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MOLECULAR MODELLING OF ORGANOPHOSPHORUS PODANDS AND THEIR COMPLEXES WITH ALKALI METAL CATIONS

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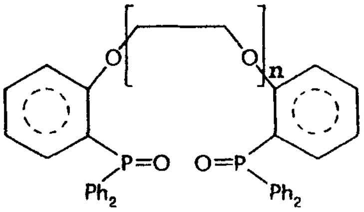
A molecular mechanics study on some organophosphorus podands, with both rigid and flexible terminal groups, and on their complexes with Li^+ and Na^+ was carried out. Na^+ causes smaller deformations of the ligands than Li^+, but its complexes are less stable, as the interaction energy with the podands is weaker. The ligands with rigid terminal groups are, in general, more pre-organized for complex formation. The cation–ligand interaction energies, including also the changes in steric energies, are always higher in complexes of flexible molecules than in those containing rigid ligands. The lower entropy losses which accompany the formation of complexes of rigid molecules with alkali metal cations probably account for the observed higher stabilities of the complexes

INTRODUCTION

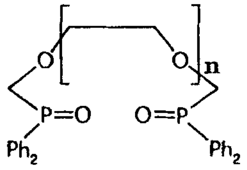
Macrocyclic polyethers are unique agents which are able to bind alkali metal cations selectively.[1] Recently, much attention has been devoted to open-chain analogues of macrocyclic compounds.[2,3] These molecules, on the one hand, are more readily available than crown ethers and, on the other, in a number of cases they possess complexation abilities similar to those of macrocycles.

Numerous investigations of podands have shown that their complexation properties are highly dependent both on the length of the polyether chain and on the character of the terminal groups. Recently, some new monopodands containing phosphoryl terminal groups have been synthesized by Tsvetkov *et al.*[4] They found that in the mixed solvent tetrahydrofuran–chloroform (4 : 1) some of these molecules possess a high complexation ability with respect to Li^+ and Na^+ cations and, as a rule, complexes of podands with rigid terminal groups have higher stabilities than those of more flexible molecules. They suggested that the stability of these complexes could be accounted for by specific features of the cation coordination polyhedra, tetrahedra or octahedra corresponding to the most stable complexes.

In order to test such a hypothesis, in this paper we consider modelling, by molecular mechanics, of some organophosphorus molecules both with rigid (**Ia–c**) and flexible (**IIa–c**) terminal groups. The complexation properties of these molecules with regard to alkali cations have been thoroughly investigated by other workers.[4–6]



n = 1(Ia) ; 2(Ib) ; 3(Ic)



n = 1(IIa) ; 2(IIb) ; 3(IIc)

Scheme

Few theoretical studies have been previously performed on polydentate organophosphorus molecules. Dashevsky *et al.*[7] carried out conformational analyses

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on a number of bidentate molecules in which two $(Ph)_2PO$ fragments are connected by methylene, ethylene or vinylene bridges. An attempt was made to use the 'fine' functions method to explain the complexation properties of the lariat ligand on the basis of a tetraazomacrocycle containing four diphenylphosphorus fragments.[8] The influence of the cation on the ligand conformational state was either indirectly considered within the 'fine' functions method or neglected. For these reasons, detailed information concerning the structures and the energetics of the complexes was not obtained.

METHOD

Conformational calculations on the free molecules and on their complexes with Li^+ and Na^+ were performed using the MM2I program package,[9,10] which includes the Allinger force field[11] for the intramolecular interactions and a modified[12] force field for the ion–molecule or the intermolecular interactions. According to Caillet and Claverie,[12] the intermolecular interaction energy (E_i) can be written as a sum of electrostatic (E_{es}), polarization (E_{pol}) and van der Waals (E_{vdw}) terms:

$$E_i = E_{es} + E_{pol} + E_{vdw} \qquad (1)$$

The electrostatic term is calculated in the point-charge approximation, the atomic charges Q_i being determined in such a way as to reproduce the molecular electrostatic potential distribution outside the van der Waals spheres of atoms (PD charges[13]). The polarization term is computed[12] using experimental data on bond polarizabilities.[14] The van der Waals interaction energy is calculated by the equation

$$E_{vdw} = \Sigma_i \Sigma_j k_{ij} \left(1 - \frac{Q_i}{N_i}\right)\left(1 - \frac{Q_j}{N_j}\right) B_0 \exp(-\alpha Z_{ij}) \qquad (2)$$

Z_{ij} being the scaled interatomic distance, N_i the number of valence electrons of the atom i and B_0 and α being taken from Ref. 9. The k_{ij} parameters were fitted to reproduce the structural and energy characteristics of model compounds.

The possibility of modelling complicated systems, including several interacting partners (ligand, cation, anion, some solvent molecules), is a specific feature of this approach, which takes into account non-additivity effects. Computations of the geometry and energy characteristics of crown ethers, of their complexes with alkali metal cations and of ion pairs[15] confirmed the reliability of the force field combination employed.

PD charges, obtained by the least-squares method, reproduce the molecular electrostatic potential on Connolly surfaces,[16] computed by the MNDO method using the MOPAC-5 package.[17] The charges were multiplied by the factor 1·42, which scales MNDO PD charges to the *ab initio* (6–31G*) values.[18]

A direct calculation of the PD charges of the molecules studied is inappropriate, because of the close dependence of the Q_i values on the molecular geometry, a result also noted by others.[19] According to Grootenhuis and Kollman,[20] we used by-fragment calculations with further averaging of Q_i. PD charges for the terminal groups of molecules **I** and **II** are shown in Figure 1. The averaged values for the atoms of polyether chains $C_2H_5O—(C_2H_4—O—)_n—C_2H_5$ (n = 1–3) were in −0·6 (O), 0·3 (C) and 0·0 (H).

