Li$^+$−Diglyme Complexes: Barriers to Lithium Cation Migration

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The potential energy surfaces of Li$^+$−diglyme and Li$^+$−triglyme complexes, which are models for poly(ethylene oxide) electrolytes, have been investigated at the HF/6-31G(d) and MP2/6-31+G(d) levels of theory. Eighteen local minima were located that correspond to coordination of Li$^+$ with one to four oxygens. The binding energies of the complexes increase with coordination of Li$^+$ by oxygen, although the binding per Li−O bond decreases. The potential energy surfaces for lithium cation migration between one- and two-coordination sites and two- and three-coordination sites in the Li$^+$−diglyme complexes were investigated, and five transition states were located. While the barriers are small (less than 2 kcal/mol) for lithium cation migration from lower to higher coordination, the barriers are large (20−30 kcal/mol) for higher to lower coordination. The latter corresponds to the barrier for transfer of Li$^+$ from one end of diglyme to the other and is approximately the difference in binding energy of the higher and lower coordination structures. The implications for Li$^+$ migration along a *single* polymer chain in lithium−poly(ethylene oxide) are discussed.

1. Introduction

Salts such as $LiClO_4$ and $LiCF_3SO_3$ may be dissolved in poly(ethylene oxide), $(CH_2CH_2O)_n$, to yield solid electrolytes that exhibit high ionic conductivities.[1,2] The conductivity is largely confined to the amorphous phase. These polymer salts have potential applications in high-energy density batteries, fuel cells, and other electrochemical devices. The ion−polymer and ion−ion interactions in these materials are believed to play an important role in their ionic conductivity but are poorly understood.

Recently, there have been a number of theoretical studies[3−16] aimed at characterizing the ion−polymer and ion−ion interactions in poly(ethylene oxide) (PEO) based polymer electrolytes. Some of the theoretical studies have used molecules such as diglyme and triglyme as models for PEO. Gejji et al.[7] investigated the Li$^+$−diglyme complex, $Li^+[CH_3(OCH_2-CH_2)_2-OCH_3]$, with ab initio molecular orbital theory at the HF/3-21G and HF/6-31G(d,p) levels and reported structures of Li$^+$ coordinated by two and three oxygens, but did not find structures of Li$^+$ coordinated by a single oxygen. Johansson et al.[8] investigated the Li$^+$−triglyme complex, $Li^+[CH_3(OCH_2-CH_2)_3-OCH_3]$, at the HF/3-21G level and reported structures of Li$^+$ coordinated by four oxygens. Related theoretical work has been reported on the complexes of Li$^+$ with 1,2-dimethoxyethane[9,10,16] and dimethyl ether.[11,12] There have also been theoretical investigations of dimethoxyethane[13] and diglyme[14,15] to study conformations of PEO by itself.

Spectroscopic investigations have been reported of the conformations of PEO oligomers (glymes),[17−19] $CH_3(OCH_2-CH_2)_nOCH_3$ for $n = 1, 2, 3$, and 6, and of PEO oligomers complexed with metal salts.[20,21] The studies on the complexes with metal salts suggest that several different conformers of the glymes exist in the presence of cations, that at low temperatures the free "ions" (i.e., Li$^+$ cations) are the dominant species, and that there may be coordination of the ion by more than one chain. Lightfoot, Mehta, and Bruce[22] have reported crystal structures of $(PEO)_3$:$LiCF_3SO_3$ which indicate no links occur between PEO chains, and coordination of the Li$^+$ cation is with both the anion and PEO oxygens. It is not certain yet whether the amorphous phase has a similar structure.

In this paper we report an ab initio molecular orbital study of the potential energy surface of the interaction of a single Li$^+$ cation with different conformers of diglyme as a model for PEO−lithium salt complexes. We have previously reported on the conformers of diglyme using ab initio molecular orbital theory.[14] The purpose of the present work was to determine the transition structures and energy barriers between Li$^+$−diglyme complexes having different Li−oxygen coordination numbers. We are not aware of any theoretical investigations of these barriers, which probably play an important role in the Li$^+$ diffusion in PEO electrolytes. Information on the barriers is also important for molecular dynamics simulations of these materials.[16] The anions present in the polymer salts may also play a role in the lithium migration and will be considered in a subsequent study. Transition structures between local minima corresponding to one-, two-, and three-coordination of Li$^+$ with the oxygens in diglyme were located, and the barriers to Li$^+$ migration were calculated. Structures of complexes corresponding to four-coordination of Li$^+$ with triglyme were also investigated.

2. Theoretical Methods

Ab initio molecular orbital theory[23,24] was used in all of the calculations reported in this paper. Initially, calculations were carried out on a complex of Li$^+$ with dimethyl ether (DME) to assess the reliability of different levels of theory for the Li$^+$−diglyme complexes. The highest level of theory used was G2-(MP2,SVP),[25] which is a variant of G2 theory[26] that uses less computational time and is accurate to about ±3 kcal/mol. On the basis of this assessment, geometry optimizations were carried out at the Hartree−Fock level with the 6-31G(d) basis set [HF/6-31G(d)], and energies were refined at the MP2/6-31+G(d) level, which includes correlation effects based on Moller−Plesset perturbation theory to second order.

