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13-Membered Azo- and Azoxycrown Compounds with Sulfur Atom in Long Side Chain

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A facile way to obtain azo- and azoxycrown ethers with sulfur atom in side chain has been developed. Applicability of these crown ethers in sodium-sensitive membrane electrodes has been studied. Formation of Langmuir-Blodgett monolayers of amphiphilic azocrown ethers on aqueous subphase has been investigated.

Keywords: azo- and azoxycrown ethers, membrane electrodes, Langmuir-Blodgett monolayers

Azo- and azoxycompounds exist in two isomeric forms: *Z* and *E*. Their reversible isomerization could be utilized for molecular switching, for construction of sensors and optical memories. Azocompounds were used as photo or redox active components of films deposited on solid substrates [1].

13-, 16-, 19- and 20-membered crown ethers bearing azo unit in the macrocycle were prepared and studied by Shiga [2]. The synthesis involved alkylation of dihydoxyazobenzene. An alternative synthetic route introduced by us consists in stannite reduction of bis(2-nitrophenoxy)-oxaalkanes [3]. Azo- and azoxycrown ethers are formed simultaneously. High sodium selectivities were found for 13-membered azo- and azoxycrown ethers applied as ionophores in ion-selective membrane electrodes [3].

Both isomers of 13-membered azocrown ethers were obtained and their geometry was established based on X-ray studies of one of them [4a]. *E*-Geometry is characteristic for their solid complexes [5]. The same geometry was found for solid azoxycrown ethers [4b]. Stereochemistry of lipophilic derivatives of 13-membered azocrown ethers in monolayers on aqueous subphases [6,7] or accumulated on a solid material [8,9] was analyzed by surface pressure and surface potential studies or by electrochemical methods [10]. The monolayers interact with salts and undergo isomerization upon illumination.

The monolayers formed on water subphase can be transferred onto various substrates usually gold films on glass slides or thin mercury films on silver electrodes. Such electrodes retain properties of the individual crown ethers. Sulfur atoms in side chain of macrocyclic compounds should increase durability of electrodes modified in this way. The aim of this work was synthesis and preliminary examination of azo- and azoxycrown ethers incorporating sulfur atom.

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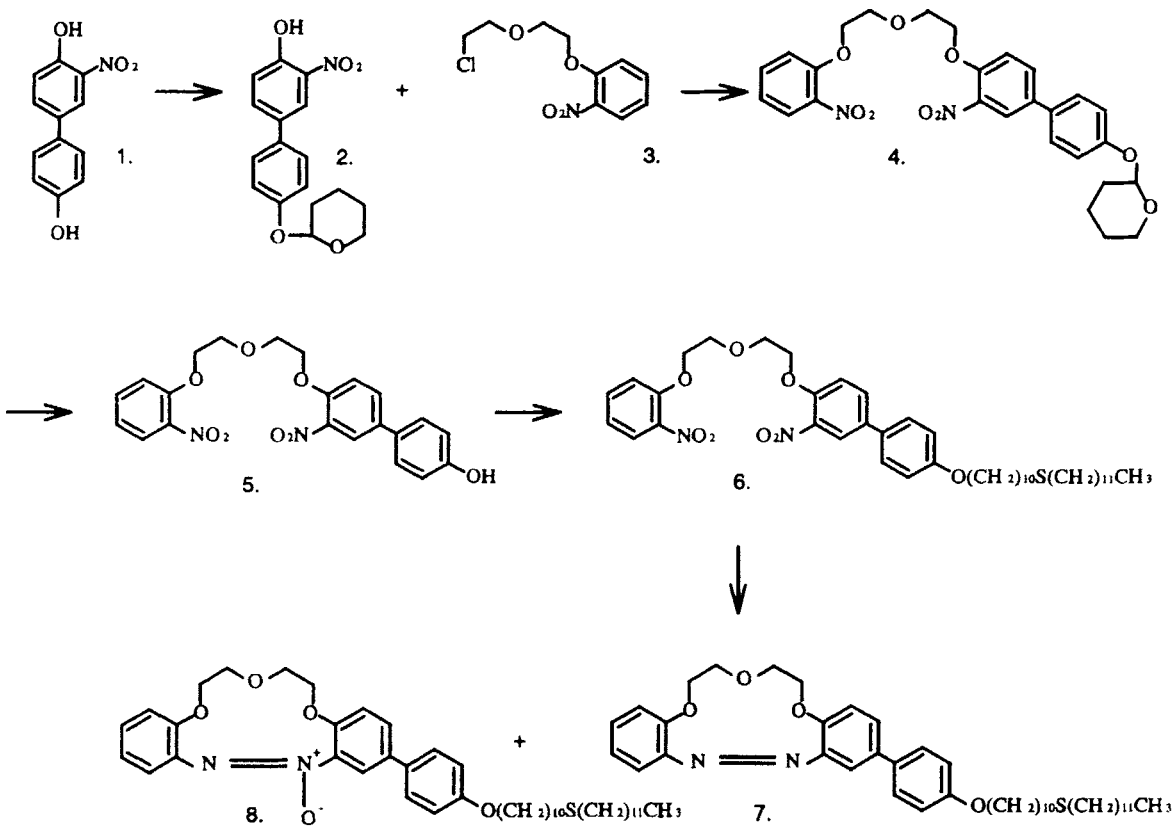