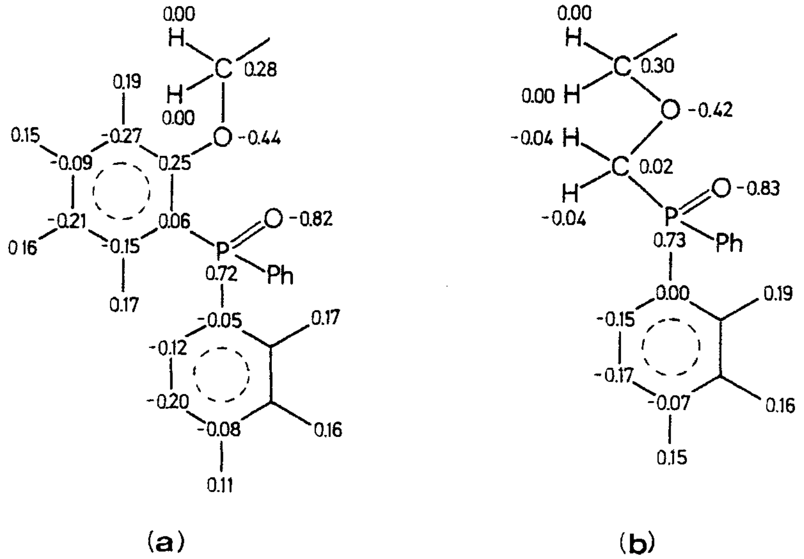

Figure 1. Pd atomic charges of terminal groups of molecules (a) **I** and (b) **II**

Table 1. Equilibrium distances (R_0, Å) and interaction energies (E_i, kcal mol^{-1}) in $H_3PO\cdots M^+$ systems ($M^+ = Li^+, Na^+$)

Method	R_0		$-E_i$	
	Li^+	Na^+	Li^+	Na^+
molecular mechanics (MM2I)	1·749	2·110	57·02	42·34
Ab initio (4–31G*)	1·749	2·107	56·40	40·90

The parameters for the van der Waals potentials, involving Li^+ and Na^+ interactions with C, H and O, were taken from Ref. 12. To obtain such parameters for the interactions of Li^+ and Na^+ with compounds including P=O bonds, we performed *ab initio* calculations on $H_3PO\cdots M^+$ ($M^+ = Li^+, Na^+$) with the 4–31G* basis set using the GAUSSIAN-88 program.[21] In the first series of calculations, we optimized all geometry parameters, whereas in the second we fixed the cation on the P=O bond line at 10 Å from the oxygen atom. The cation–oxygen equilibrium distances and the cation–H_3PO interaction energies, reported in Table 1, show that the fitted force field parameters reproduce reliably structural and energetic characteristics of the model compounds.

Previously unknown parameters of the Allinger force field, corresponding to intramolecular interactions in molecules **I** and **II**, were determined in such a way as to reproduce the geometry of the terminal groups of these molecules obtained from MNDO calculations with full optimization.

STRUCTURAL CHARACTERISTICS OF PODANDS AND THEIR COMPLEXES

The choice of the starting conformation in molecular-mechanical computations of molecules such as podands **Ia–c** and **IIa–c** presents considerable difficulties, because there is an exceedingly large number of possible conformers corresponding to various sequences of the torsion angles of the polyether chains. At the same time, one might assume that only a specific conformation ('pseudo-cavity' conformation) for each molecule allows the most effective contacts of the cation with all donor atoms of the ligand. In simulating pseudo-cavities of molecules **I** and **II**, we assumed that the starting conformation had to meet the requirements that oxygen lone pairs should be oriented inside the pseudocavity and that the torsion angles of the polyether chain should not differ too much from their 'ideal' values (180° for C—O and ± 60° for C—C bonds[22]).

To describe the conformations of the free molecules **I** and **II** and of their metal complexes, it is convenient to use the Klyne and Prelog[23] classification of the torsion angles:

Torsion angle (°)	Conformation
0 ± 30	∓ synperiplanar (∓ *sp*)
60 ± 30	+ synclinal (+ *sc*)
120 ± 30	+ anticlinal (+ *ac*)
180 ± 30	∓ antiperiplanar (∓ *ap*)
− 120 ± 30	− anticlinal (− *ac*)
− 60 ± 30	− synclinal (− *sc*)

According to this classification, the sequence of torsion angles ('conformational formula') provides a sufficiently good description of the conformational state of a molecule.

The structural features of molecules **I** and **II** and of their complexes are discussed in more detail in the following sections.

MOLECULES **Ia–c** AND THEIR COMPLEXES

n = 1

The sequence of the torsion angles of the polyether chain (starting with C_bO_aCC[*]) is the same both in the free molecule **Ia** and in its complexes. The interaction with the cation increases considerably the planarity of the pseudo-cavity oxygens framework; thus, the torsion angle $O_{ph1}O_{a1}O_{a2}O_{ph2}$ is 7·5° in the Li^+ complex and 8·6° in the Na^+ complex, whereas it is 36·1° in the free molecule. The cation coordination polyhedron may be regarded as a distorted square (Figure 2). The pseudo-cavity size is 2·80 Å both in the Li^+ and Na^+ complexes. The shift out of the oxygens plane is 0·4 Å for Li^+ and 1·1 Å for Na^+.

The macrocyclic ligand 12-crown-4 may be considered as an analogue of this molecule. Its cavity size is 3·7–3·9 Å and the cation shift out of the oxygens plane in the complex with LiNCS is 0·87 Å and it is as large as 1·53 Å in the complex $(12\text{-crown-}4)_2\cdot NaClO_4$[24].

Stacking of phenyl groups is not observed in either the free molecule or its complexes. The oxygen lone pairs are oriented inside the pseudo-cavity in both cases.

n = 2

The conformational formulae reported in Table 2 show that in the Li^+ complex the ligand undergoes considerable conformational changes (larger than in the Na^+

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[*] The following abbreviations are used: C_b = benzene carbon; O_{ph} = phosphoryl oxygen; O_e = ether oxygen; O_a = aryl oxygen (for molecules **I**); O_t = terminal oxygen (for molecules **II**).

