# Elementary Steps of Lithium Ion Transport in PEO via Quantum Mechanical Calculations

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A first attempt to model lithium ion transport along a poly(ethylene oxide), PEO, chain by quantum mechanical calculations is reported here. The PEO oligomer diglyme ($CH_3O-(CH_2CH_2O)_2-CH_3$) has been used as a model system for a PEO polymer. Different transition states have been calculated with ab initio methods for conformational changes leading to changes in coordination number for lithium from three to two in the lithium−diglyme complexes. The imaginary frequencies for the transition states and the associated intrinsic reaction coordinate paths have been calculated. Energy barriers of ∼90 kJ $mol^{-1}$ are found along all the paths. The use of a bidentate structure as an intermediate between the two different tridentate structures is suggested. All structures have been optimized at the HF/6-31G** level of theory, and the total energy calculations have been performed at different levels of sophistication (HF/6-31G** and MP2/6-311+G**//HF/6-31G**). Furthermore, two equivalent transition states for the next oligomer in size, triglyme, complexed with a lithium ion have been calculated to test and show the stability of the calculations of the present model when elongating the oligomer. The results are compared with NMR data for the activation energies of conformational transformations in complexed PEO. A transport path for $Li^+$ along a single PEO chain involving tri- to "tetra-" to tridentate coordination changes with small energy differences has been calculated.

## Introduction

Mixtures of poly(ethylene oxide), PEO, with lithium salts of low lattice energy have gained much interest as polymer electrolytes—materials that, owing to their high ionic conductivity, mechanical properties, and processing flexibility, are suitable in various electrochemical applications such as solid-state thin film batteries and electrochromic windows.[1] There is, however, a lack of basic understanding of the conduction mechanism of lithium ions in these preferably amorphous PEO polymer electrolytes. Dynamic properties of polymer electrolytes have earlier been calculated by well-known computational methods like Monte Carlo (MC) and molecular dynamics (MD) simulations.[2,3] However, these methods do not explicitly treat the electrons and are, therefore, in some cases not sufficient to give the needed and/or relevant chemical information. To allow the electronic structure to be explicitly treated in quantum mechanical calculations, the system must, however, be severely limited in size for computational reasons. For this purpose diglyme ($CH_3O-(CH_2CH_2O)_2-CH_3$) and triglyme ($CH_3O-(CH_2CH_2O)_3-CH_3$) have been used as model systems for a PEO long-chain polymer.[4,5] The present study is based on the idea that conformational changes of the polymer chain promote the lithium ion transport via the making and breaking of oxygen−lithium bonds.[6,7] The total transport of lithium ions probably consists of both interchain and intrachain movements, the latter being modeled in this work by the use of a single oligomer chain. Such movements are mainly affected by the changes in the local surroundings of the cation (i.e., the coordinating ether oxygens). A possible anion-assisted lithium ion transport as suggested in ref 3 has not been explicitly treated in the present work.

For a short fragment, $-O-CH_2-CH_2-O-$, occurring in a glyme or a PEO chain, the conformation can be specified by the torsion angles about the three central bonds O−C, C−C, and C−O. These angles can be of an anti (a) or gauche (g) character. The C−C torsion angles are denoted with capital letters to simplify recognition. In previous calculations on complexes between a metal ion and a polyether, where all consecutive ether oxygens are involved in bonding to the metal ion, only two kinds of conformations were obtained for the basic oxyethylene unit, $aG^{\pm}a$ and $g^{\pm}G^{\pm}a$.[4,5] Units of O−C−C−O with $aG^{\pm}a$ conformation with alternating signs are often found in crown ether complexes.[8] In some complexes and other situations where a sharper folding of the chain is required, the $g^{\pm}G^{\pm}a$ conformation, referred to as a "genuine corner", is found.[9]

In a calculation of possible minimum energy structures for complexes between a lithium ion and diglyme, two distinct combinations of the basic oxyethylene conformations were found with tridentate coordination and with nearly the same energy.[4] The conformational sequences of these two cases are $aG^-aaG^+a$ and $aG^+g^+aG^+a$ and were referred to as structure **1** (D1) and **2** (D2), respectively. Different combinations of these two prototype structures were then used in calculations of minimum energy structures of triglyme with several alkali and alkaline earth cations.[5]

Conformational changes in a long-chain PEO system leading to a lithium ion transport or a stepwise complexation in a lithium ion oligoether system involve both the breaking and the formation of lithium oxygen bonds. Lithium−diglyme is the simplest system where transition states and reaction paths in an elementary step can be studied for such processes when the change from tridentate to bidentate coordination has to be considered. Also, conformational changes resulting in a transfer from the tridentate structures D1 and D2 are clearly of interest.