FIGURE 1 Synthesis of azo- and azoxycrown ethers with sulfur atom in side chain

The synthesis of 13-membered azocrown ethers proceeds by the following route (Figure 1): 4,4′-Dihydroxybiphenyl was nitrated with conc. nitric acid in a mixture of chloroform and acetic acid at 0°C to give 4,4′-dihydroxy-3-nitrobiphenyl with 65% yield. The 4′-hydroxy group of the nitro compound **1** was selectively protected with 3,4-dihydro-2*H*-pyran and the monoether **2** was alkylated with 1-chloro-5-nitrophenoxy-3-oxapentane **3** to give compound **4**. After deprotection the product **5** was condensed with 1-chloro-11-thiatricosane in dry boiling dimethylformamide in the presence of anhydrous potassium carbonate to form the desired derivative **6**. The last compound was in turn reduced in a two phase system with sodium stannite to produce macrocyclic 13-membered azo- and azoxycrown ethers **7** and **8** with overall 30% yield.

Compound **7** ^{1}H NMR 200 MHz δ($CDCl_3$): 0.90, t, (J = 6.84 Hz), 3H; 1.28 – 152, m, 30H; 1.56 – 1.63, m, 4H; 1.79 – 1.83, m, 2H; 2.52, t, (J = 7.04 Hz), 4H; 3.94 – 4.05, m, 6H; 4.31, q, (J = 5.10 Hz), 4H; 6.99, dd, (J_1 = 1.99 Hz, J_2 = 8.79 Hz), 2H; 7.12 – 7.22, m, 3H; 7.34 – 7.39, m, 1H; 7.58, dd, (J_1 = 2.04 Hz, J_2 = 8.8 4Hz), 3H; 7.82, dd, (J_1 = 1.84 Hz, J_2 = 7.86 Hz), 1H; 7.99, d, (J = 2.36 Hz); MS calcd. for $C_{44}H_{64}N_2O_4S$ 717,1; LSIMS(+) (M+Na) 739.5; (M+H) 717.

Compound **8** ^{1}H NMR 200 MHz δ($CDCl_3$): 0.90, t, (J = 6.80 Hz), 3H; 1.28 – 1.33 m, 30H; 1.52 – 1.63, m, 4H; 1.78 – 1.86, m, 2H; 2.52, t, (J = 7.12 Hz), 4H; 3.95–4.04, m, 6H; 4.25 – 4.33, m, 4H; 6.95 – 7.00, m, 2H; 7.08 – 7.16, m, 3H; 7.40 – 7.47, m,

