq 23$
Reflections collected/unique	6540/2648 [$R(int)$ = 0.1024]	13244/2826 [$R(int)$ = 0.0222]
Completeness to θ = 28.45	96.9%	96.3%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	2648/0/164	2826/0/176
Goodness-of-fit on F^2	0.751	0.961
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0566, $wR2$ = 0.1059	$R1$ = 0.0331, $wR2$ = 0.0848
R indices (all data)	$R1$ = 0.1837, $wR2$ = 0.1290	$R1$ = 0.0643, $wR2$ = 0.0924
Largest diff. peak and hole	0.167 and –0.165 e. Å^{-3}	0.122 and –0.125 e. Å^{-3}

The bond lengths and angles in ethylenedioxy chain are ordinary. Conformation of this chain may be described by the following set of torsion angles: -ac, sc, sc, -ac and ac starting from C(10)–O(1) bond. The sequence of two sc angles on the C(2) atom forms so called corner (angular) fragment [17], which is also typical for larger azo- and azoxy macrocycles [9,10,18,19]. The torsion angles of the ethylenedioxy chain indicate its depressed stretch conformation as compared with the *trans*-isomer. One can conclude that stability of *trans*-isomer of 10-membered azocrown compound is stimulated by strong π-conjunction of azo group with the adjacent benzene ring that overbalances the steric strain in molecule, while the *cis*-isomer exists in stress-free conformation.

Table 2. Selected bond lengths [Å] and angles [°] for *E*-**1** and *Z*-**1**.

Atoms	*E*-**1**	*Z*-**1**
Bond lengths		
O(1)–C(10)	1.387(3)	1.380(1)
O(1)–C(2)	1.443(3)	1.438(2)
C(2)–C(3)	1.509(4)	1.493(2)
C(3)–O(4)	1.422(3)	1.433(1)
O(4)–C(5)	1.380(3)	1.369(1)
C(5)–C(6)	1.410(3)	1.389(2)
C(6)–N(7)	1.431(3)	1.446(2)
N(7)–N(8)	1.234(3)	1.251(1)
N(8)–C(9)	1.397(3)	1.441(2)
C(9)–C(10)	1.388(4)	1.387(2)
Angles		
C(10)–O(1)–C(2)	119.8(2)	116.0(1)
O(1)–C(2)–C(3)	115.9(2)	112.9(1)
O(4)–C(3)–C(2)	109.2(2)	107.1(1)
C(5)–O(4)–C(3)	120.4(2)	117.5(1)
O(4)–C(5)–C(18)	117.8(2)	123.4(1)
O(4)–C(5)–C(6)	122.6(3)	116.7(1)
C(15)–C(6)–N(7)	116.6(2)	120.2(1)
C(5)–C(6)–N(7)	124.6(3)	119.2(1)
N(8)–N(7)–C(6)	110.3(2)	119.9(1)
N(7)–N(8)–C(9)	118.9(2)	120.3(1)
C(10)–C(9)–N(8)	114.0(3)	120.3(1)
N(8)–C(9)–C(14)	126.9(3)	119.4(1)
O(1)–C(10)–C(11)	117.6(3)	121.9(1)
O(1)–C(10)–C(9)	121.7(3)	118.6(1)

Table 3. Selected torsion angles [°] for *E*-**1** and *Z*-**1**.

	E-**1**	*Z*-**1**
C(9)–C(10)–O(1)–C(2)	54.6(4)	–113.5(1)
C(10)–O(1)–C(2)–C(3)	–100.8(3)	44.3(2)
O(1)–C(2)–C(3)–O(4)	122.7(2)	49.1(2)
C(2)–C(3)–O(4)–C(5)	–138.5(2)	–142.3(1)
C(3)–O(4)–C(5)–C(6)	80.3(3)	136.1(1)
O(4)–C(5)–C(6)–N(7)	–1.0(4)	–0.5(2)
C(5)–C(6)–N(7)–N(8)	–28.1(3)	–67.3(1)
C(6)–N(7)–N(8)–C(9)	174.6(2)	–7.7(2)
N(7)–N(8)–C(9)–C(10)	–175.4(2)	116.2(1)
N(8)–C(9)–C(10)–O(1)	–3.3(4)	–7.6(2)

Spectroscopic properties of isomers of azocrown 1 and interactions with cations. Isomers of 10-membered azocrown ethers are easily distinguishable by chromatographic and spectroscopic methods. For example, Rf values (TLC, methylene chloride) are equal 0.65 and 0.20 for *E*-**1** and *Z*-**1**, respectively.

UV-Vis spectra of both isomers and of their mixtures are shown in Figure 3.

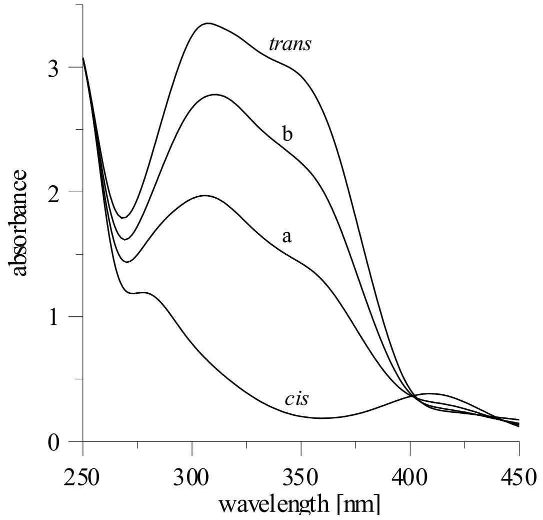


Figure 3. UV-Vis spectra of isomer *cis*, *trans*, mixture of 70% *cis* – 30% *trans* (a), and 30% *cis* – 70% *trans* (b) of **1**.