There is a number of crystal structure determinations of complexes between a metal ion and glymes or low molecular weight poly(ethylene glycol)s where conformations are found,

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**TABLE 1: Total (au) and Relative Energies (kJ mol$^{-1}$) for Lithium Di- and Triglyme Complexes and Transition States**

| | computational method | | | |
|---|---|---|---|---|
| structure | HF/6-31G**// HF/6-31G** | HF/6-31G**// HF/6-31G** | MP2/6-311+G**// HF-6-31G** | MP2/6-311+G**// HF-6-31G** |
| Li$^+$−diglyme | | | | |
| Li$^+$−D1 | −467.291 664 | 0 | −468.890 599 | 0 |
| Li$^+$−D1 | −467.288 660 | 7.9 | −468.888 019 | 6.8 |
| Li$^+$−bidentate | −467.258 088 | 88.2 | −468.857 389 | 87.2 |
| Li$^+$−TS1 | −467.255 160 | 95.9 | −468.855 414 | 92.4 |
| Li$^+$−TS2 | −467.253 355 | 100.6 | −468.854 199 | 95.6 |
| Li$^+$−triglyme | | | | |
| Li$^+$−T1 | −620.235 106 | 8.4 | −622.364 715 | 7.1 |
| Li$^+$−T4 | −620.238 299 | 0 | −622.367 405 | 0 |
| Li$^+$−tridentate | −620.211 724 | 69.8 | −622.339 126 | 74.3 |
| Li$^+$−tridentate2 | −620.208 616 | 77.9 | −622.336 525 | 81.1 |
| Li$^+$−TS3 | −620.208 655 | 77.8 | −622.336 900 | 80.1 |
| Li$^+$−TS4 | −620.203 914 | 90.3 | −622.333 470 | 89.1 |

which could be described as different combinations of structures D1 and D2.[10−16] In the crystal structures of $(PEO)_3LiCF_3SO_3$ [17] and $(PEO)_3Li[N(CF_3SO_2)_2]$,[18] the lithium ions are coordinated to three ether oxygens of the same chain and two oxygens belonging to the anions. Contrary to what was observed for the short-chain oligomers, the conformational sequences in the latter structures are not combinations of structures D1 and D2 but contain the sequence $(aG^+aaG^+aaG^-a)_n$. It is, however, probable that in amorphous systems containing more ether oxygens per lithium ion and in plasticized systems, the PEO chains have more freedom to adopt the sequences of structures D1 and D2.

Crown ether or acyclic oligoethers have been suggested to act as carriers for lithium ions in plasticized polymer electrolytes.[19] The occurrence of the complexes at the electrodes of lithium batteries was also suggested to minimize unfavorable initial reactions at the surface of the electrodes that otherwise could lead to damage of the electrode.[19] The dynamics of the complexation is clearly of vital importance under such circumstances.

## Computational Method

Ab initio Hartree−Fock (HF) self-consistent field (SCF) molecular orbital calculations have been performed using the GAUSSIAN 94 program.[20] The basis set used for the HF calculations was 6-31G**, and all geometries were optimized at this computational level. Second-order Møller−Plesset perturbation function calculations (MP2)[21] were carried out for the obtained stationary points to include electron correlation to better evaluate the total energies using the larger 6-311+G** basis set, MP2/6-311+G**//HF/6-31G** (Table 1). The four different transition states (Table 2) were obtained by using the quasi synchronous transit method QST3,[22] which uses the input from the relevant minima (reactant and product) and an estimate of the transition state. Several different guesses were obtained from single-point calculations at the same computational level. The transition states were characterized by vibrational frequency calculations, and intrinsic reaction path (IRC) calculations were performed to confirm that the transition states truly connect the reactant and the product. The step size parameter in these calculations was varied, the final calculations performed with a step size of 30. The conformations of the reactants and products have in most cases been calculated before but with simpler basis sets.[4,5] The notation of the conformer sequences occurring in the text and tables below refers to the dihedral angles as described in the Introduction.

