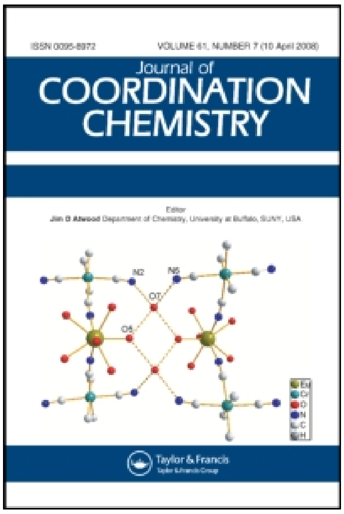

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ON Li-CHELATING ADDITIVES TO ELECTROLYTES FOR Li BATTERIES

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The relative affinity of several electrochemically stable bi- and polydentate organic ligands (containing ether, amino, carbonate or phosphonate moieties) to Li ion was estimated by *ab initio* calculations at the MP2/6-31G(d) level comparing their calculated binding energies (BEs). Polyether 12-crown-4 and a bisphosphonate, which is covalently locked in a cyclic "chelating" conformation, are stronger Li^+ chelators than isosparteine and 1,2-methylenebisphosphonate (an open-chain compound). Organic biscarbonates are the weakest complexing agents among the ligands considered. Although BE values were calculated for the gas phase, the order of ligand complexation ability obtained is also considered relevant to solutions since the difference between the BEs for these three groups of ligands is significant. The same calculations that were performed for complexes of Li ion and different organic carbonate diesters (solvents usually used in Li-ion batteries) allowed singling out of conformationally locked bisphosphonates as new battery life-prolonging additives to carbonate electrolytes.

Keywords: Chelation; Bisphosphonates; Biscarbonates; Lithium; *Ab initio* calculations

INTRODUCTION

All currently available Li-ion batteries suffer from capacity-fading problems, especially at elevated temperatures. Capacity-fading mechanisms of Li-ion battery systems usually relate to continuous side-reactions of solution species (organic carbonates) with both the anode and cathode materials [1–3]. One of the most important strategies to improve the performance of Li-ion batteries is the use of additives that positively affect the surface chemistry of the electrodes, either by acting as scavengers that remove detrimental contaminants such as HF or H_2O [4] or as species that react directly on the electrodes and attenuate their surface chemistry towards the formation of better passivating surface films [5a,b].

There are also reports on the improvement of Li/Li-ion battery electrodes in solutions containing Li chelators (e.g. polyamines or polyethers) [6a–d]. For instance, graphite electrodes that are deactivated upon cathodic polarization into pure propylene carbonate (PC)/Li salt solutions insert lithium reversibly when they contain a crown

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ether additive [6b]. Another careful study of Li complexes in propylene carbonate (PC) solutions [7] concluded that complexating ligands may be promising additives in lithium batteries.

Systematic studies of chelation-associated processes in nonaqueous Li salt solutions have not been undertaken, and it is still difficult to single out essential mechanisms of their positive effects. In any event, the binding of Li-ions in solutions by different ligands is not necessarily the primary factor that determines their usefulness as additives to Li-ion battery solutions. A key issue is their possible reaction on the electrode's surface and to what extent their reaction may induce the formation of surface films with better passivating properties than those formed in standard (additive-free) solutions. Nevertheless, the ability to chelate metal cations (including Li^+) in solutions was considered as an important factor for the positive effects of some complexating agents in carbonate electrolytes or the behavior of Li-graphite anodes [6b,d]. Chelation of Li ions may decrease their electrophilicity. Some surface reactions may be facilitated by electrophilic assistance from Li ions. For instance, it was demonstrated that the presence of crown ether in solution reduces the rate of decomposition of solvents such as propylene carbonate on Li metal electrodes [8].

Despite the high solvation energy of lithium ions by organic carbonates [9a–c], crown as well as azacrown ethers can lead to strong binding of Li^+ in PC [7]. Equilibrium constants for the equilibrium Li-PC complex–Li-crown ether complex range between 5×10^3 and 1.5×10^4 at 298 K for different lithium salts. However, it is questionable whether other bi- or polydentate ligands that can form stable Li complexes in moderately polar organic solvents (e.g. sparteine **1** in ethers or acetone [10a,b]) are capable of chelating this ion to an appreciable extent in organic carbonate media.