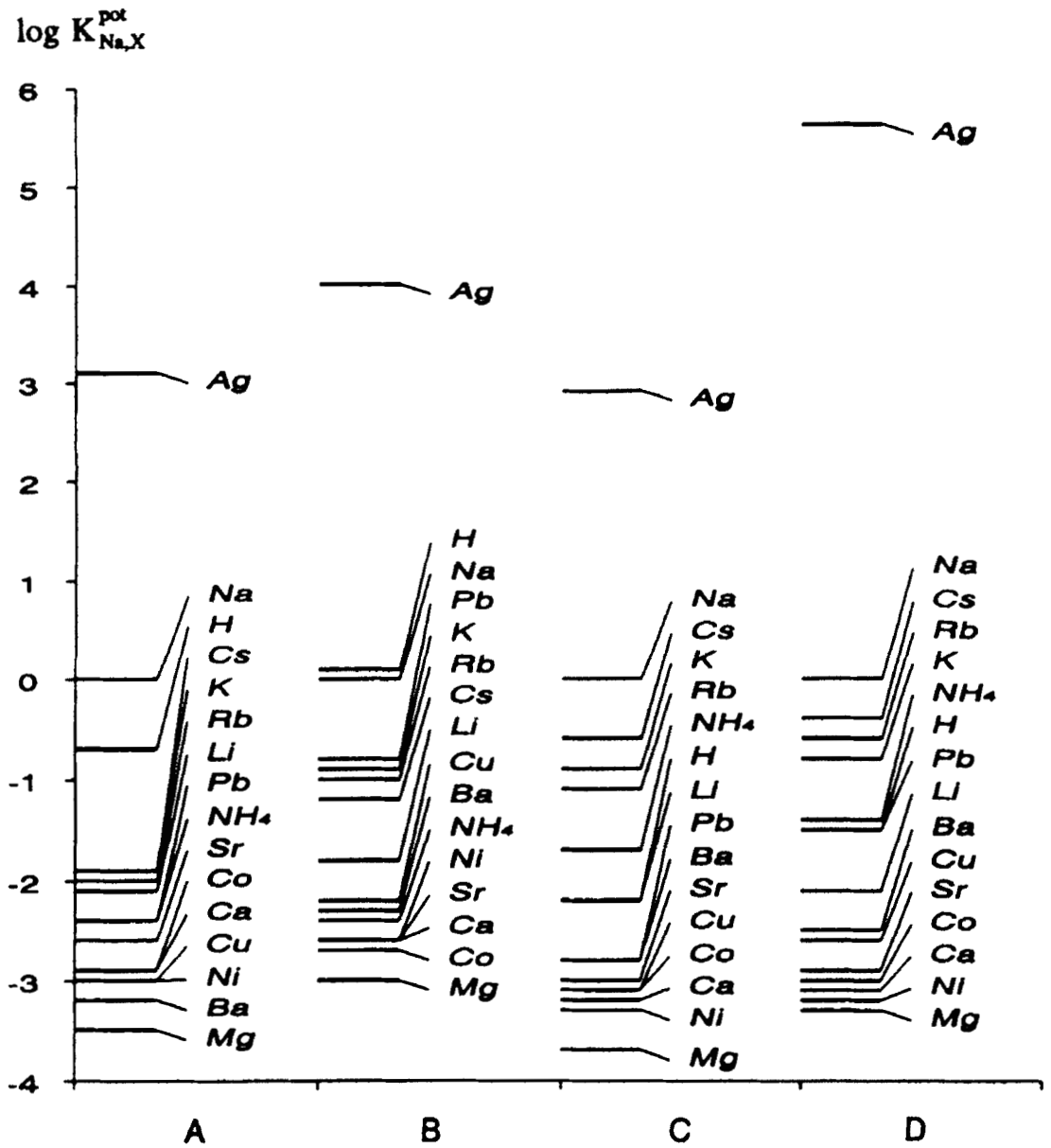

FIGURE 2 Sodium selectivities of membrane electrodes based on 13-membered azo- and azoxycrown ethers: **(A)** 13-membered phenylazocrown ether, **(B)** compound **7**; **(C)** 13-membered phenyloxycrown ether, **(D)** compound **8**

1H; 7.48 – 7.55, m, 2H; 7.58 – 7.63, m, 1H; 7.58 – 7.63, m, 1H; 7.73, dt, (J_1 = 1,46 Hz, J_2 = 7.98 Hz), 1H; 7.89, t (J = 2.36 Hz) 1H. MS calcd. for $C_{44}H_{64}N_2O_5S$ 733.1 LSIMS(+) (M+Na) 755.5; (M+H) 733.