For evaluation of the suggested lithium migration mechanism, Hartree−Fock calculations employing the 3-21G* basis set were performed with the Spartan program.[23] In these calculations the lithium ion position was optimized and all other atoms kept fixed in specific positions to mimic a simplified reaction path.

**TABLE 2: Selected Geometry Parameters for the Obtained Transition States (HF/6-31G**)[a]**

| | Li$^+$−TS1 | Li$^+$−TS2 | Li$^+$−TS3 | Li$^+$−TS4 |
|---|---|---|---|---|
| Bond Lengths (*r*) in Å | | | | |
| *r*(Li−O1) | 4.064 | 4.367 | 4.054 | 4.378 |
| *r*(Li−O2) | 1.882 | 1.869 | 1.945 | 1.923 |
| *r*(Li−O3) | 1.879 | 1.879 | 1.919 | 1.932 |
| *r*(Li−O4) | | | 1.939 | 1.935 |
| Bond Angles (*a*, *d*) in deg | | | | |
| *a*(O1−Li−O2) | 57.1 | 47.4 | 57.5 | 47.6 |
| *a*(O1−Li−O3) | 143.7 | 133.6 | 139.4 | 132.4 |
| *a*(O2−Li−O3) | 89.2 | 89.5 | 85.4 | 86.2 |
| *a*(O1−Li−O4) | | | 134.7 | 120.4 |
| *a*(O2−Li−O4) | | | 163.7 | 141.1 |
| *a*(O3−Li−O4) | | | 85.2 | 86.5 |
| *d*(C1−O1−C2−C3) | −170.7 | −186.4 | −170.8 | −186.8 |
| *d*(O1−C2−C3−O2) | −131.0 | 125.0 | −130.9 | 124.7 |
| *d*(C2−C3−O2−C4) | −174.5 | −184.7 | −172.5 | −184.5 |
| *d*(C3−O2−C4−C5) | 174.3 | 161.4 | 176.0 | 163.9 |
| *d*(O2−C4−C5−O3) | 49.5 | 47.5 | 51.9 | 51.6 |
| *d*(C4−C5−O3−C6) | 167.0 | 166.5 | −166.6 | −168.7 |
| *d*(C5−O3−C6−C7) | | | 167.9 | 88.4 |
| *d*(O3−C6−C7−O4) | | | −50.3 | 45.8 |
| *d*(C6−C7−O4−C8) | | | −168.8 | 168.1 |
| imaginary freq (cm$^{-1}$) | −112 | −120 | −107[a] | −118[a] |

[a] At HF/3-21G*.

## Results and Discussion

In the following sections we will first investigate possible reaction paths and transition states in lithium−diglyme complexes involving bidentate−tridentate and tridentate−tridentate transitions. We will then repeat the process for lithium−triglyme complexes to test the stability of the results to changes in chain length, and on the basis of this, we will discuss a possible lithium ion transport mechanism.

**Conformational Transitions in Lithium−Diglyme Complexes**. *Path 1: Transition from Tridentate Structure **1** to Bidentate Coordination*. Starting from the global minimum geometry of the tridentate lithium−diglyme complex, Li$^+$−D1,[4] with the oligomer chain in an $aG^-aaG^+a$ conformation, only one major internal change, in one of the dihedral angles O−C−C−O, is needed to construct the bidentate minimum, $aAaaG^+a$, Li$^+$−bidentate.[4] Investigation of the total energy as a function of this dihedral angle by single-point calculations gave a local energy maximum at about 140°, which was then used as a starting value in a calculation with the QST3 option in search