In order to estimate the relative ability of polydentate ligands of different chemical functionalities to afford Li complexes, we have carried out the present computational study. We also suggest that the *ab initio* quantum mechanic estimates obtained may be used as a basis for consideration of new additives to electrolyte solutions of rechargeable batteries.

EXPERIMENTAL

Amber* and OPLS* force fields implemented into the Macromodel6.5 package [11a–c] were used for geometry optimization of Compounds **2**–**6** as well as monocarbonate diesters using *no solvent* and *distance-dependent dielectric electrostatics* options. The Monte-Carlo option (a Macromodel6.5 component) was used for conformational analysis (generation of 5×10^3 structures for cyclic compounds **2** and **6** and 4×10^4 structures for open-chain compounds **3**, **4** and **5**, with the energy upper limit of 3 kcal/mol from the lowest energy conformer found). Energy minimization for polycycle **1** was performed using the 1996 version of the MM3 package possessing an explicit parameterization for amines [12a–c].

The geometry of conformers obtained by molecular mechanics-based optimization was used as the starting geometry for *ab initio* calculations (Gaussian98 package [13]) for Compounds **1**–**6** as well as for monocarbonate diesters in the gas phase. Optimized structures of selected conformers of **1**–**6** and monocarbonates were used as starting geometry for these ligands in the corresponding Li complexes (gas phase). The difference, ΔE, between full electron energies is not corrected to the zero-point energy.

Initial *ab initio* geometry optimization was performed at the restricted Hartree–Fock level using the 6-31G(d) basis set. The resulting geometry was reoptimized at the MP2/6-31G(d) level.

RESULTS AND DISCUSSION

Compounds **1** and **2** (see Fig. 1) were chosen because of their affinity for Li cations [10a,b,14a] while for Compounds **3**–**6** we presume that Li^+ can be chelated (see below). Our choice of biscarbonates **3** and **4** as well as bisphosphonates **5** and **6** was motivated by successful use of biscarbonates [15a] and bisphosphonates [15b] as

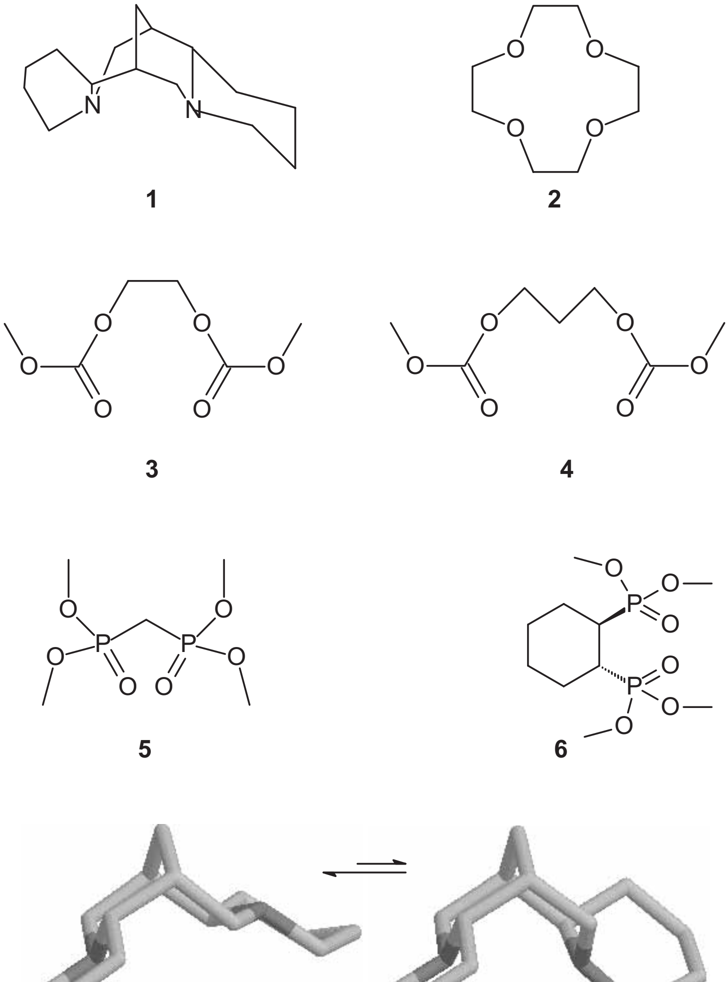


FIGURE 1 Compounds **1**–**6**. Conformational equilibrium is shown for the two lowest energy conformers for diamine **1** (H-atoms are omitted for clarity).

additives in model systems for Li-ion batteries. It should be mentioned that our choice of potential chelators was strongly restricted because of the electrochemical lability of many organic functions, which obviously may be quite stable chemically (e.g. sulfones and sulfoxides).