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TABLE 1: Energies for the Li$^+$−Dimethyl Ether (DME) Complex at Different Levels of Theory[a]

method[b]	d(Li−O)[c]	ΔE_e	ΔE_0	ΔH_{298}	ΔG_{298}
HF/3-21G//HF/3-21G	1.748	57.8	56.2	56.8	49.7
HF/6-31G(d)//HF/6-31G(d)	1.827	41.4	40.1	40.5	33.7
HF/6-31+G(d)//HF/6-31G(d)	(1.827)	39.7			
HF/6-31+G(d)//HF/6-31+G(d)	1.812	39.7	38.4	38.9	32.1
HF/6-31G(d,p)//HF/6-31G(d)	(1.827)	41.5			
HF/6-31+G(2df,p)//HF/6-31G(d)	(1.827)	39.0			
HF/6-31+G(3df,2p)//HF/6-31G(d)	(1.827)	39.2			
MP2/6-31G(d)//HF/6-31G(d)	(1.827)	43.4			
MP2/6-31+G(d)//HF/6-31G(d)	(1.827)	40.0			
MP2/6-31+G(2df,p)//HF/6-31G(d)	(1.827)	38.6			
MP2/6-311+G(d)//HF/6-31G(d)	(1.827)	40.5			
MP2/6-311+G(2df,p)//HF/6-31G(d)	(1.827)	38.8			
MP2/6-31G(d)//MP2/6-31G(d)	1.840	43.3	42.0	42.4	35.7
MP2/6-311+G(3df,2p)//MP2/6-31G(d)	(1.840)	38.1			
G2(MP2,SVP)	(1.840)	37.9	36.6	37.0	30.2
experiment			39.4 ± 2.5[d]	39.9 ± 2.4[d] 39.4 ± 2[e]	

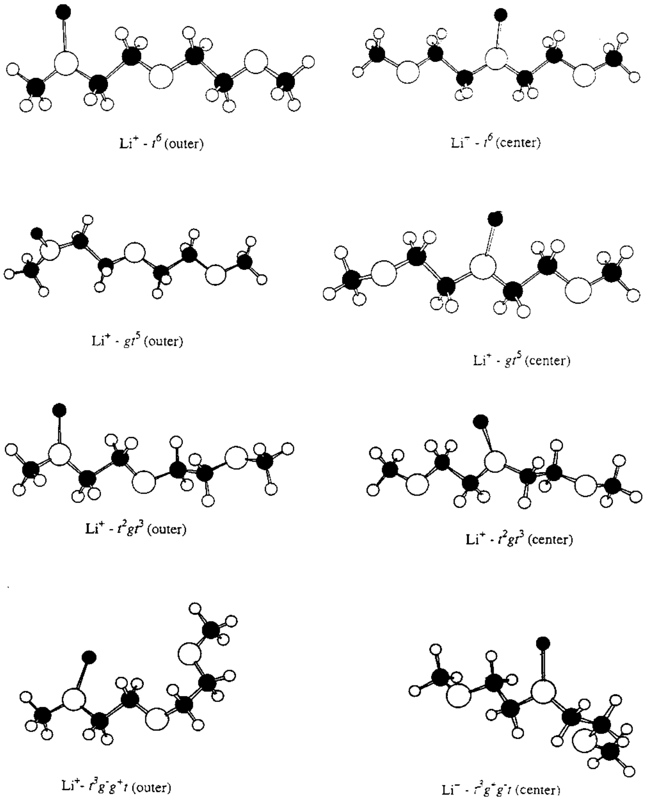
[a] Energies (in kcal/mol) for the reaction DME-Li$^+$ → DME + Li$^+$. Scaled frequencies [0.893 for HF/6-31G(d) and HF/6-31+G(d), 0.94 for MP2/6-31G(d)] used to calculate ΔE_0, ΔH_{298}, and ΔG_{298}. [b] "//" = "at the geometry of". [c] Li−O distance in Å. [d] Reference 11. [e] Reference 28.

Local minima were obtained by full geometrical optimizations, and transition-state structures were determined using traditional transition-state optimization methods based on the Berny algorithm with internal coordinates.[27] The transition-state structures had one imaginary frequency, and the equilibrium structures had all positive frequencies. The interaction energies of the Li$^+$−diglyme (or triglyme) complexes are defined relative to the *all-trans*-diglyme (or triglyme) conformer. The conformers of diglyme in the complexes are denoted by combinations of *t* and *g*, where *t* refers to a trans arrangement of a four-atom-segment dihedral angle between 160° and 180° of the backbone, while *g* refers to a gauche arrangement of a four-atom-segment dihedral angle between 50° and 90°.