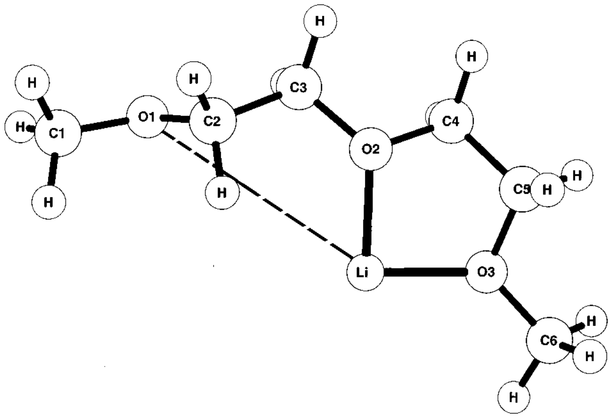

**Figure 1.** Geometry of transition state $Li^+-TS1$.

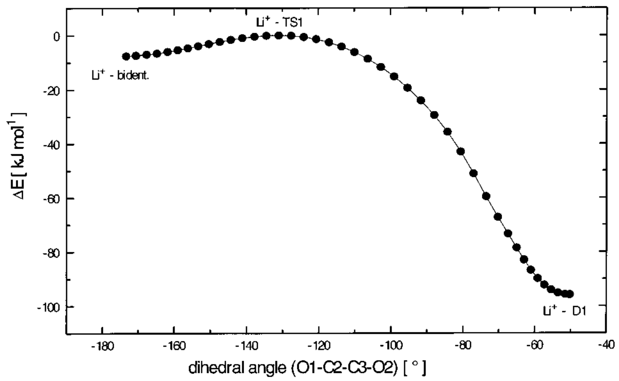

**Figure 2.** Calculated IRC path for $Li^+-TS1$.

of the relevant transition state. The resulting geometry of the transition state ($Li^+-TS1$) is given in Table 2 and Figure 1. The transition state was verified by a vibrational frequency calculation that gave an imaginary frequency of $-112$ $cm^{-1}$. It was clear that the transition state was the one searched for, i.e., connecting the reactant and the product, both from an IRC calculation (Figure 2) and from analysis of the vibrational mode, which is a mode almost solely contributed to by a changing O−C−C−O dihedral angle.

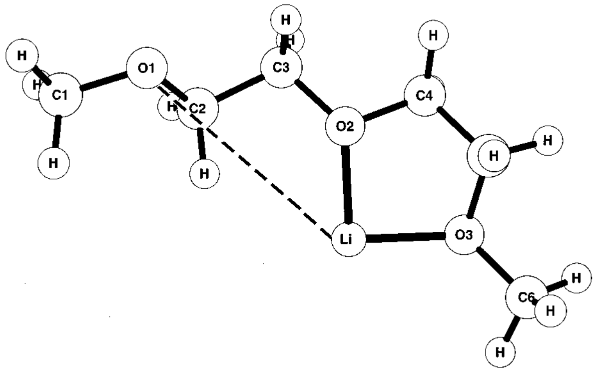

**Figure 3.** Geometry of transition state $Li^+-TS2$.

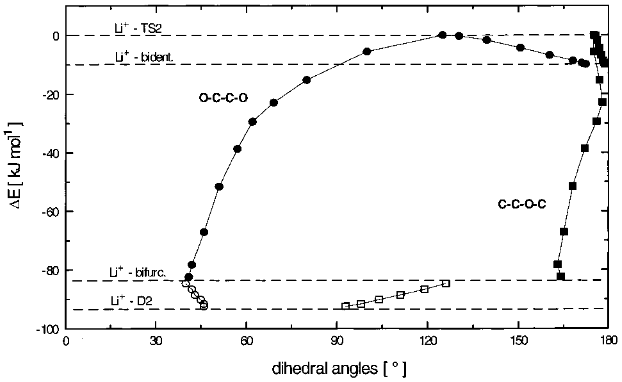

**Figure 4.** Calculated IRC path for $Li^+-TS2$ with circles for the O−C−C−O dihedral and squares for the C−C−O−C dihedral.

**TABLE 3: Selected Geometry Parameters in the Vicinity of the Bifurcation Point (HF/6-31G**)**

| | $Li^+-bifurc$ |
|---|---|
| Bond Lengths ($r$) in Å | |
| $r$(Li−O1) | 1.981 |
| $r$(Li−O2) | 1.861 |
| $r$(Li−O3) | 1.980 |
| Bond Angles ($a$, $d$) in deg | |
| $a$(O1−Li−O2) | 82.2 |
| $a$(O1−Li−O3) | 164.1 |
| $a$(O2−Li−O3) | 82.2 |
| $d$(C1−O1−C2−C3) | 160.8 |
| $d$(O1−C2−C3−O2) | 41.2 |
| $d$(C2−C3−O2−C4) | 163.8 |
| $d$(C3−O2−C4−C5) | 153.7 |
| $d$(O2−C4−C5−O3) | 39.0 |
| $d$(C4−C5−O3−C6) | 160.1 |