As a measure of the relative affinity of Compounds **1**–**6** to the lithium cation we used the calculated BE (the difference between calculated electronic energies of starting species and products; see below and Table I) of these ligands (L) to Li^+ for reaction (1) in the gas phase. Such BE values "neglect" solvation effects and are, of course, only a rough estimate of absolute affinity when considered for a ligand in real electrolytes, dimethylcarbonate (DMC), ethylene carbonate (EC), vinylene carbonate (VC) or PC-based solvent mixtures comprising Li salts in very high concentrations. However, ΔBE values taken for different ligands are obviously significantly more accurate as a *relative* estimate of their complexation ability in solutions. To avoid residual inaccuracy, only compounds for which ΔBE is more than 10 kcal/mol are accepted here as ligands whose affinity to Li^+ is indeed different and the increase in BE corresponds to a stronger capture of the Li cation. Thus, ΔBE values were a basis for the final qualitative comparison of the strength of the chelation.

$$\mathrm{Li}^+ + \mathrm{L} = \mathrm{LLi}^+. \tag{1}$$

Compounds **1**–**6** are conformationally flexible and it is generally difficult to conclude *a priori* which conformation leads to the formation of the lowest energy Li complex. Only in the case of **1** did backbone geometry restrictions permit consideration of the minor conformer (see Fig. 1; for conformational analysis of **1** see [16a,b]) as a conformation capable of Li chelation. Conformational analysis was carried out to identify chelating conformations of ligands **2**–**6**. A set of low-energy conformers was generated by the Monte-Carlo conformational search followed by geometry optimization using the Amber force field (see Experimental for details) [17]. Parameterization in this force field, as well as other common force fields, has not been extended explicitly to carbonates or phosphonates. Hence, the molecular mechanics-derived results, for example for spatial structure and relative stability of conformers, are not reliable when considered for these ligands. Therefore, the geometry of the lowest energy conformers generated by Amber (occupying a 2 kcal/mol range over the

TABLE I Calculated BE values, O–Li bond lengths and "endocyclic" heteroatom–Li–heteroatom bond angles for complexes of ligands **1**–**6** as well as EC, PC, VC and DMC with Li^+ in the gas phase

	BE (kcal/mol)	*O–Li* (Å)	*HetLiHet*[a] (°)
1-Li	84.0	1.97, 1.98	96.1
2-Li	100.1	2.02[b]	83.1
3-Li	71.2	1.88, 2.02, 2.09	154.3
4-Li	70.8	1.82[b]	123.9
5-Li	86.4	1.85[b]	110.0
6-Li	95.6	1.82[b]	110.1
EC–Li–EC	92.7	1.84	179.6
PC–Li–PC	94.7	1.84	177.2
VC–Li–VC	85.0	1.84	179.2
DMC–Li–DMC	94.7	1.88	161.6

[a] Het = N for **1**-Li and Het = O for **2**-Li to **6**-Li. [b] Equal length for both $Li^+\cdots O$ bonds.

global minimum of steric energy) was reoptimized by *ab initio* calculations at the MP2/6-31(d) level.