3. Results and Discussion

A. Li$^+$−Dimethyl Ether Complex. Table 1 lists the interaction energies of the Li$^+$−dimethyl ether complex at various levels of theory. The most accurate level, G2(MP2,SVP) theory, gives an interaction energy, ΔE_e, of 37.9 kcal/mol. This calculation is effectively at the QCISD(T)/6-311+G(3df,2p) level. Inclusion of zero-point energies and thermal corrections gives a reaction enthalpy at 298 K (ΔH_{298}) of 37.0 kcal/mol. A previous high-level calculation[11] gave 37.8 kcal/mol at 298 K. Experimentally, values of 39.9 ± 2.4 kcal/mol[11] and 39.4 ± 2.0 kcal/mol[28] have been reported for the reaction enthalpy at 298 K. The results in Table 1 indicate that all levels of theory, with the exception of HF/3-21G, give a reasonable account of the interaction energy and Li−O bond distance. The 3-21G basis set does poorly for the energy and Li−O distance as it differs with the more accurate calculations by about 20 kcal/mol for the interaction energy and 0.07 Å for the Li−O distance. In the following calculations, we have optimized geometries at the HF/6-31G(d) level, and the energies of selected structures are refined at the MP2/6-31+G(d) level.

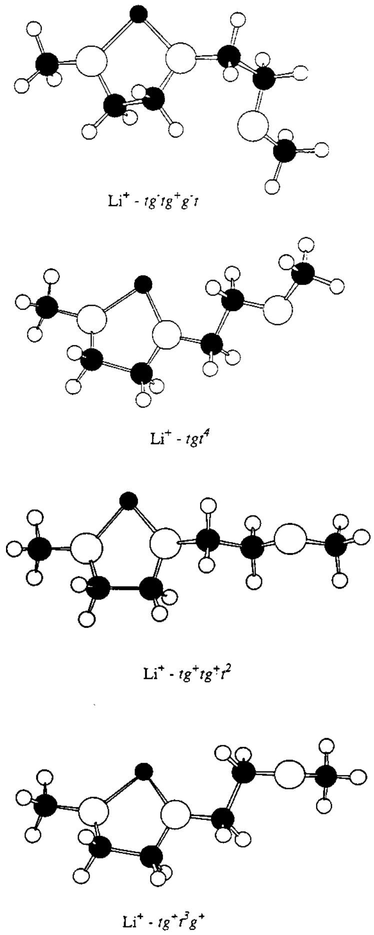
B. Li$^+$−Diglyme Complex. The one-, two-, and three-coordination Li$^+$−diglyme complexes are shown in Figures 1, 2, and 3, respectively, and their interaction energies are listed in Table 2. We located 14 local minima, and there are certain to be additional local minima of similar energy on the potential energy surface because of the large number of conformers of diglyme.[14] The ones that we report should be representative of the different possible structures.



Li$^+$ - t^6 (outer)
Li$^+$ - t^6 (center)
Li$^+$ - gt^5 (outer)
Li$^+$ - gt^5 (center)
Li$^+$ - t^2gt^3 (outer)
Li$^+$ - t^2gt^3 (center)
Li$^+$- $t^3g^-g^+t$ (outer)
Li$^+$ - $t^3g^+g^-t$ (center)

Figure 1. Optimized HF/6-31G(d) structures for coordination of Li$^+$ with a single oxygen in a Li$^+$−diglyme complex.

The eight local minima of the one-coordination complex that were located contain t^6, gt^5, t^2gt^3, $t^3g^-g^+t$, and $t^3g^+g^-t$ conformers of diglyme. For all of the conformers there are two possible locations for the cation: (a) Li$^+$ coordinated with one of the outer oxygens or (b) Li$^+$ coordinated to the center oxygen. No one-coordination structure was found for the tgt^4 diglyme conformer as it forms a two-coordination structure. The Li$^+$−$t^3g^-g^+t$ (outer) structure has the lowest energy of the local minima investigated for the one-coordination complexes. It has an interaction energy (ΔE_e) of 44.0 kcal/mol [45.1 kcal/mol at the MP2/6-31+G(d)//HF/6-31G(d) level]. The other local minima are within 7 kcal/mol (see Table 2). The Li−O bond length is 1.839 Å in the most stable structure and differs by about 0.02 Å in the other structures. The structures containing two gauche dihedrals are more stable than the one-gauche and t^6 structures (see Table 2) because of shorter Li$^+$···O distances



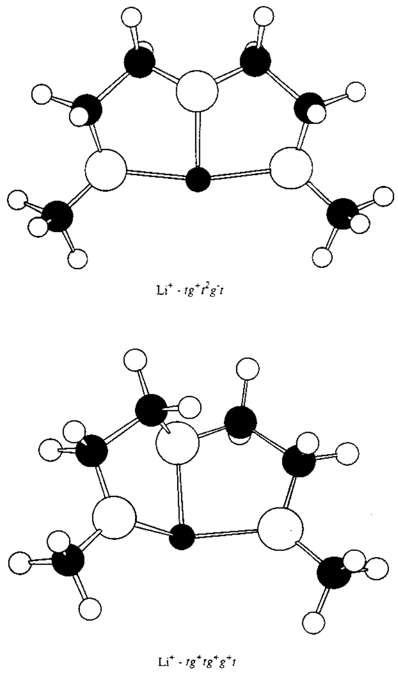
Li^+ - $tg^-tg^+g^-t$

Li^+ - tgt^4

Li^+ - $tg^+tg^+t^2$

Li^+ - $tg^+t^3g^+$

Figure 2. Optimized HF/6-31G(d) structures for coordination of Li^+ with two oxygens in a Li^+−diglyme complex.