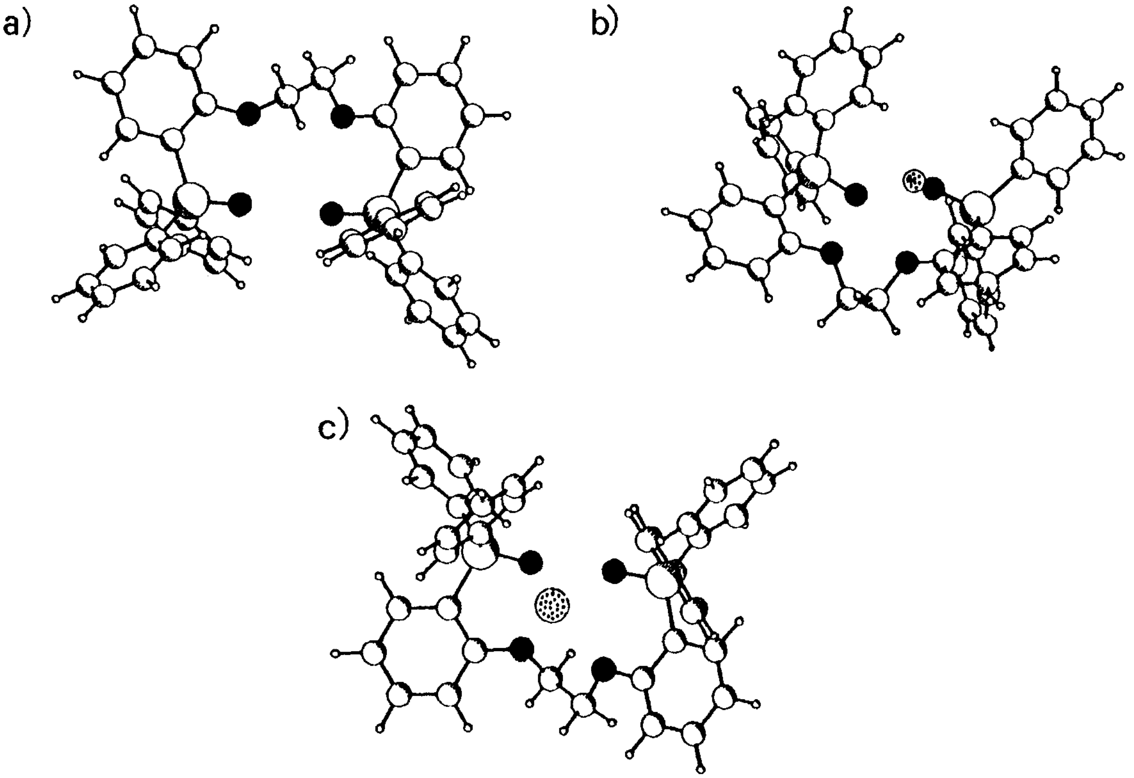

Figure 2. Structure of (a) of free molecule **Ia** and its complexes with (b) Li^+ and (c) Na^+. Black spheres, oxygens; dotted spheres, cation

Table 2. Sequence of torsion angles[a] in polyether chains of the molecules **Ia–c** and **IIa–c** and their complexes with Li^+ and Na^+

Molecule	Conformational formula												
Ia	−*ap*	−*sc*	−*ac*										
Ia·Li^+	−*ap*	−*sc*	−*ac*										
Ia·Na^+	−*ap*	−*sc*	−*ac*										
Ib	−*ac*	−*sc*	−*ap*	−*ap*	*sc*	*sc*							
Ib·Li^+	−*ap*	−*sc*	−*ac*	*ap*	*sc*	*ac*							
Ib·Na^+	−*ap*	−*sc*	−*ap*	−*ap*	*sc*	*ac*							
Ic	−*ac*	−*sc*	−*ap*	*ap*	*sc*	*ap*	−*ap*	−*sc*	−*ap*				
Ic·Li^+	−*ap*	−*sc*	−*ac*	−*ap*	*sc*	*ac*	−*ap*	−*sc*	−*ap*				
Ic·Na^+	−*ap*	−*sc*	−*ap*	−*ap*	*sc*	*ap*	−*ap*	−*sc*	−*ap*				
IIa	*sc*	−*sc*	*ac*	−*ap*	*ac*	−*sc*	*sc*						
IIa·Li^+	*sc*	*ap*	*ap*	−*sc*	*ap*	*ap*	*sc*						
IIa·Na^+	*sc*	*ap*	−*ap*	−*sc*	−*ap*	*ap*	*sc*						
IIb	*sc*	−*ap*	*ac*	−*sc*	*ap*	*ap*	*sc*	*sc*	*ap*	*sc*			
IIb·Li^+	*sc*	*ap*	−*ac*	−*sc*	−*ap*	*ap*	*sc*	−*ap*	*ap*	−*sc*			
IIb·Na^+	*sc*	*ap*	−*ac*	−*sc*	−*ap*	*ap*	*sc*	−*ap*	*ap*	−*sc*			
IIc	*sc*	−*ap*	*ap*	−*sc*	*ap*	*ap*	*sc*	*ap*	*ap*	−*sc*	*ap*	−*ap*	*sc*
IIc·Li^+	*sc*	−*ap*	*ap*	−*sc*	*ap*	*ap*	*sc*	*ap*	*ap*	−*sc*	*ap*	−*ap*	*sc*
IIc·Na^+	*sc*	−*ap*	*ap*	−*sc*	*ap*	*ap*	*sc*	*ap*	*ap*	−*sc*	*ap*	−*ap*	*sc*

[a] Starting from the angles C_bO_aCC for molecules **I** and from the angles $O_{ph}PCO_t$ for molecules **II**.

complex) with respect to the free molecule **Ib**. The largest change [from −98° (for the Li^+ complex) to −157° (for the Na^+ complex)] is observed for one of the CCO_eC angles.