Our conformational analysis demonstrates that conformers possessing spatially near X=O fragments (“cyclic” conformations; X = C, P; see Fig. 2) predominate over conformers with remote X=O fragments (“linear” conformations) for open-chain compounds **3**–**5**. The difference in electron energy (ΔE) between the lowest energy conformer (i.e. a “cyclic” one) and the second in energy conformer (i.e. a “linear” one) is 1.6, 2.5 and 1.9 kcal/mol for **3**–**5**, respectively. The calculated distance between the

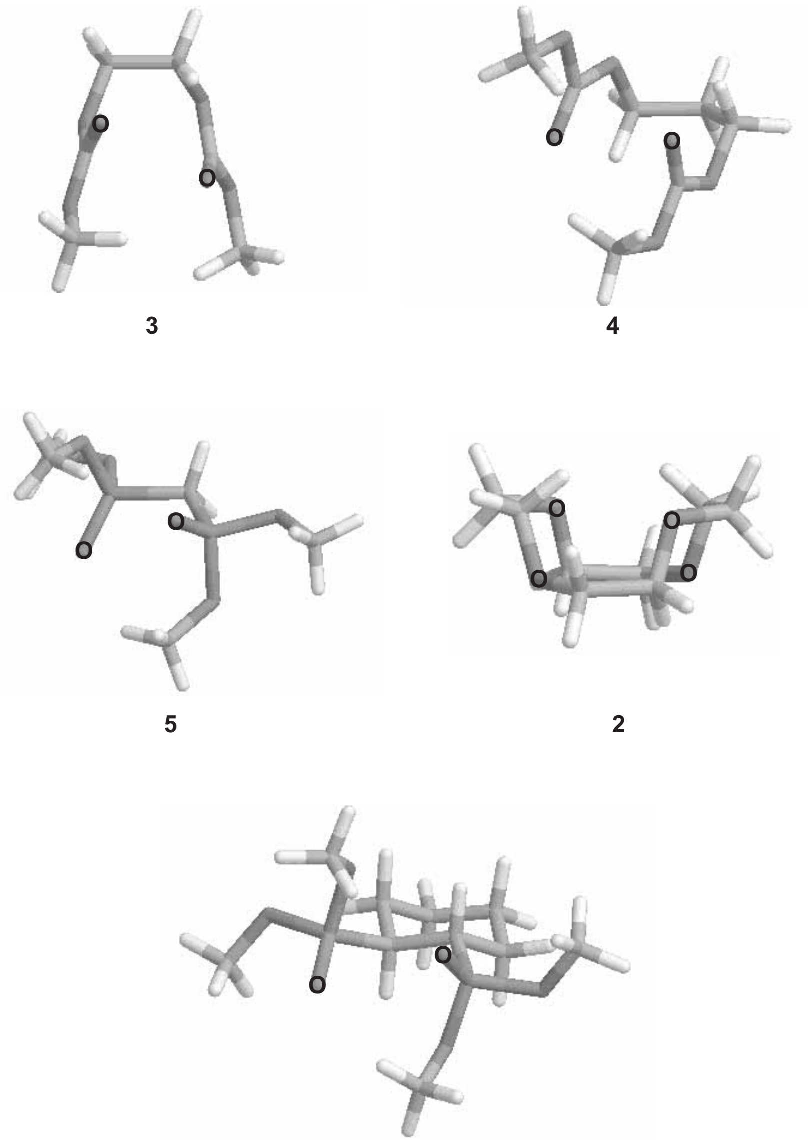


FIGURE 2 Lowest energy (“cyclic”) conformers of ligands **2**–**6** with the geometry optimized at the MP2/6-31G(d) level.