Li^+ - $tg^+t^2g^-t$

Li^+ - $tg^+tg^+g^+t$

Figure 3. Optimized HF/6-31G(d) structures for coordination of Li^+ with three oxygens in a Li^+−diglyme complex.

for the oxygens not directly bonded to Li^+. The bond lengths and angles of the conformers change by less than 0.05 Å and 10°, respectively, relative to their values in the corresponding uncomplexed diglymes (i.e., no Li^+). Gejji et al.[7] were unable to locate any one-coordination Li^+−diglyme complexes in their study.

In the case of the two-coordination Li^+−diglyme complex, we located the four structures shown in Figure 2. The interaction energies of two-coordination complexes are in the 63−69 kcal/mol range. The Li^+−$tg^-tg^+g^-t$ complex has the largest interaction energy [ΔE_e = 68.8 kcal/mol at the HF/6-31G(d) level]. The Li−O bond length of two-coordination structures is about 1.87 Å, which is about 0.05 Å longer than in the one-coordination structures. The interaction energy of the most stable two-coordination complex, Li^+−$tg^-tg^+g^-t$, is 24.8 kcal/mol [23.9 kcal/mol at the MP2/6-31+G(d)//HF/6-31G(d) level] larger than the most stable one-coordination structure, Li^+−$t^3g^-g^+t$ (outer). Gejji et al.[7] located only the Li^+−tgt^4 two-coordination complex at the HF/3-21G level. From our calculations at the HF/6-31G(d) level, the Li^+−tgt^4 complex is less stable by 3 kcal/mol than the Li^+−$tg^-tg^+g^-t$ complex.

Two local minima were found for the three-coordination complex, namely, Li^+−$tg^+t^2g^-t$ and Li^+−$tg^+tg^+g^+t$ (see Table 2 and Figure 3). The three-coordination complexes have HF/6-31G(d) binding energies of 87.1 and 85.2 kcal/mol, respectively, with Li−O bond lengths of less than 1.94 Å. The three-coordination complexes are about 20 kcal/mol more stable than the two-coordination complexes because of the third Li−O bond, and the Li−O bond length in the three-coordination complexes is elongated by 0.04 Å or more relative to the two-coordination complexes. Similar three-coordination complex structures were obtained by Gejji et al.[7]

C. Li^+−Triglyme Complex. The Li^+−triglyme complex was investigated with the cation coordinated by four oxygens. The structures of the local minima are shown in Figure 4, and the binding energies are listed in Table 3. The four-coordination complexes have interaction energies of about 103 kcal/mol, which is about 16 kcal/mol more stable than the three-coordination complex with diglyme. The Li−O bond lengths in the four-coordination structures are about 2.00 Å. Johansson et al.[8] have reported the same structures for four-coordination Li^+−triglyme using the 3-21G basis set. The relative stability of the structures with the HF/3-21G basis set is different from the HF/6-31G(d) basis set, as shown in Table 4. We also carried out geometry optimizations at the HF/6-31+G(d) level and found the relative stabilities from this level to be in good agreement with the HF/6-31G(d) calculations. Although the binding energies of the complexes increase with Li^+ coordination number, the binding per Li−O bond in the Li^+−diglyme and Li^+−triglyme complexes decreases from about 40 kcal/mol per Li−O bond to about 25 kcal/mol per bond.

D. Barriers for Li^+ Migration in Diglyme. Bruce and Gray[1] suggested that the migration of the Li^+ cation in PEO electrolytes occurs by segmental motion which involves breaking and making Li−O bonds and allowing the cation to move from one coordination site to another. Lightfoot, Mehta, and Bruce[22] reported that, in the crystal structures of $(PEO)_3{:}LiCF_3SO_3$, there are no links between PEO chains, and coordination of the Li^+ cation is with both the anion and PEO oxygens. We have investigated the potential energy surface of the Li^+−diglyme complex to find the transition structures between one- and two-coordination sites (pathway I) and between two- and three-coordination sites (pathway II). These pathways are models for Li^+ migration along a single PEO chain. Schematics of the potential energy surfaces for pathways I and II are shown in Figures 5 and 6, respectively. The energies are summarized in Table 5.

TABLE 2: Equilibrium Structures and Energies for Li^{+}$-$Diglyme Complexes[a]

