EFFECT OF A CATECHOL SEGMENT IN A POLYETHER CHAIN ON THE COMPLEXING ABILITY OF SOME PHOSPHONATE AND QUINOLINE MONOPODANDS

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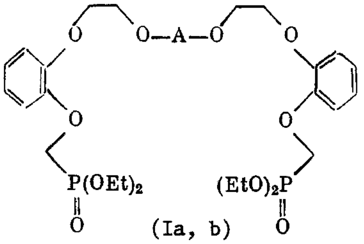
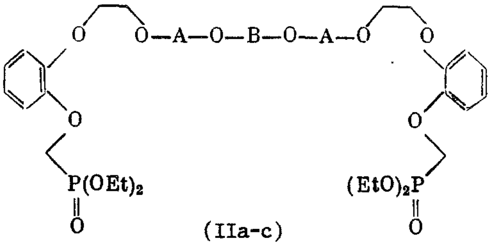
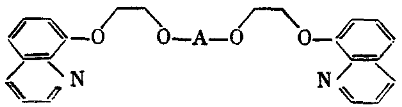
The complexing ability of monopodands with o-diethoxyphosphinylmethoxyphenyl and 8-quinoline end groups, containing both ethylene glycol and catechol units in the polyether chain, was studied by conductimetry in tetrahydrofuran—$CHCl_3$. Replacement of ethylene glycol by catechol changes the efficiency insignificantly, but in a number of cases leads to some increase in K/Li and K/Na selectivity of phosphonate podands, and the K/Li and Na/Li selectivity of quinoline podands.

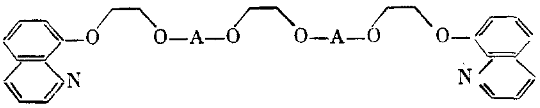
The factors that determine the selectivity of crown ethers and their analogs (the podands) can include rigidity of complexing molecule, type and basicity of donor atoms, and the distance between those atoms in the conformation that is favorable for cation binding. The most common structural units in the polyether chain of crown ethers and podands are ethylene glycol and catechol residues; but the relative effect of those segments on ligand properties has been insufficiently studied. For example, in the crown ether series, with rare exceptions [2] the stability constants [1] of the complexes of ethylene glycol and catechol type ligands can be compared only by comparing the results obtained by different authors. In this connection the ionophoric and complexing properties of the diamides of the polyethers of dicarboxylic acids (e.g., [3]) have been studied in more detail. The features of the change in podand properties of this type have been formulated [4, 5]; these features are related to the varying basicity and conformational structure of the polyether chain. For a series of neutral podands containing phosphorus [6] the effects of catechol and ethylene glycol units on the stability of complexes with alkali metals are illustrated only by isolated examples.

The purpose of the present work was to study the effect of catechol segments in the polyether chain on the efficiency and selectivity of two classes of podands, viz., compounds (I), (II), and (III), (IV), containing terminal o-diethoxyphosphinylmethoxyphenyl and 8-quinoline groups:


(Ia, b)


(IIa-c)


(IIIa, b)


(IVa, b)

A = CH_2CH_2 (Ia), (IIIa), (IVa), o-C_6H_4 (Ib), (IIIb), (IVb); A = B = CH_2CH_2 (IIa), A = CH_2CH_2, B = o-C_6H_4 (IIb), A = o-C_6H_4, B = CH_2CH_2 (IIc).

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In each group ligands with the same number of donor centers are distinguished from one another only by the structure of the polyether chain. The complexing ability of compounds (I)-(IV) was estimated from the stability constants of the M^+L complexes which are determined by conductimetry.

EXPERIMENTAL

Synthesis of ligands (I) and (IIa, b) has been described in [7]. ^1H and ^{31}P NMR spectra were recorded with a Bruker CXP-200 Fourier spectrometer; internal standard was TMS and external standard was 85% H_3PO_4. Melting points were taken with a Boetius RNMK apparatus. For column chromatography we used silica gel L, 100-250 μ. Reactions were carried out in a dry Ar atmosphere. Yields, constants, PMR spectroscopic data, and analytical data of compounds (III) and (IV) are shown in Table 1. Tri- and pentaethylene glycol ditosylates [8], bis(2-hydroxyethyl) ether of catechol [9] and 1,2-bis[2-(2-hydroxyethoxy)phenoxy]ethane [10] were obtained by published methods. Conductimetric measurements were carried out [11] with alkali 2,4-dinitrophenolates in THF—$CHCl_3$ (4:1 by volume). The random error in the determination of log stability constant (log β) of 1:1 complexes did not exceed ±0.1.