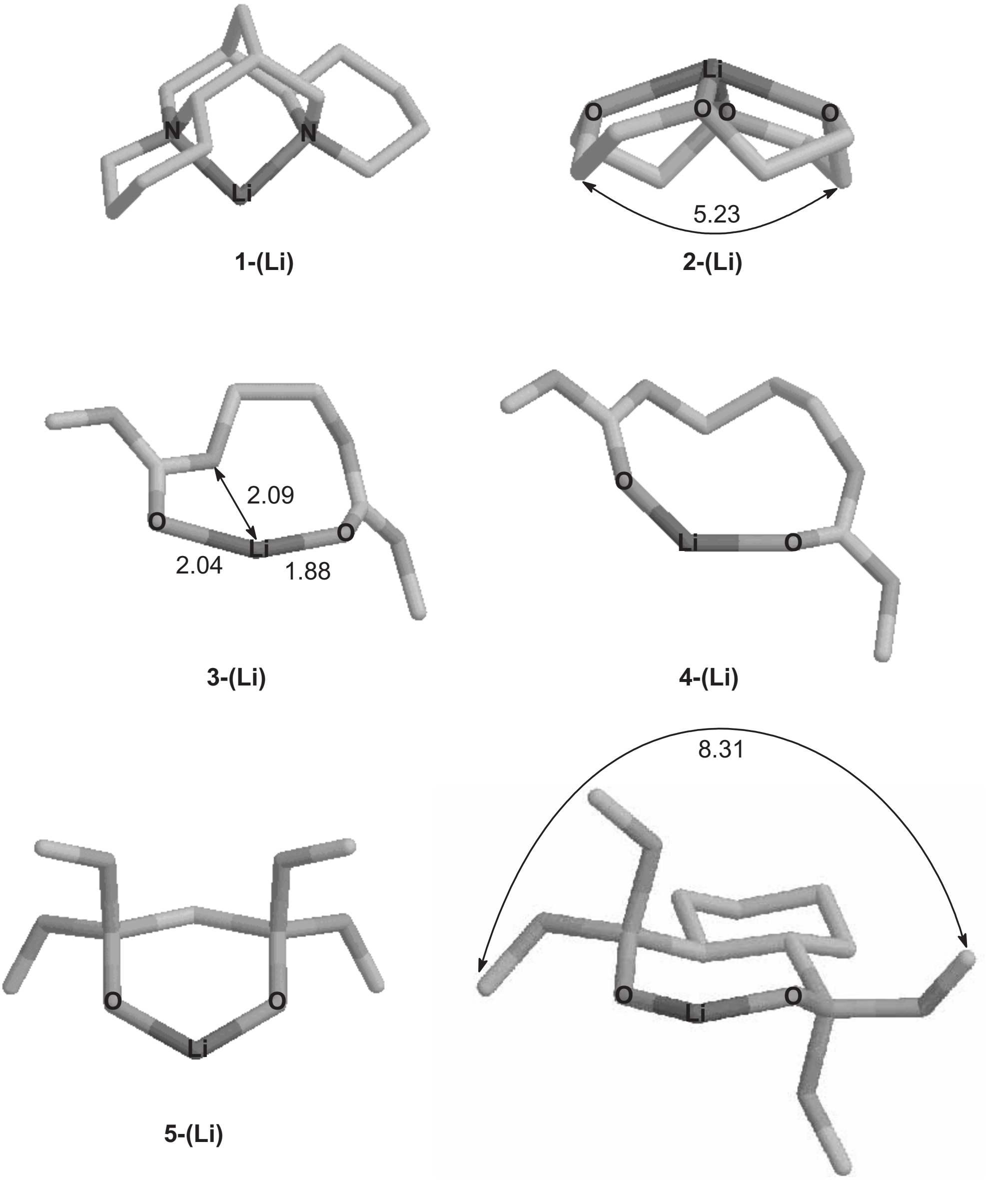
oxygen atoms of the two X=O fragments of bidentate ligands **3**–**5** is 3.28, 3.01 and 3.63 Å, respectively, for the "cyclic" conformers. A "cyclic" conformation (the calculated P=O···O=P distance is 3.2 Å) is also preferable for less flexible *trans*-disubstituted cyclohexane **6**. Thus, as expected, the spatial structure of these ligands should facilitate Li chelation. The structures of these "cyclic" conformers were used as starting structures for the geometry optimization of the corresponding ligands in their Li complexes.

Interestingly, even though Amber is unable to take into account "through space" repulsion of electron lone pairs (e.g. in 1,2-heteroatom disubstituted systems), it singled out the lowest energy conformer of macrocycle **2** (Fig. 2) correctly: its spatial structure corresponds to the X-ray determined geometry of **2** [18]. Nevertheless, for the modeling of complex Li-**2** we used the same "crown" conformation (see Fig. 3), which was accepted [14a] for **2**, to be responsible for Li complexation. This conformation is less stable by 1.0 kcal/mol than the lowest energy conformation (by Amber). Its Li complex, however, is more stable than the complex with the ligand at its lowest energy conformation [14a]. For the more rigid polycycle **1**, the geometry of its minor conformer (see above, as well as Fig. 1) represents a 3D structure of this ligand at its Li complex before energy minimization.