The Li^+ coordination polyhedron may be considered as a distorted trigonal bipyramid, the cation lying in the plane of an ether and two phosphoryl oxygens, while the aryl oxygens are in axial positions [Figure (3b)]. The Na^+ coordination polyhedron is close to a planar pentagon with sides 2·52–2·70 Å, the cation lying in this plane [Fig. (3c)]. In both the free molecule and in its complexes there is a stacking of two phenyl groups with a distance of 4·3 Å between them.

n = 3

As in the previous case, the sequence of the ligand torsion angles in the Li^+ complex differs considerably from that in the free molecule **Ic** and in its Na^+ complex (Table 2). The largest change, from ±105° in the Li^+ complex to ±165° in the Na^+ complex, was observed for the CCO_eC torsion angles. There is no

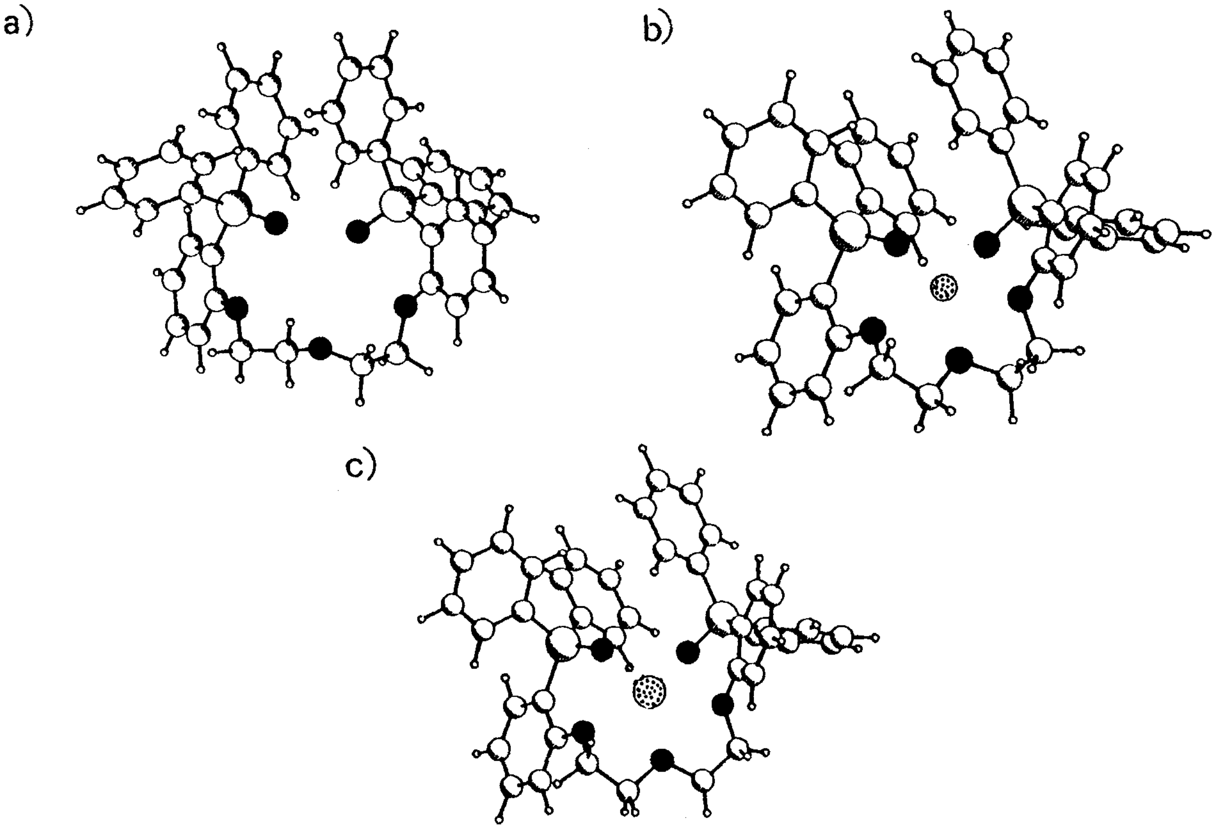

Figure 3. Structure of (a) free molecule **Ib** and its complexes with (b) Li^+ and (c) Na^+. Black spheres, oxygens; dotted spheres, cation

Table 3. Cation—oxygen coordination bond lengths (Å) in complexes of molecules **Ia**–**c** with Li^+ and Na^+

	$M^+\cdots O_{ph}$		$M^+\cdots O_a$		$M^+\cdots O_e$	
Molecule	Li^+	Na^+	Li^+	Na^+	Li^+	Na^+
Ia	1·71	2·03	2·03–2·15	2·34–2·46	—	—
Ib	1·72–1·73	2·03	2·22–2·33	2·38	1·92	2·27
Ic	1·76	2·05	2·32	2·52	2·05	2·25