1,2-Bis<2-{2-[2-(diethoxyphosphinylmethoxy)phenoxy]ethoxy}phenoxy>ethane (IIc). A mixture of 2.7 g of 1,2-bis[2-<2-{2-[hydroxy(ethoxy)phosphinylmethoxy]phenoxy}ethoxy>phenoxy]ethane [12] and 10 ml of ortho-formic ester was boiled for 2 h, with removal of alcohol and ethyl formate. After cooling, the solution was evaporated and the residue was chromatographed (eluent 3:1 C_6H_6—acetone). There was obtained 1.9 g (66%) of (IIc), mp 53-55°C (ether). PMR spectrum ($CDCl_3$, δ, ppm): 1.28 t (12H, CH_3), 4.18 quintet (8H, $POCH_2$), 4.32 m (16H, PCH_2 and OCH_2CH_2), 6.93 m (16H, C_6H_4). ^{31}P NMR spectrum ($CDCl_3$, δ, ppm): 19.86. Found: C, 52.6; H, 7.1; P, 9.5%. $C_{28}H_{44}O_{12}P_2$. Calculated: C, 53.0; H, 7.0; P, 9.8%.

1,8-Bis(8-quinolyloxy)-3,6-dioxaoctane (IIIa), 1,2-bis[2-(8-quinolyloxy)ethoxy]benzene (IIIb), 1,14-bis(8-quinolyloxy)-3,6,9,12-tetraoxatetradecane (IVa), 1,2-bis{2-[2-(8-quinolyloxy)ethoxy]phenoxy}ethane (IVb). A mixture of 15 mmoles of anhydrous Cs_2CO_3, 15 mmoles of 8-hydroxyquinoline, and 7 mmoles of the respective diol ditosylate in 30 ml of anhydrous THF was boiled for 3 h with stirring. After cooling, the precipitate was filtered off and the filtrate was evaporated in vacuum. The residue was dissolved in 30 ml of $CHCl_3$ and the solution was washed with water (2 × 50 ml), dried with Na_2SO_4, and evaporated in vacuo. Chromatography of the residue gave (IIIa) (20:1 $CHCl_3$—i-PrOH), (IIIb) ($CHCl_3$), (IVa) (1:2 C_6H_6—acetone), and (IVb) ($CHCl_3$).

RESULTS AND DISCUSSION

The logarithms of the stability constants (log β) of complexes (I)-(IV) with alkali metal and the ratios β(Na)/β(Li), β(K)/β(Li), and β(K)/β(Na) that characterize ligand selectivity are shown in Table 2. For comparison we also show log β and selectivity for 18-crown-6- and dibenzo-18-crown-6 which we obtained previously under the same conditions [11].

For the crown ether shown in Table 2 the differences in log β for the same cation when ethylene glycol units are replaced by catechol units, reach nearly an order of magnitude (in the case of Li^+). However, podands (I)-(IV) with the same structural modification show a less significant change in complexing properties. Thus, for the phosphonate podands (Ia, b) and (IIa-c) the analogous difference in log β lies between −0.2 and +0.5 and is usually 0.2-0.3. Li and Na are most sensitive to changes in phosphonate podand structure. As a result of the overall lowering of log β of these metals, the K/Li and K/Na selectivity ratios increase for compounds (Ib) and (IIc). But this relation does not apply to the decadentate podand (IIb), which contains one catechol unit in the polyether chain; it is characterized by the most stable complex with Li^+ among compounds (IIa-c).

With changing structure of the polyether chain the stability of the quinoline podands (III) and (IV) does not decrease so sharply as with the crown ethers, but the decrease is different from that with the phosphonate ligands (I) and (II). As with compounds (I) and (II), log β decreases for Li^+, but when catechol units are introduced into the polyether chain the K/Na selectivity of ligands (III) and (IV) is practically unchanged; on the other hand their Na/Li selectivity ratio increases. A similar relation is typical of the crown ethers that we studied.