			ΔE_e[d,e]	
structure	d(Li$-$O)[b]	E_e[c]	HF/6-31G(d)	MP2/6-31+G(d)
One-Coordination				
$\mathrm{Li}^{+}{-}t^{3}g^{-}g^{+}t$(outer)	1.839	$-$467.201 19(0)	44.0	45.1
$\mathrm{Li}^{+}{-}t^{3}g^{+}g^{-}t$(center)	1.823	$-$467.197 53(0)	41.8	
$\mathrm{Li}^{+}{-}t^{6}$(outer)	1.830	$-$467.193 73(0)	40.6	39.4
$\mathrm{Li}^{+}{-}gt^{5}$(outer)	1.824	$-$467.194 73(0)	40.0	
$\mathrm{Li}^{+}{-}t^{6}$(center)	1.834	$-$467.193 73(0)	39.4	
$\mathrm{Li}^{+}{-}t^{2}gt^{3}$(center)	1.828	$-$467.193 46(0)	39.2	
$\mathrm{Li}^{+}{-}t^{2}gt^{3}$(outer)	1.832	$-$467.192 63(0)	38.7	
$\mathrm{Li}^{+}{-}gt^{5}$(center)	1.837	$-$467.190 66(0)	37.5	
Two-Coordination				
$\mathrm{Li}^{+}{-}tg^{-}tg^{+}g^{-}t$	1.875, 1.866	$-$467.240 55(0)	68.8	69.0
$\mathrm{Li}^{+}{-}tgt^{4}$	1.876, 1.880	$-$467.236 21(0)	66.0	
$\mathrm{Li}^{+}{-}tg^{+}tg^{+}t^{2}$	1.882, 1.872	$-$467.235 08(0)	65.3	
$\mathrm{Li}^{+}{-}tg^{+}t^{3}g^{+}$	1.876, 1.878	$-$467.232 30(0)	63.6	
Three-Coordination				
$\mathrm{Li}^{+}{-}tg^{+}t^{2}g^{-}t$	1.917, 1.933, 1.938	$-$467.269 83(0)	87.1	86.6
$\mathrm{Li}^{+}{-}tg^{+}tg^{+}g^{+}t$	1.933, 1.932, 1.931	$-$467.266 79(0)	85.2	

[a] All structures are local minima from HF/6-31G(d) optimizations. See Figure 2 for structures. Number of imaginary frequencies in parentheses. [b] Li$-$O distance in Å. [c] Total HF/6-31G(d) energy in hartrees. [d] $\Delta E_e = E(\mathrm{Li}^{+}) + E(t^{6}) - E(\mathrm{Li}^{+}{-}\mathrm{diglyme})$ where t^{6} is the *all-trans*-diglyme conformer (in kcal/mol). At the HF/6-31G(d) level, $E(\mathrm{Li}^{+}) = -7.235\,54$ hartrees and $E(t^{6}) = -459.895\,43$ hartrees. [e] MP2/6-31+G(d) results are at the HF/6-31G(d) geometries.

TABLE 3: Equilibrium Structures and Energies for Li^{+}$-$Triglyme Complexes[a]

			ΔE_e[d,e]	
	d(Li$-$O)[b]	E_e[c]	HF/6-31G(d)	MP2/6-31+G(d)
$\mathrm{Li}^{+}{-}tg^{+}t^{2}g^{-}t^{2}g^{+}t$	2.006, 2.015 2.014, 2.007	$-$620.210 36(0)	103.0	104.6
$\mathrm{Li}^{+}{-}tg^{-}t^{2}g^{+}tg^{+}g^{+}t$	1.977, 1.992 2.015, 1.981	$-$620.208 59(0)	101.9	
$\mathrm{Li}^{+}{-}tg^{+}g^{+}tg^{+}tg^{+}g^{+}t$	1.963, 1.998 1.998, 1.962	$-$620.207 12(0)	101.0	
$\mathrm{Li}^{+}{-}tg^{-}t^{2}g^{+}g^{+}tg^{+}t$	2.010, 1.983 2.051, 1.986	$-$620.206 83(0)	100.8	

[a] All structures are local minima from the HF/6-31G(d) optimizations. See Figure 4 for structures. Number of imaginary frequencies in parentheses. [b] Li$-$O distance in Å. [c] Total HF/6-31G(d) energy in hartrees. [d] $\Delta E_e = E(\mathrm{Li}^{+}) + E(t^{9}) - E(\mathrm{Li}^{+}{-}\mathrm{triglyme})$, where t^{9} is the *all-trans*-triglyme conformer (in kcal/mol). At the HF/6-31G(d) level, $E(\mathrm{Li}^{+}) = -7.235\,537$ and $E(t^{9}) = -612.810\,68$ hartrees.

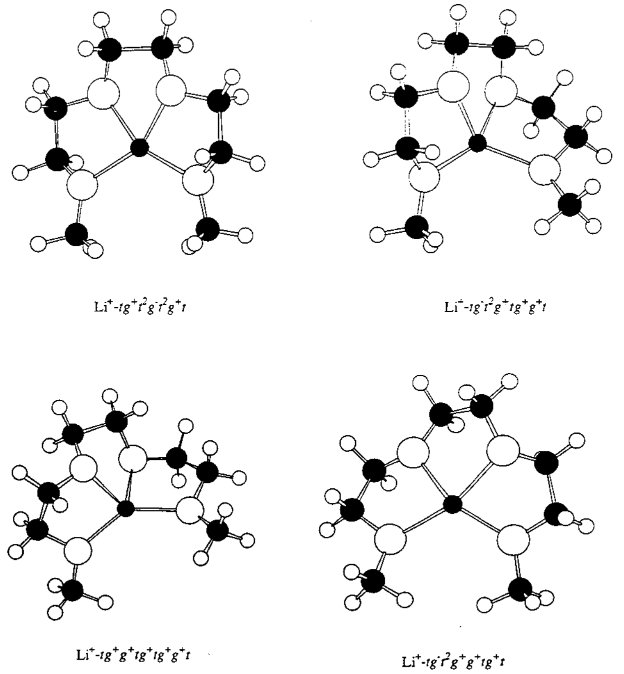


Figure 4. Optimized HF/6-31G(d) structures for coordination of Li^{+} with four oxygens in a Li^{+}$-$triglyme complex.