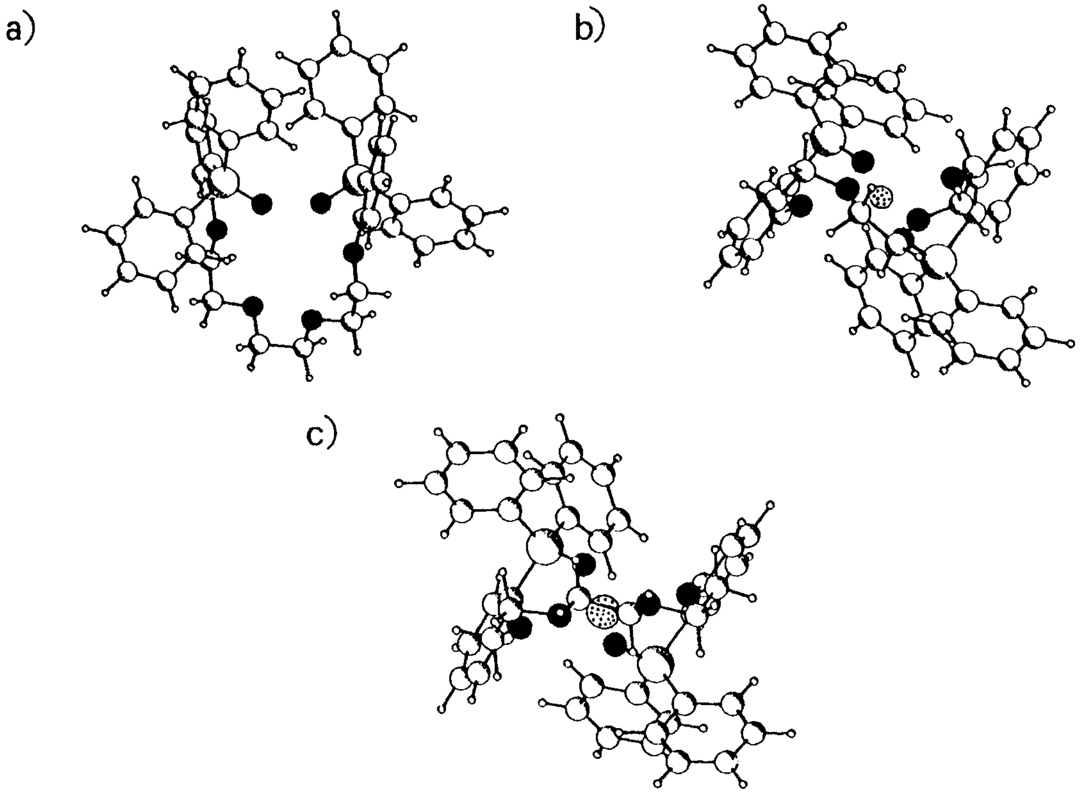

Figure 4. Structure of (a) free molecule **Ic** and its complexes with (b) Li^+ and (c) Na^+. Black spheres, oxygens; dotted spheres, cation

stacking of phenyl groups in either the free molecule or its complexes (Figure 4).

The Li^+ and Na^+ coordination polyhedra in the complexes of the molecule **Ic** appear as distorted tetragonal bipyramids. Still some structural characteristics of these complexes differ significantly: Li^+ is coordinated by two ether oxygens in the equatorial plane and the aryl oxygens lie in axial positions [Figure 4(b)]; the equatorial plane of the Na^+ polyhedron contains ether and aryl oxygens, whereas the phosphoryl group oxygens occupy axial positions [Figure 4(c)].

MOLECULES IIa–c AND THEIR COMPLEXES

n = 1

The oxygens of the free molecule **IIa** do not lie in a plane, the torsion angle $O_{ph1}O_{t1}O_{t2}O_{ph2}$ being 45·5°. The lone pairs of one of the terminal oxygens are oriented outside the pseudo-cavity [Figure 5(a)]. Almost all the torsion angles have non-optimum values (Table 2); thus, the torsion angles along the C—O bonds could be referred to as *ac* or $-sc$ types, and along the C—C bonds as *ap* type, whereas the optimum values correspond to $\pm ap$ (for C—O) and $\pm sc$ (for C—C) types.[24]

The interaction of the ligand with Li^+ and Na^+ leads to the same conformation with an optimum sequence of torsion angles, the ligand oxygens becoming more planar, with a decrease in the $O_{ph1}O_{t1}O_{t2}O_{ph2}$ torsion angle to 27°. Under the influence of the cation field, the pseudo-cavity is compressed: the distance between the terminal oxygens decreases from 3·60 to 2·37 Å (Li^+) and 2·62 Å (Na^+), along with the pseudo-cavity size, which can be defined as the $O_{ph1}O_{t2}$ ($O_{t1}O_{ph2}$) distance, its values being 4·5 Å (free molecule), 3·6 Å (Li^+) and 3·8 Å (Na^+). The polyether chain twines around the cation forming a helix-like polyhedron, characteristic of podands [Figures 5(b) and (c)]. The distances between the cation and the phosphoryl oxygens are in a narrower range than those between the cation and the terminal oxygens (Table 4), owing to the difference in charge–dipole interactions of the cation with the corresponding groups.

There is no stacking of phenyl groups. These bulky substituents on the various P=O groups are oriented towards different sides of the pseudo-cavity.

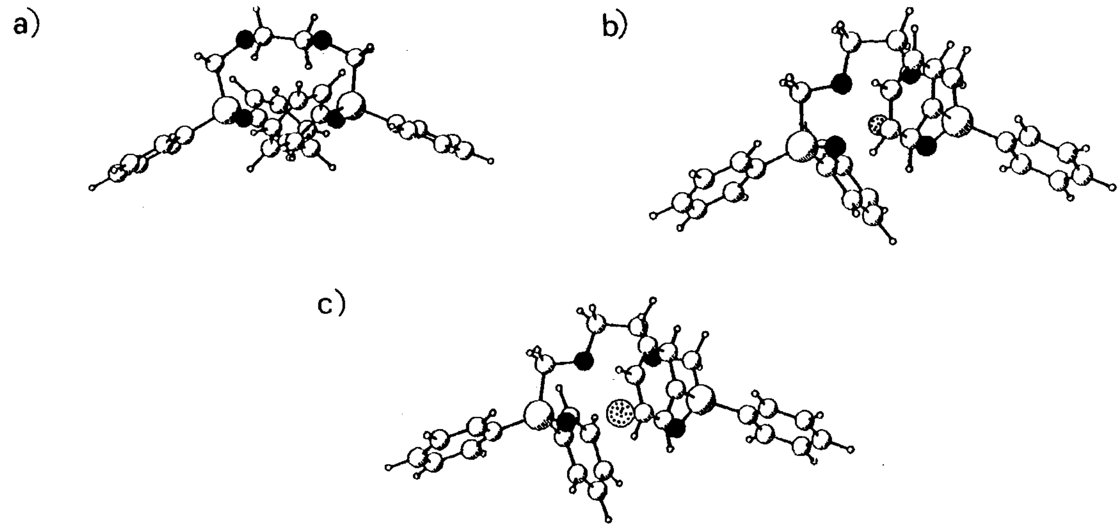

Figure 5. Structure of (a) free molecule **IIa** and its complexes with (b) Li^+ and (c) Na^+. Black spheres, oxygens; dotted spheres, cation