^{1}H NMR spectra are shown in Figure 4. Typical differentiation of chemical shifts for protons *ortho* to azo group was observed. The shift is 7.72 ppm for isomer *trans*, whereas that for isomer *cis* it is equal 6.67 ppm. Ethylene protons in isomer *trans* are equivalent. For isomer *cis* the ethylene protons are nonequivalent. It is reflected by the presence of two broad peaks around 3.9 and 4.4 ppm at room temperature. At low temperature (–60°C) the peaks narrowed to form two characteristic multiplets of nonequivalent protons.

The influence of alkali metal cations on chemical shifts of azocrown ethers was studied by ^{1}H NMR in acetonitrile. The spectra of 10-membered azocrown ethers were compared with the respective spectra of larger azocrown ethers (13- and 16-membered) for which the stability constants for 1:1 complexes in acetonitrile are known. The respective stability constants are *E*-**3**·LiI logK = 4.0; NaI = 3.69 and *E*-**2**·LiI log K = 4.1 [2]; for *tert*-octyl-**2**·$NaClO_4$ logK = 2.2 [20]. The differences in chemical shifts of selected protons in the presence of an excess of lithium or sodium perchlorates are shown in Table 4.

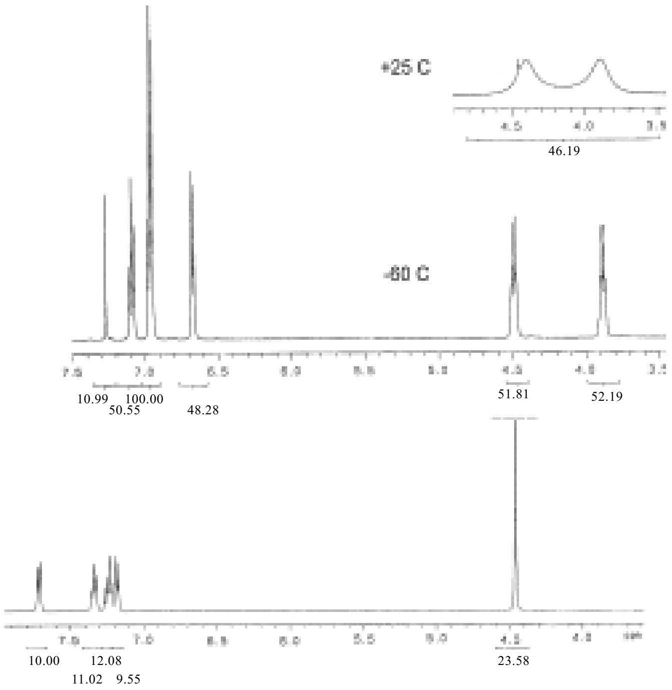
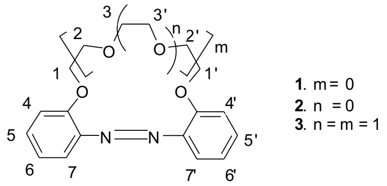


Figure 4. ^{1}H NMR spectra ($CDCl_3$) of isomers of azocrown **1**. Top: *cis*; bottom *trans* form.

Table 4. Effect of lithium and sodium perchlorates on ^{1}H NMR chemical shift of azocrown protons.



Compound	Δδ [ppm]: shift of a proton in the presence of $LiClO_4$ minus shift in free ligand					Δδ [ppm]: shift of a proton in the presence of $NaClO_4$ minus shift in free ligand				
	1,1′	2,2′	3,3′	4,4′	7,7′	1,1′	2,2′	3,3′	4,4′	7,7′
E-**3**	0.11	0.12	0.15	0.11	0.33	0.11	0.11	0.17	0.13	0.40
E-**2**	0.24	0.10	–	0.17	0.27	–0.02	0.01	–	0.03	0.07
E-**1**	–0.13	–	–	–0.03	–0.06	–0.02	–	–	~0	–0.01
Z-**3**	0.04	#	0.02	0.04	~0	0.18	#	0.10; 0.04	0.07	0.07
Z-**2**	–0.04	–0.03	–	–0.03	–0.02	~0	~0	–	~0	~0
Z-**1**	–0.05	–	–	–0.04	–0.03	–0.01	–	–	–0.01	~0

Exact determination of shift was not possible.

Under conditions favoring formation of 1:1 complexes of *trans* isomers with stability constants in the range of 3.7–4.1 [2] a significant downfield proton shifts are observed. In this case the protons *ortho* to azo group are the most deshielded (up to 0.4 ppm). Similar changes are characteristic for complexes of *Z*-**3**, but they are less pronounced. In this case the contribution of azo unit in the stabilization of complexes is poorer. Lithium and sodium cations affect *Z*-**2** and both isomers of **1** to a very low extent and in the opposite direction.

Supplementary data are deposited with the Cambridge Crystallographic Data Centre as a supplementary publication no CCDC 197625 and 197626 (CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; E-mail deposit@ccdc.cam.ac.uk).

Acknowledgments

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