Properties of membrane electrodes were determined by standard SSM procedure. Figure 2 shows diagram of log $k_{Na/X}{}^{pot}$ values of ion-selective membrane electrodes. The electrode contain: **(B)** compound **7**; **(D)** compound **8**;

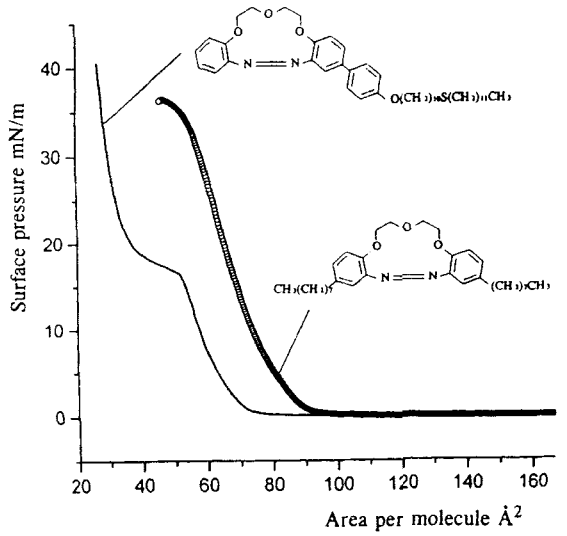

FIGURE 3 Isotherm of azocrown 7 compared to isotherm of di-*n*-octylazocrown ether

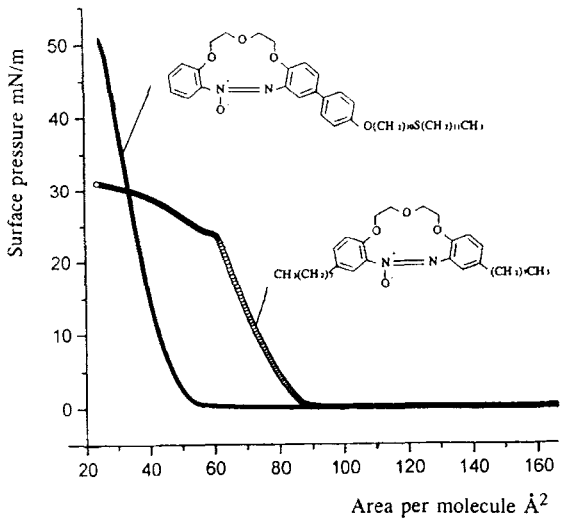

FIGURE 4 Isotherm of azoxycrown 8 compared to isotherm of di-*n*-octylazoxycrown ether

for comparison are shown data for electrode containing 13-membered phenylazocrown ether (**A**) and doped with 13-membered phenyloxy-crown ether (**C**).

Properties of Langmuir-Blodgett monolayers of amphiphilic azo and azxycrown ethers are shown in Figure 3 and 4. Figure 3 presents isotherm of azocompound 7 as compared to isotherm of di-*n*-octylazocrown ether. Figure 4 shows isotherms of analogous azoxyderivatives.

CONCLUSIONS

The procedure presented is a convenient way to obtain crown ethers bearing the azo or azoxy group in the macrocyle and sulfur atom in side chain. Lipophilic azo- and azoxycrown ethers 7and 8 applied in ion-selective membrane electrodes are sodium selective. Compounds 7 and 8 were found to form stable monolayer films on water-air interface.

Acknowledgements

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