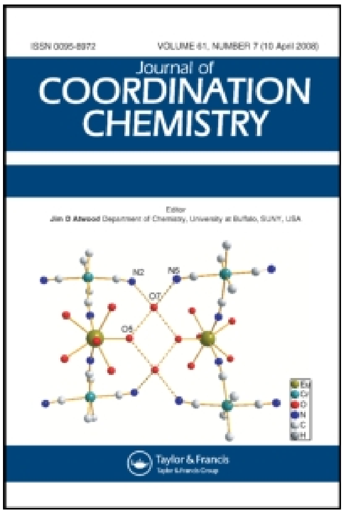

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Jan F. Biernat[a]; Elzbieta Luboch[a]; Andrzej Cygan[a]
[a] Faculty of Chemistry, Technical University of Gdańsk, Gdańsk, Poland

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NEW MACROCYCLES CONTAINING THE AZOXY SUBUNIT AND THEIR PROPERTIES

JAN F. BIERNAT,* ELŻBIETA LUBOCH and ANDRZEJ CYGAN

Faculty of Chemistry, Technical University of Gdańsk, 80–952 Gdańsk, Poland

A new macroring closure reaction leading to crown-like macrocycles containing the azoxy group as a new macroring subunit has been introduced. The possibility of complex formation with cations has been examined by studying these compounds in membrane ion-selective electrodes.

Keywords: Synthesis, macroring, azoxy group, crown ethers, ion-selective electrodes

The complexation ability of crowns may be modified, first of all, by changing the type of electron donating group in the macroring. The list of electron donating groups forming parts of a macroring in crown ethers includes, in addition to groups containing oxygen atoms, mainly groups with nitrogen, sulphur or phosphorus atoms.[1] The nitrogen atoms are found in the macroring, for example, in the form of amino,[2] amide,[3] sulphonamide,[4] urethane,[5] oxime,[6] azo,[7] pyridine,[8] pyridine N-oxide[9] or pyrimidine[10] subunits. Now we would like to add an azoxy subunit as part of a macroring. Compounds incorporating this residue were obtained as shown in Figure 1. Their properties are given in Table I. Strongly alkaline conditions are favourable for termination of the reduction on higher oxidation states of nitrogen thus preferring accumulation of the azoxy compound in the reaction mixture. As reducing reagent usually methanol is used. Unfortunately in our case in the presence of methanol a base catalysed nucleophilic substitution of the oxyalkyl residue takes place and azoxyanisole was isolated as the main product in very high yield. It is formed independently of the length of the oxyethylene chain joining both *o*-nitrophenyl residues of the substrate. Thus the use of alkali metal stannites as reducing reagents[11] seems to be a good option as the reaction is to be run under rather mild conditions; therefore the above mentioned side reaction is strongly reduced. Acetone was used as solvent increasing the solubility of the starting material in an organic-aqueous solvent mixture. The role of acetone is uncertain. Apart from increasing the solubility of the substrate it probably is also engaged in the chemical process. When acetone is replaced by *e.g.* dioxane, which also increases the solubility, the reduction does not proceed.

The above reaction presents a new method of macroring closure consisting of nitrogen to nitrogen double bond formation.

A unique feature of the above described synthetic procedure is associated with the possibility of formation of an azoxy group with *cis* orientation of phenyl substituents. The *trans* azoxy group was previously used to link two crown ether moieties with the formation of a biscrown ether.[12]

The macrocyclic compounds are rather difficult to isolate because they have similar properties to the starting material and because polymeric substances are formed during this reaction. The best results were obtained when the crude products were chromatographed two times on a column with Silicagel LSL_{254} 5/40μ with gypsum