Starting geometries of Li complexes of **3**–**6** were obtained by placing a Li cation between two oxygen atoms, *sp*^{2}- and *sp*^{2}-hybridized or *sp*^{2}- and *sp*^{3}-hybridized, that belong to different ester functions of the corresponding "cyclic" conformer and are separated by not more than 4 Å. The backbone rigidity of the tetra-chair conformer of **1** permitted consideration of only one starting structure of its Li complex with a Li atom at the predicted crossing point of the orientation of the lone pairs of the two nitrogen atoms. For **2**, a geometry similar to the reported geometry of its Li complex [14a] was used.

Geometry optimization at the MP2/6-31(d) level [19] for each starting structure provided only two Li complexes of different spatial structures for each flexible ligand **3**–**6** (some nonidentical starting structures led to the same geometry when optimized). The lowest energy complexes, **3**-Li, **4**-Li, **5**-Li and **6**-Li (Fig. 3), as well as Complex **1**-Li, indeed possess a chelate structure, binding the metal cation intramolecularly by electron-donating atoms belonging to two differently positioned functional groups. Complex **2**-Li is of the same "crown" structure as in earlier calculations [14] using the MP2/6-31+G(d) hybrid level: C–C, C–O, O–Li bond distances and dihedral angle OCCO are 1.515, 1.440, 2.021 Å and 53.2°, respectively, according to our present calculations, compared to 1.515, 1.440, 2.019 Å and 52.7° by the previous ones.

As our calculations show, Li cation is bound most strongly by polyether **2** (see Table I for the corresponding BE as well as geometry parameters) and by the conformationally restricted bisphosphonate **6**. Diamine **1** and open-chain bisphosphonate **5** are better chelators than biscarbonates **3** and **4**. There is no correlation between the BE of the ligands and the length of the Li$^+$···Het bond (Het = N, O; see Table I) in their complexes. Indeed, a single geometry parameter cannot represent the affinity of **1**–**6** to Li$^+$ since their chelating moieties as well as the spatial structures of chelates **1**-Li to **6**-Li are quite different. This affinity is also characterized by the HetLiHet bond angle and also by the number of atoms involved in complexation (electron pair donors). For instance, Complex **3**-Li is additionally stabilized by coordination of the Li cation with the "endocyclic" oxygen of one of the carbonate moieties (see Fig. 3 for the corresponding interatomic distances).



1-(Li) **2-(Li)**

3-(Li) **4-(Li)**

5-(Li) **6-(Li)**

FIGURE 3 Calculated geometry of **1**-Li, **2**-Li, **3**-Li, **4**-Li, **5**-Li and **6**-Li (H-atoms are omitted for clarity). Interatomic distances are shown in Å.

In general, a Li^+ ion that coordinates to an sp^2-hybridized oxygen atom is located "linearly", that is on an imaginary continuation of the double bond [14b]. Hence, the OLiO bond angle has a tendency to have a 180° value for Li complexes with two sp^2-O-containing groups, which belong to different molecules or are connected very flexibly (see, for example, Table I for Li complexes with carbonate solvents).

In bent structures **3**-Li, **4**-Li, **5**-Li and **6**-Li this tendency is limited due to the ring geometry constraints: the considered angles are appreciably less than 180° (Table I). Nevertheless, the OLiO bond angles for the larger rings **3**-Li and **4**-Li are bigger than the corresponding angles for the smaller-sized rings **5**-Li and **6**-Li.

As mentioned above, higher BE values are found for chelates **5**-Li and **6**-Li (complexes with not quite optimal OLiO angles) compared to BE values for **3**-Li and **4**-Li (complexes with near-optimum OLiO angles). This means that better Li coordination to phosphonate ligands **5** and **6** rather than to carbonate ligands **3** and **4** is determined more by the chemical difference between the phosphoryl and the carbonyl fragments (e.g. easier polarizability of P=O) than by the shape of the ligand backbone.