*Path 2: Transition from Tridentate Structure **2** to Bidentate Coordination.* The conformational change involving a single dihedral angle as calculated above is not the only conformational transformation occurring in this system. From our earlier calculations[4] a second stable tridentate complex of lithium and diglyme can be found, $Li^+-D2$, with the conformational sequence $aG^+g^+aG^+a$ and an energy slightly higher than that of $Li^+-D1$. Conversion of this complex into the bidentate complex clearly requires at least two internal dihedral angles to be altered. Single-point calculations were made, varying both relevant dihedrals systematically, to construct a surface to locate the appropriate starting geometries for the transition state involved in this conversion. The starting geometries were used as earlier in calculations with the QST3 option, and the only resulting transition state ($Li^+-TS2$) is shown in Table 2 and Figure 3. For this transition state we expected a larger energy barrier than for $Li^+-TS1$, since we have changed two dihedrals to reach the transition state. Indeed, the barrier going from the bidentate complex to the transition state $Li^+-TS2$ is somewhat higher, +8.4 kJ $mol^{-1}$, than the corresponding value for $Li^+-TS1$, 5.2 kJ $mol^{-1}$. However, the large energy barrier when going from the tridentate structure to the transition state is somewhat lower, 88.8 kJ $mol^{-1}$ along path 2 compared with 92.4 kJ $mol^{-1}$ along path 1. The imaginary frequency was $-120$ $cm^{-1}$ and an IRC calculation confirmed that it was the correct transition state (Figure 4). During this IRC calculation, the part of the path leading to the $Li^+-D2$ structure reaches a bifurcation point, $Li^+-bifurc$ (Table 3 and Figure 5), where the geometry of the complex has an approximate $C_2$ symmetry (end of filled symbols). From this bifurcation point the IRC calculation can follow either one of two equivalent paths. The products will be two identical $aG^+g^+aG^+a$ lithium−diglyme complexes, the difference between these final products being which part of the diglyme that changes its dihedral angles from the bifurcation sequence. Since the IRC calculation cannot be performed at a bifurcation point, the imaginary frequencies at the bifurcation point were calculated. After that, the mode involving a conformational change of the oligomer chain was used to force a displacement along the mode from this point and a new IRC calculation was made that reached the expected product(s). The other part of the reaction path reaches the expected bidentate reactant structure without any complications.

*Transition from Tridentate to Tridentate Coordination.* Can

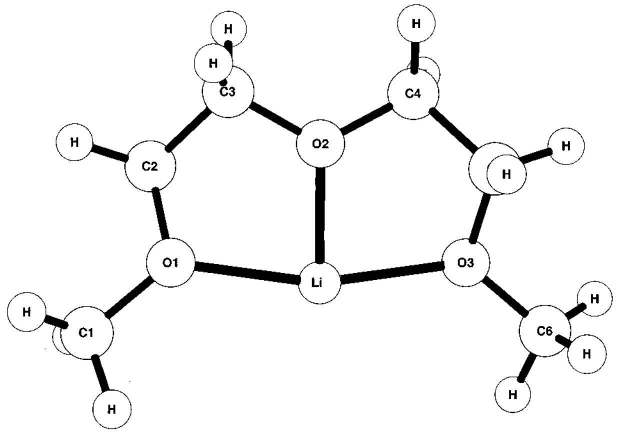

**Figure 5.** Li$^+$−bifurc geometry.

there be transition states where the coordination number of lithium does not change? The answer is yes; the conversion between the aG$^-$aaG$^+$a, Li$^+$−D1, and the aG$^+$g$^+$aG$^+$a, Li$^+$−D2, structures would certainly be such a case. However, when searching for such a transition state, we always arrived at either one of the two already obtained transition states. Thus, we suggest that a conversion of this type occurs via the bidentate structure as an intermediate.