TABLE 4: Relative Energies (in kcal/mol) of Li^{+}$-$Triglyme Complexes

	HF/3-21G	HF/6-31G(d)	HF/6-31+G(d)
$\mathrm{Li}^{+}{-}tg^{+}t^{2}g^{-}t^{2}g^{+}t$ (T1)	0.00	2.03	2.11
$\mathrm{Li}^{+}{-}tg^{-}t^{2}g^{+}tg^{+}g^{+}t$ (T2)	2.14	2.21	2.18
$\mathrm{Li}^{+}{-}tg^{+}g^{+}tg^{+}tg^{+}g^{+}t$ (T3)	0.03	1.11	1.18
$\mathrm{Li}^{+}{-}tg^{-}t^{2}g^{+}g^{+}tg^{+}t$ (T4)	2.03	0.00	0.00

Pathway I (Figure 5) contains three one-coordination local minima and two two-coordination local minima. The pathway corresponds to movement of the lithium cation from one end of the diglyme to the other. We located the four transition structures, each having one imaginary frequency, between the five local minima. The structures for the minima and the barriers are shown in Figure 5. The reaction coordinate corresponds to rotation about an OCCO dihedral angle that *makes* a second Li$-$O bond (one-coordination → two-coordination) or *breaks* the second Li$-$O bond (two-coordination → one-coordination). The barriers for one-coordination → two-coordination are small (0.2$-$1.7 kcal/mol), while the barriers for two-coordination → one-coordination are large (24$-$28 kcal/mol). The barrier between the *two* two-coordination complexes ($\mathrm{Li}^{+}{-}tg^{-}tg^{+}g^{-}t \rightarrow \mathrm{Li}^{+}{-}tgt^{4}$) in pathway I is 28.3 kcal/mol [27.1 kcal/mol at the MP2/6-31+G(d)//HF/6-31G(d) level].

Pathway II (Figure 6) is symmetric and contains the two-coordination structure, $\mathrm{Li}^{+}{-}tgt^{4}$, and three-coordination structure, $\mathrm{Li}^{+}{-}tg^{-}t^{2}g^{+}t$. The transition-state structure between these structures is a $\mathrm{Li}^{+}{-}td^{+}t^{2}g^{-}t$ structure. The dihedral angle OCCO, d, is 130° and is the reaction coordinate for this pathway. The barrier is 1.8 kcal/mol [1.0 kcal/mol at the MP2/6-31+G-