Table 4. Cation—oxygen coordination bond lengths (Å) in complexes of molecules **IIa–c** with Li^+ and Na^+

	$M^+\cdots O_{ph}$		$M^+\cdots O_t$		$M^+\cdots O_e$	
Molecule	Li^+	Na^+	Li^+	Na^+	Li^+	Na^+
IIa	1·72	2·01	2·11	2·40	—	—
IIb	1·76	2·05	2·02	2·31	1·88	2·25
IIc	1·73	2·05	2·11	2·31	1·95	2·22

$n = 2$

The interaction with a cation leads to conformational changes of the free molecule **IIb**: the $O_{ph}PCO_t$ torsion angle changes from 60° to -34° (Li^+) and to 40° (Na^+); the CO_tCC angles change from -68°, 105° to -98°, -162° (Li^+) and to -108°, -169° (Na^+). The distance between the phosphoryl oxygens changes from 3·21 Å to 2·85 Å (Li^+) and to 3·8 Å (Na^+). The coordination polyhedra appear as trigonal bipyramids [Figures 6(b) and (c)], the cations lying nearly in the plane of the O_{t1}, O_e and O_{t2} atoms, and the $O_{t1}O_eO_{t2}M^+$ torsion angles being equal to $9{\cdot}6^\circ$ (Li^+) and 12° (Na^+). The oxygens of the phosphoryl groups coordinate the cation in axial position, the $M^+\cdots O_{ph}$ distances being 1·76 Å (Li^+) and 2·05 Å (Na^+). The cation—ether oxygen bond lengths [1·88 Å (Li^+) 2·25 Å (Na^+)] are slightly shorter than the $M^+\cdots O_t$ distances [2·02 Å (Li^+) and 2·31 Å (Na^+)].

It is worth mentioning that the stacking of the phenyl groups in the neutral molecule almost disappears in the complexes, owing to their shifts in parallel planes.

$n = 3$

Although the conformational formulas in the free ligand **IIc** and in its Li^+ and Na^+ complexes are identical, the values of some torsion angles change appreciably, the variations of the $O_{ph}PCO$ torsion angles being in the range 32 to 55° and of the O_tCCO_e angles being in the range -60 to 28°. The $O_{e1}CCO_{e2}$ angle in the Li^+ complex ($31{\cdot}5^\circ$) is slightly larger than that in the free molecule ($29{\cdot}3^\circ$), whereas it increases considerably in the Na^+ complex ($41{\cdot}3^\circ$). A helix-like coordination of the cation by the donor atoms occurs in the complexes [Figures 7(b) and (c)]. There is stacking of phenyl groups both in the free molecule and in the complexes.

The structural characteristics both of molecules **I** and **II** and of their complexes are now summarized. A specific feature of the free molecules **IIa** and **IIb** is the absence of conformations pre-organized for complexation, as the lone pairs of one or two oxygens of the polyether chains are oriented outside the pseudo-cavity [Figures 5(a) and 6(a)]. Hence the interaction with a cation drastically changes the molecular conformation, and the torsion angle sequences in the chains become closer to the ideal one (± *ap* for angles along the C—O bond and ± *sc* for angles along the C—C bond). The structures of the Li^+ and Na^+ complexes are similar and correspond to a helix-like cation coordination by the donor atoms of the molecule.

Unlike molecules **II**, the more rigid molecules **I** may occur in conformations with all the oxygens oriented inside the pseudo-cavity [Figures 2(a), 3(a) and 4(a)]. The coordination polyhedra of Li^+ and Na^+ are similar only in complexes with the molecule **Ia**, but they differ