TABLE 1. Yields, Constants, PMR Spectra, and Analytical Data for Podands (III) and (IV)

Compound	Yield,* %	Mp, °C (solvent for recrystallization)	PMR spectrum ($CDCl_3$, δ, ppm)**			Found, %			Empirical formula	Calculated, %		
			CH_2	C_6H_4, m	C_9H_6N	C	H	N		C	H	N
(IIIa)	70	100–102 (ether)	3,77 s (4H), 3,97 m (4H), 4,33 (4H)	—	7,16 m (2H), 7,44 m (6H), 8,23 d.d (2H), 8,85 m (2H)	70,9	6,1	6,9	$C_{24}H_{24}N_2O_4$	71,3	6,0	6,9
(IIIb)	80	152,5–153.5 (dioxane)	4,58 s (8H)	6,97 (4H)	7,12 d.d (2H), 7,37 m (6H), 8,09 d.d (2H), 8,92 d.d (2H)	74,0	5,4	5,9	$C_{28}H_{24}N_2O_4$	74,3	5,4	6,2
(IVa)	84	oil	2,64 s (4H), 2,67 m (4H), 2,75 m (4H), 3,05 t (4H), 3,42 t (4H)	—	7,12 d.d (2H), 7,40 m (6H), 8,10 d.d(2H), 8,94 d.d(2H)	67,9	6,7	6,0	$C_{28}H_{32}N_2O_6$	68,3	6,6	5,7
(IVb)	85	140–141 (dioxane)	4,35 s (4H), 4,54 m (8H)	6,92 (8H)	7,14 d.d (2H), 7,37 m (6H), 8,10 d.d (2H), 8,91 d.d (2H)	73,2	5,9	4,8	$C_{36}H_{32}N_2O_6$	73,5	5,5	4,8

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*After column chromatography.

**For (IIIa), acetone-d_6.

TABLE 2. Logarithm of Stability Constant, log β, of M+L Complexes of Alkali Metals with Podands (I)-(IV) and Crown Ethers, and Selectivity Factors of Complexation in 4:1 THF—$CHCl_3$ at 25°C

Ligand	Cation					$\frac{\beta(Na)}{\beta(Li)}$	$\frac{\beta(K)}{\beta(Li)}$	$\frac{\beta(K)}{\beta(Na)}$
	Li	Na	K	Rb	Cs			
(Ia) [13]	4,0	4.9	5,1	4.9	4,2	7,9	12,6	1,6
(Ib)	3.7	4.4	4.9	4.7	4,2	5,0	15,9	3,2
(IIa) [13]	3.7	4,7	5.1	5,3	4,8	10,0	25,0	2,5
(IIb)	3.9	4.5	5.0	5.0	4,7	4.0	12.6	3,2
(IIc)	3,6	4,5	5,2	5,3	4,8	7,9	40,0	5,0
(IIIa)	4,9	5,8	5,2	4,7	4,2	7,9	2,0	0,2
(IIIb)	4,4	5,5	5,0	4,6	3,9	12,6	4,0	0,3
(IVa)	4,4	5,8	5,9	5,6	4,9	25,0	31,6	1,3
(IVb)	4,1	5,8	5,8	5,4	4,9	50,0	50,0	1,0
18-Crown-6 [11]	5,5	6.5	5,5	4,9	4,5	10,0	1,0	0,1
Dibenzo-18-crown-6 [11]	4,6	6,0	5.0	4,6	4,4	25,0	2,5	0,1

In efficiency of reaction with K^+, Rb^+, and Cs^+, both the decadentate phosphonate (II) and the octadentate quinoline podands (IV) are comparable to or exceed 18-crown-6 and dibenzo-18-crown-6; in this case the K/Li selectivity ratio is substantially greater than for the macrocyclic complex formers. The quinoline podands (IVa, b) also show high Na/Li selectivity; for compound (IVb) which contains two catechol units the ratio of β(Na) to β(Li) reaches 50.0.

The main reason for the increase in K/Li selectivity both for crown ethers and for podands (I)-(IV) is apparently the decrease in basicity of the ether oxygens. At the same time the structure of the end groups in the acyclic ligands (I), (II), and (III), (IV) is responsible for the different changes in their Na/Li and K/Na selectivities when ethylene glycol units are replaced by catechol units in the polyether chain.

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