Our results demonstrate that it is difficult to estimate the influence of the length of the methylene bridge between two functionalities (carbonate groups in **3** and **4** or phosphonate groups in **5** and **6**) on Li chelation without performing a conformational analysis. The shape of "cyclic" structures formed by such chelation does not correspond to well-known minimum energy forms of saturated carbocycles [20a–e]. For instance, a six-membered "cyclic" structure of **5**-Li is neither a chair, a distorted chair, or a twist (stable conformations of cyclohexane and related heterocyclic rings), but a flattened boat (the usual boat is a transition state in an interconversion of twist forms of six-membered cycles [20a,b]). This is not surprising since the geometry of Li^+-containing cycles is strongly influenced by the length of the $Li^+\cdots O$ bond, which deviates significantly from the values for covalent endocyclic C–C bonds. Classical conformations of saturated carbocycles cannot be taken into account when considering complexes of the corresponding ring size formed via Li^+ coordination. Therefore, there is no basis for an *a priori* prediction of the geometry of bidentate Li complexes of **3**–**5** and, thus, a relative stability of these cycles. However, consideration of compounds possessing a favored "chelating" conformation (for compounds with electron-donating moieties covalently fixed proximally as, for example, in polycycle **1** or monocycle **6**) may facilitate such a prediction.

In order to estimate a relative Li^+ complexation ability of different solvents and chelating additives, we also calculated BEs at the same theory level for coordination of the Li cation by two molecules of PC, EC, VC or DMC (i.e. for reaction (2); it is known that two ligand-containing carbonate complexes L–Li–L predominate over tetracoordinated complexes in concentrated solutions of $LiPF_6$ used in Li-ion batteries [21]. See also [14a] and [19] for calculations at other theory levels).

$$Li^+ + 2L = L_2Li^+. \tag{2}$$

The BE values obtained (Table I) show that there is a strong interaction between organic carbonates and the Li cation. As expected, VC, as a carbonate bearing a fragment with −I-effect (the endocyclic C=C bond) and therefore the less electron-donating C=O group, possesses a lower affinity to the Li ion among these carbonate solvents (see Fig. 4 for the structure of VC–Li–VC).

Considering ligands **1**–**6** and using a 10 kcal/mol comparison condition (see above), we concluded that crown ether **2** and cyclic bisphosphonate **6** belong to one group of Li complexing agents (the strongest) *in solution*, diamine **1** and open-chain bisphosphonate **5** form the second group (moderate), while biscarbonates **3** and **4** are weak complexing agents.

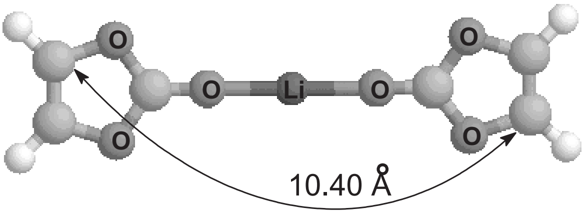


FIGURE 4 Optimized structure of complex VC–Li–VC.

Formally, the carbonate solvents lie between the moderate and the strongest chelator groups as Li^+ complexing agents. However, the comparison does not clarify whether the complexation ability of PC, EC and DMC is similar to that for compounds of one of the two groups or if it is indeed intermediate between the activities of these two groups (compounds **1**, **5** and **2**, **6**). Nevertheless, these results clearly show that at least biscarbonates cannot be considered as Li^+ chelators in DMC, VC, EC or PC solutions.

The mobility of the coordinated Li cation in carbonate solutions should be increased in the presence of **2** or **6**. Indeed, calculated interatomic distances between the maximally remote carbon atoms for complexes **2**-Li and **6**-Li (see Fig. 3) are 5.23 and 8.31 Å, respectively, whereas, for example, for solvate VC–Li–VC the corresponding distance (see Fig. 4) is 10.40 Å. In other words, 1 : 1 Li^+–ligand complexes **2**-Li and **6**-Li have more compact molecular structures than a 1 : 2 Li^+–ligand solvate (i.e. carbonate–Li–carbonate) and therefore may be more mobile in a liquid phase in the interelectrode space than the above solvates, ensuring an efficient transport of Li ions to the negative electrode's surface.

Hence, conformationally locked bisphosphonates (similar to Compound **6**) may be suitable additives to electrolyte solutions for Li batteries due to their high complexation ability and increased electrophoretic mobility. The first computational studies, which were strongly oriented on identification of "Li-ion battery-friendly" ligands, singled out organic carbonates as coordinating solvents possessing some desired properties [22a–c]. The present study is the first example of the use of a computation-supported approach to the design of additives for battery electrolytes. Synthesis and electrochemical examination of these novel bisphosphonate additives has been started quite recently [23].

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