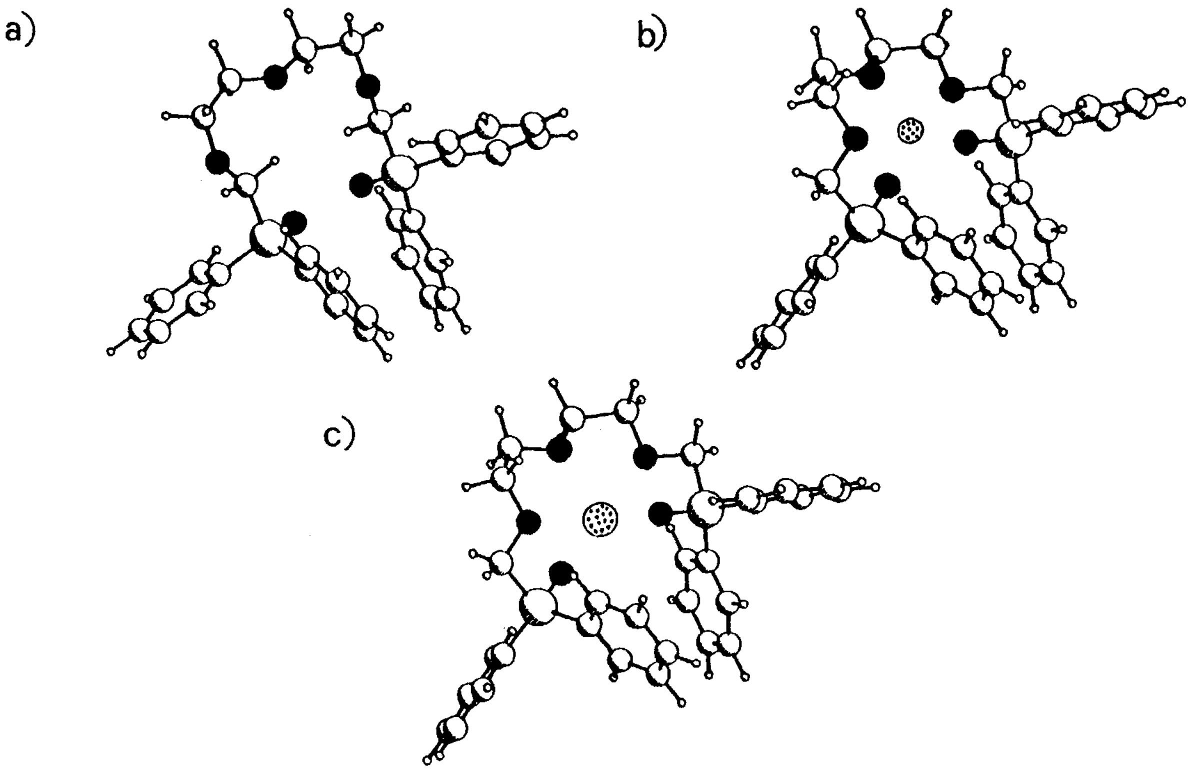

Figure 6. Structure of (a) free molecule **IIb** and its complexes with (b) Li$^+$ and (c) Na$^+$. Black spheres, oxygens; dotted spheres, cation

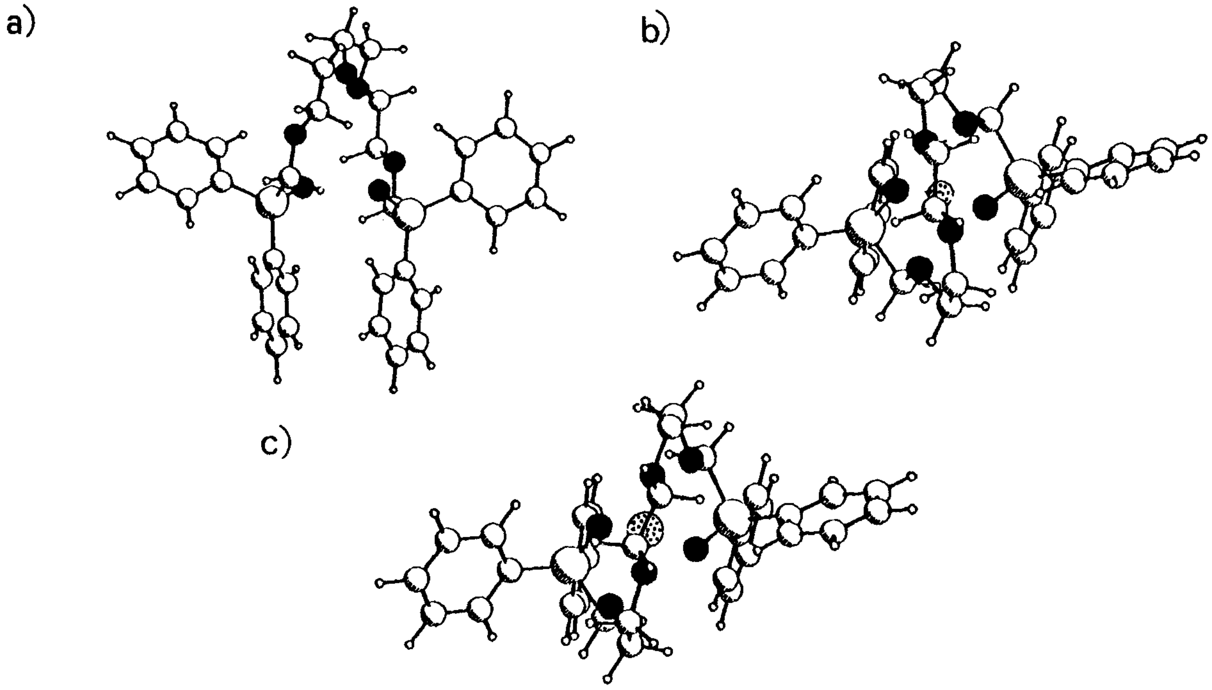

Figure 7. Structure of (a) free molecule **IIc** and its complexes with (b) Li$^+$ and (c) Na$^+$. Black spheres, oxygens; dotted spheres, cation

essentially in complexes with **Ib** and **Ic**, where the largest difference is found in the geometry of the polyether chain. Li^+ complexes show a more distorted (helix-like) coordination, whereas Na^+ complexes present an approximately planar arrangement of aryl and ether oxygens.

Stacking of phenyl groups occurs in the free molecules **Ib**, **IIb** and **IIc**. The complexes **Ib** and **IIc** are also characterized by a planar arrangement of phenyl groups, whereas in the complexes **IIb** the stacking disappears, owing to parallel shifts of the phenyl groups with respect to each other during the complexation. This result proves that the role of the stacking effect, as a factor providing the stability of a complex, is not significant.

The analysis of the results reported in Tables 3 and 4 indicates that the oxygens of the phosphoryl groups are the strongest coordination centres of the molecules considered. In fact, the lengths of the $M^+\cdots O_{ph}$ coordination bonds, much shorter than the other contacts in the cation polyhedra, are in narrow ranges 1·71–1·76 Å (Li^+) and 2·01–2·05 Å (Na^+). In the complexes of the molecules **Ia–c**, the ether oxygens make a bond with the cation stronger than the aryl oxygens, owing to their higher electron density (and, consequently, higher PD charges) compared with the O_a atoms; this explains the shortening of the $M^+\cdots O_e$ bonds [1·92–2·05 Å (Li^+) and 2·25–2·27 Å (Na^+)] compared with the $M^+\cdots O_a$ bonds [2·03–2·33 Å (Li^+) and 2·33–2·52 Å (Na^+)].