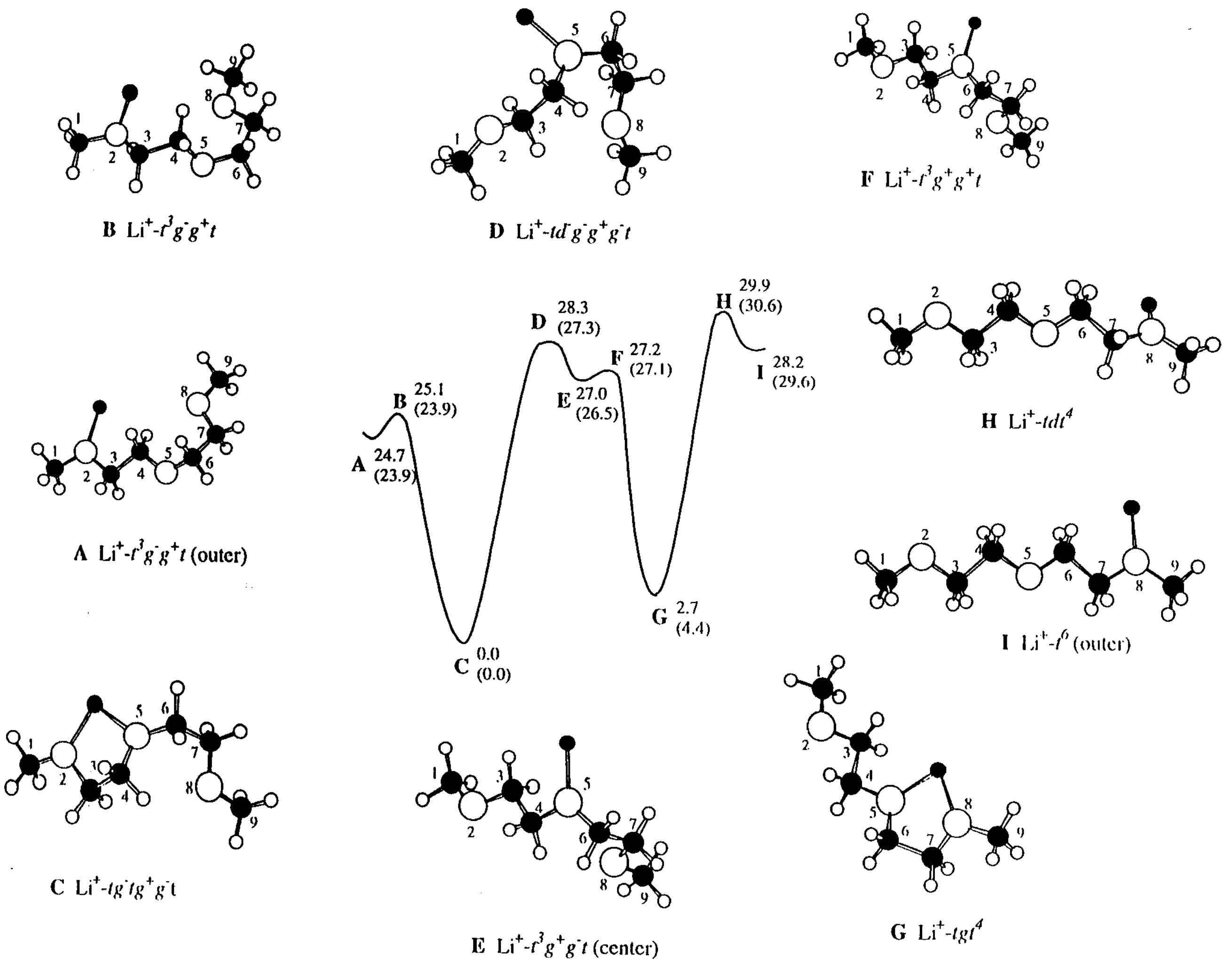


Figure 5. Pathway for lithium cation migration between one- and two-coordination sites of the Li$^+$$-$diglyme complex. The numbers (1, 2, 3, ..., 9) denote the atoms of the backbone of diglyme. The letters represent the structures at the local minima and barriers. The values represent the relative energies at the HF/6-31G(d) and MP2/6-31+G(d) levels (the latter are in parentheses).

TABLE 5: Transition-State (TS) Energies for Li$^+$ Migration in Diglyme

	TS structure[a]	E_e[b]	$\Delta E_e^{TS}(n \rightarrow n+1)$[c] HF/6-31G(d)	$\Delta E_e^{TS}(n \rightarrow n+1)$[c] MP2/6-31+G(d)
one- to two-coordination pathway				
Li$^+$$-$$t^3g^-g^+t$(outer) → Li$^+$$-$$tg^-tg^+g^-t$	Li$^+$$-$$t^3g^-g^+t$[e]	−467.200 62(1)	0.4	0.0
Li$^+$$-$$t^3g^+g^-t$(center) → Li$^+$$-$$tg^-tg^+g^-t$	Li$^+$$-$$td^-g^-g^+g-t$[f]	−467.195 43(1)	1.3	0.8
Li$^+$$-$$t^3g^+g^-t$(center) → Li$^+$$-$$tgt^4$	Li$^+$$-$$t^3g^+g^+t$[g]	−467.197 24(1)	0.2	0.6
Li$^+$$-$$t^6$(outer) → Li$^+$$-$$tgt^4$	Li$^+$$-$$tdt^4$[h]	−467.192 97(1)	1.7	1.0
two- to three-coordination pathway				
Li$^+$$-$$tgt^4$ → Li$^+$$-$$tg^-t^2g^+t$	Li$^+$$-$$td^+t^2g^-t$[i]	−467.233 34(1)	1.8	1.0

[a] Transition-state structures (see Figures 5 and 6). [b] In hartrees. [c] Energy barrier (in kcal/mol) for n-coordination → $(n + 1)$-coordination. [d] Energy barrier (in kcal/mol) for $(n + 1)$-coordination → n-coordination. [e] Reaction coordinate, t, is ∠2345 (160° at the barrier). [f] Reaction coordinate, d^-, is ∠2345 (−136° at the barrier). [g] Reaction coordinate, g^+, is ∠5678 (103° at the barrier). [h] Reaction coordinate, d, is ∠5678 (130° at the barrier). [i] Reaction coordinate, d^+, is ∠5678 (130° at the barrier).

(d)//HF/6-31G(d) level] for two-coordination → three-coordination and 22.9 kcal/mol [23.0 kcal/mol at the MP2/6-31+G(d)//HF/6-31G(d) level] for three-coordination → two-coordination.

The results for pathways I and II indicate that migration of the lithium cation from one coordination site to the next occurs with the making or breaking of Li$-$O bonds. Pathway I (Figure 5) illustrates how this can result in movement of the cation from one end of the diglyme to the other end. The barrier between the *two* two-coordination sites is about 28 kcal/mol when it goes through the one-coordination site; i.e., it is approximately the difference in binding energies of structures having n and $(n + 1)$ Li$^+$ coordination. If longer chains are used, a similar Li$^+$ migration between three-coordination sites could be shown for pathway II. In this case, the diglyme results indicate that the barrier would be about 23 kcal/mol between two sites. While we have not investigated four-coordination → three-coordination barriers, the differences in binding energies of the three- and four-coordination complexes in Tables 2 and 3 suggest that it would be >16 kcal/mol. These trends suggest that smaller barriers to migration could be obtained by higher Li$-$oxygen coordination, due to the decrease in binding per Li$-$O bond with increasing coordination. However, since the coordination