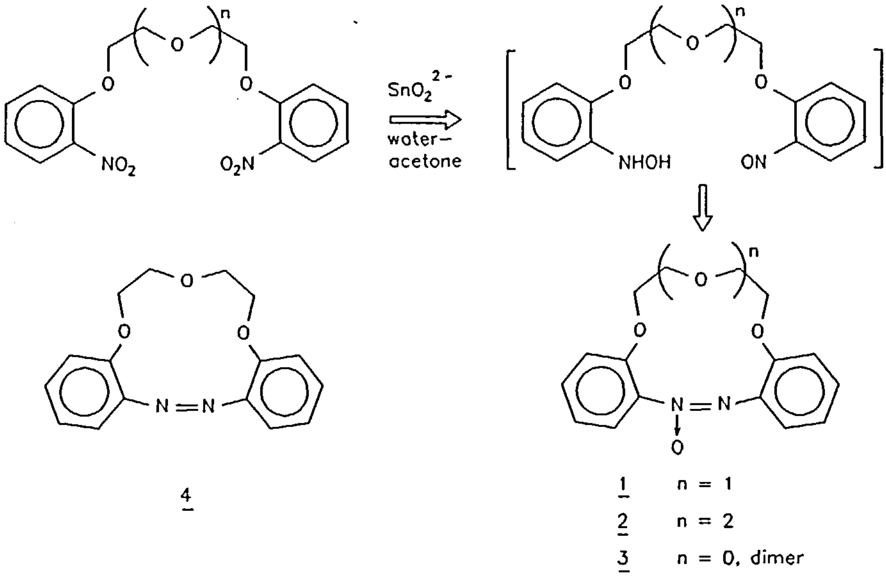

FIGURE 1 Compounds synthesized in this study.

TABLE I
Properties of azoxy and azo compounds.

Compounds	Ring size	M.p [°C]	Yield [%]	M/z	Electrode properties $\log k^{pot}_{Na,K}$	Electrode properties $\log L_D$
1	13	114–16	22	300	−1.2	−3.8 (Na^+)
2	16	122–4	15	344	1	−5.0 (K^+)
3	20 dimeric	180–2	5	512	1.8	−4.2 (K^+)
4	13	65–7	—	284	−1.7	−4.6 (Na^+)

for thin layer chromatography (Chemapol, Czechoslovakia). Carbon tetrachloride or *n*-butyl acetate were used for final crystallization.

The 1,2-bis-*o*-nitrophenoxyethane reacts to form dimeric bisazoxy compound **3** with an unknown configuration of the azoxy residues.

The azoxy compounds were identified by elemental analysis and by spectroscopic methods. ^1H NMR spectra confirm the structures. Mass spectra unequivocally showed the parent peaks (P) and the P-16 peaks. The 78, 91, 106, 120, 134 and 214 peaks also confirm the structures.

The synthesis of azoxy compounds is always accompanied by formation of the respective azo compounds. They are more soluble in organic solvents of low polarity (*e.g.* heptane) and may be isolated by extraction of the evaporated mother liquors obtained during crystallization of the respective azoxy compounds. Azo compound **4** was isolated and characterized. It possesses a *cis* configuration of the -N=N- residue.[13]

The complex formation of the reported compounds with cations was examined by using them as electroactive substances in ion selective membrane electrodes. The alkali and alkaline earth cations as well as some transition metal cations were examined. Compound **2** is potassium sensitive in membrane electrodes while compound **1** is sensitive towards sodium cations however their solubility in water is high. On the other hand azo compound **4** exhibits very good properties as an electroactive substance in membrane electrodes. It is sensitive towards sodium cations and the selectivity over potassium is high. The selectivity coefficient $\log K^{\mathrm{pot}}_{\mathrm{Na,K}}$ is equal to -1.7.

A typical synthetic procedure: To a mixture of 3.48 g (10 mmole) of 1,5-bis-*o*-nitrophenoxy-3-oxa-pentane, 8 g (200 mmole) of sodium hydroxide, 30 ml of water and 20 ml of acetone 6.2 g (32.7 mmole) of anhydrous stannous chloride was added. The mixture was stirred vigorously and refluxed for 1.5 hour. The mixture was then extracted with toluene (40 ml) and the organic layer was washed with water. The extract was evaporated to dryness under reduced pressure (3.5 g), dissolved in methylene chloride and passed through a short column with silica gel. The effluent was evaporated (2.1 g) and rechromatographed. The first methylene chloride fraction contained 0.4 g of the yellowish substrate; the desired product was eluted with the next portion of methylene chloride and finally with chloroform. The combined fractions were evaporated and the residue was crystallized from *n*-butyl acetate. Yield of compound **1**: 670 mg.

To summarize:

- a new reaction leading to macrocycles has been introduced
- the azoxy group is a new macroring subunit in crown ethers
- the macrocyclic azo compound **4** is interesting as an ion-carrier for sodium ion-selective membrane electrodes.

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