This result is in qualitative agreement with the x-ray structure[25] of a RbI complex with a podand having a three-oxygen polyether chain and 8-quinoline fragments as terminal groups. The $Rb\cdots O$ distances of the aromatic oxygens, larger than those of the ether oxygens, are interpreted in terms of a lowering of the basicity of the aromatic oxygens.[26]

The higher conformational flexibility of the molecules **II** allows better contacts of the cation with the donor atoms of the polyether chain. Hence the cation—oxygen distances are shorter than in the complexes of molecules **Ia–c**. Their values differ only slightly and lie in the ranges 2·02–2·11 Å ($Li^+\cdots O_t$), 2·31–2·40 Å ($Na^+\cdots O_t$), 1·88–1·95 Å ($Li^+\cdots O_e$) and 2·22–2·25 Å ($Na^+\cdots O_e$).

It is interesting to compare the calculated cation—oxygen distances with the known experimental x-ray data. For Li^+ compounds the structural data have recently been summarized.[27] The average $Li\cdots O_e$ distances in Li–ether complexes lie in the range 1·951 Å (pyramidal coordination)–2·265 Å (octahedral coordination). On the whole, these values correspond to the calculated distances between Li^+ and ether oxygens. Several data for Na^+ complexes with neutral organic molecules were given in a review.[28] The range 2·16–2·45 Å is found for $Na\cdots O_e$ bond lengths, in agreement with our theoretical results.

A distance of 1·77 Å for the $Li^+\cdots O_{ph}$ coordination bond in the crystal $[Li\{OP[N(CH_3)_2]_3\}_4]$ — $[Li(N{=}CPh_2)_6]$ — $[O{=}P[N(CH_3)_2]_3]$ was obtained;[29] this is slightly longer than the distances obtained here (1·71–1·75 Å). In the crystal of $[NaL_3]^+Br^-\cdot 3H_2O$ [L = methylenebis(phosphine oxide)],[30] where the cation coordination polyhedron is a trigonal prism and the coordination number is six, the average cation—oxygen distance is 2·45 Å, *ca* 0·4 Å longer than the calculated value. Presumably this difference is not due to the force field used, but could be accounted for by packing effects and/or ligand–ligand interactions. Such effects were observed for $Li\cdots O_{ph}$ coordination bonds in Li compounds. Indeed, in the complex $[LiL_4]^+\cdot LI^-$ (L = triphenylphosphine oxide), where the cation has tetragonal coordination, the average $Li\cdots O_{ph}$ distance is 1·97 Å;[31] in the crystal $[Li\{OP[N(CH_3)_3]_2\}_3](H_2O)_2]Cl$, where the cation is also present, with tetragonal coordination, distances of 1·984 Å and 2·013 Å were obtained.[32]

ENERGETICS OF INTRAMOLECULAR AND ION–MOLECULE INTERACTIONS

The cation–ligand interaction energies (E_{ML}) and the extra-steric molecular energies (ΔE_{st}), differences in the ligand conformational energies in the complex and in the free molecule, are reported in Table 5.

ΔE_{st} increases from 5·4 to 22·6 kcal mol^{-1} in Li^+

Table 5. Cation–ligand interaction energies (E_{ML}, kcal mol^{-1}) and extra-steric ligand energies (ΔE_{st}, kcal mol^{-1}) in complexes of the molecules **Ia–c** and **IIa–c** with Li^+ and Na^+

	Li^+			Na^+		
Molecule	$-E_{ML}$	ΔE_{st}	$-(E_{ML}+\Delta E_{st})$	$-E_{ML}$	ΔE_{st}	$-(E_{ML}+\Delta E_{st})$
Ia	194·2	5·4	188·8	148·7	4·6	144·1
Ib	215·9	8·6	207·3	161·7	5·7	156·0
Ic	249·4	22·6	226·8	190·4	5·2	185·2
IIa	212·9	12·1	200·8	168·7	9·1	159·6
IIb	244·9	12·9	232·0	189·1	10·2	178·9
IIc	278·1	19·7	258·4	213·2	8·4	204·8

complexes of molecules **Ia–c** and from 12·1 to 19·1 kcal mol^{-1} in complexes of **IIa–c** (1 kcal = 4·184 kJ). The large excess steric energy of ligand **Ic** in its complexes is due to the relevant conformational transformation of the free molecule. The same reason may also account for the high values of ΔE_{st} in the Li^+ complex of **IIa** and **b**.

The formation of the $\mathrm{Li}^+\cdot$**IIc** complex does not change the conformational formula of the free molecule as for **IIa** and **b**. However, the reduction in the pseudo-cavity size under the influence of the cation field results in a high steric energy value.

The increase in the ligand steric energies in Li^+ complexes is compensated for by the increase in cation–ligand interaction energies; the $-E_{\mathrm{ML}}$ values and the sums $-(E_{\mathrm{ML}}+\Delta E_{\mathrm{st}})$ gradually increase in the series **Ia**, **Ib** and **Ic** and **IIa**, **IIb** and **IIc** (Table 5).

The interaction with Na^+ leads to essentially lower deformations of the ligands, the extra-steric energies being lower in Na^+ than in Li^+ complexes. The Na^+–ligand interaction energy, as in Li^+ complexes, increases gradually with increasing number of donor atoms.

The data in Table 5 prove that the cation–ligand interaction energy, taking into account the steric energy changes, is always higher in complexes of molecules **II** than in those of molecules **I**. This is not surprising, because the higher conformational flexibility of **IIa–c** allows more effective contacts with the cation in the complexes.

The question arises of how the stability of Li^+ and Na^+ complexes, higher for molecules **Ia–c** than for **IIa–c**, can be accounted for. The present results indicate that the entropy losses during complexation are lower for the rigid molecules **I** than for the flexible molecules **II**. Probably this is the reason why the complexes have different stabilities. This suggestion is strengthened by the experimental results on the complexation of some glymes and glycols with alkali metal cations in methanol.[33] In some cases the complex stability decreases in spite of the reduction in the enthalpy term. Our results further emphasize the major role of entropy changes in reactions involving open-chain polydentate ligands.

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