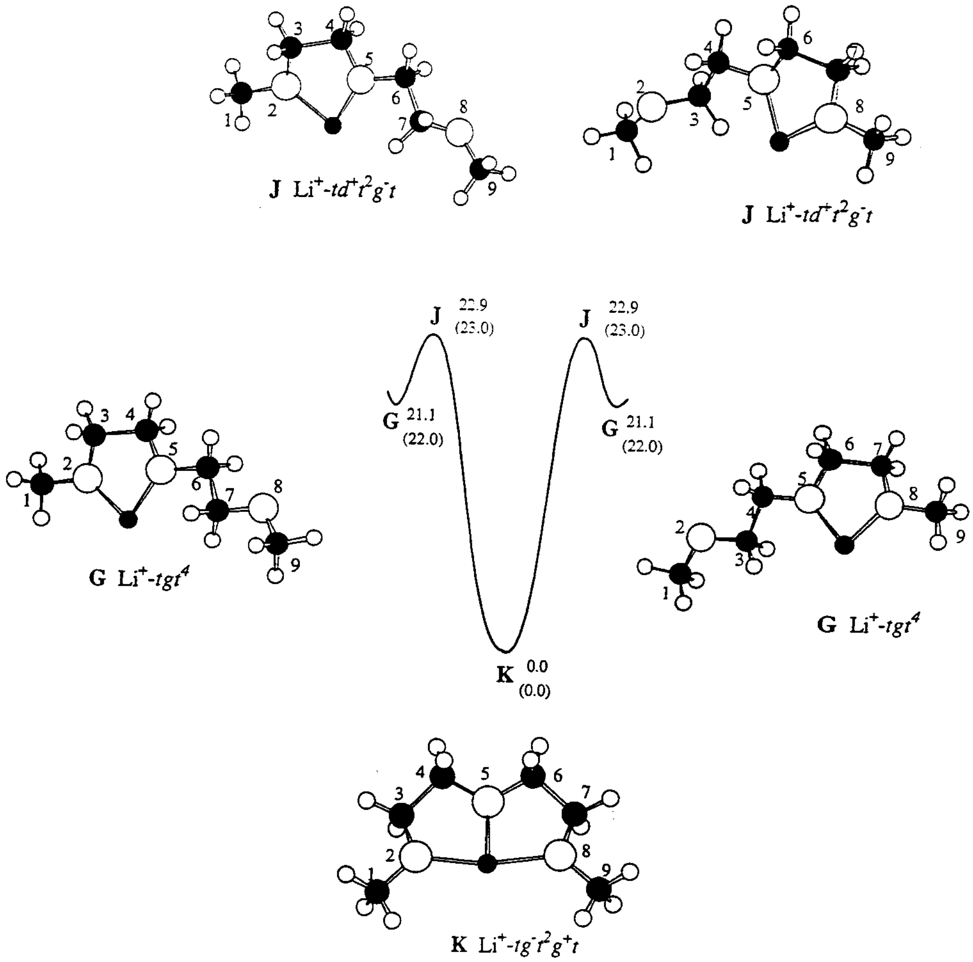


Figure 6. Pathway for lithium cation migration between two- and three-coordination sites of the Li$^+$−diglyme complex. The numbers (1, 2, 3, ..., 9) denote the atoms of the backbone of diglyme. The letters represent the structures at the local minima and barriers. The values represent the relative energies at the HF/6-31G(d) and MP2/6-31+G(d) levels (the latter are in parentheses).

number that can be attained with a single chain is probably limited to three or four, these results suggest that Li$^+$ movement along a *single* polymer chain in poly(ethylene oxide) electrolytes would have large barriers and may be prohibitive. Lower barriers might be achieved through interaction of the cation with more than one chain that would allow larger coordination numbers to be attained. The effect of anions on the barriers is uncertain and will be considered in future studies.

4. Conclusions

We have presented a study of the potential energy surface, at the HF/6-31G(d) and MP2/6-31+G(d) levels of theory, of Li$^+$−diglyme and Li$^+$−triglyme complexes as models for poly(ethylene oxide)-based polymer electrolytes. The following conclusions can be drawn from this study:

1. There are many local minima on the potential energy surface of the Li$^+$−diglyme and Li$^+$−triglyme complexes with coordination of Li$^+$ by up to four oxygen and different conformations of the diglyme or triglyme. The different conformations have similar stabilities for the same coordination number. For example, four structures were located for lithium cation coordination by two oxygens in diglyme with binding energies in the range 64−69 kcal/mol. The binding energies of the complexes increase with coordination number, although the binding per Li−O decreases.

2. The barriers for lithium cation migration between one- to two-coordination and two- to three-coordination complexes are small (less than 2 kcal/mol) for lower → higher coordination and large (20−30 kcal/mol) for higher → lower coordination. The latter corresponds to the barrier for transfer of Li$^+$ from one end of diglyme to the other end.

3. The barrier for cation migration from one coordination site to another corresponds approximately to the difference in binding energies of the complexes having different lithium−oxygen coordination numbers. On the basis of the results for Li$^+$ complexes with diglyme and triglyme, the barriers for migration along a *single* PEO chain are likely to be 20−30 kcal/mol. The results suggest that higher Li$^+$ coordination with oxygen, which may be achieved through involvement of two or more chains, could reduce the migration barriers.

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