**Transitions in Triglyme Complexes**. Following our earlier proposal that all conformational sequences of longer glymes with all their oxygens coordinated can be derived from combinations of the two diglyme tridentate structures,[5,24] unless steric hindrance occurs, a prolongation of the oligomer chain in the transition state calculations also seems appropriate. If these calculations are to be valid as a model for ion transport in polymers, then independence of oligomer size is a requirement; the structures of the transition states and the energy barriers must be approximately the same, independent of the number of ethylene oxide units in the chain. Also, they must be rather insensitive to the actual coordination number of the cation but not to the type of cation. The complexes of lithium and triglyme in the sequences of aG$^-$aaG$^+$aaG$^-$a,[5] Li$^+$−T4, and the tridentate structure aAaaG$^+$aaG$^-$a, Li$^+$−tridentate (comparable to the bidentate lithium−diglyme complex), were therefore calculated and used as starting structures to locate a transition state. An initial guess of the transition state was based on the knowledge obtained from the calculations on diglyme and the QST3 calculation option employed. The resulting transition state is listed as Li$^+$−TS3 (Table 2 and Figure 6). Having the O−C−C−O angle basically the same (+0.1°) and the small energy barrier differing by only 0.6 kJ mol$^{-1}$ compared with the analogous diglyme case, our proposal seems to be correct. The larger barrier, on the other hand, differs more, 12.3 kJ mol$^{-1}$, probably because of the lower energy per bond as the number of ether oxygens coordinated increases. This value is thus suggested to converge when the optimum coordination number for lithium in these systems is reached, which is suggested to be five.[24] The calculation of the imaginary frequency was made at the HF/3-21G* level for computational reasons but still shows only a 5 cm$^{-1}$ difference.

This same approach was made for the other type of transition state starting from the sequences aG$^+$g$^+$aG$^+$ag$^+$Ga, Li$^+$−T1, and the tridentate structure aAaaG$^+$a g$^+$G$^+$a, Li$^+$−tridentate 2, which both were calculated and used as starting structures. One transition state was obtained and is listed as Li$^+$−TS4 (Table 2 and Figure 7).

Also in this case the differences compared with the comparable diglyme case in geometry and imaginary frequency are small; 0.3° in the relevant O−C−C−O dihedral and 2 cm$^{-1}$ in frequency. The small energy barrier differs by only 0.4 kJ mol$^{-1}$, and this further strengthens our belief of the size independence.

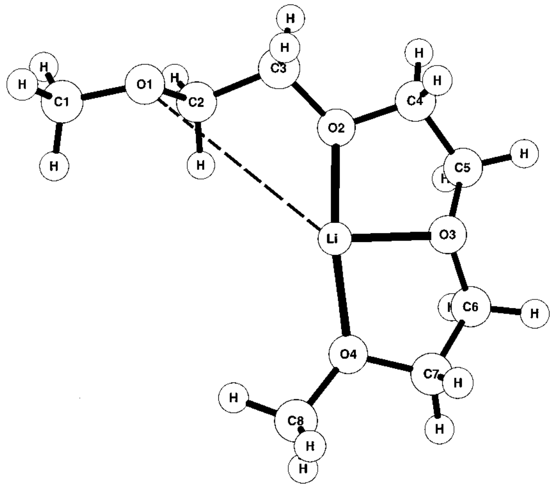

**Figure 6.** Geometry of transition state Li$^+$−TS3.

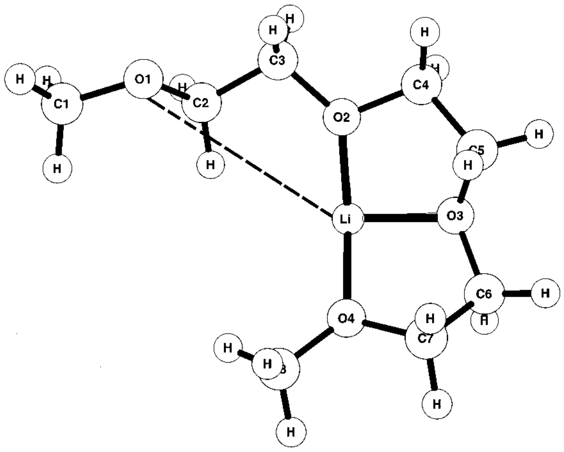

**Figure 7.** Geometry of transition state Li$^+$−TS4.

**Comparison with Experimental Results**. Earlier NMR experiments show that the introduction of a salt into the polymer matrix drastically changes the chain mobility and the associated activation energies for chain movement by the coordination of the cations. Even though, to our knowledge, there are no reported measurements of activation energies for lithium-containing systems such as the present ones, we can compare with analogous systems with Sr$^{2+}$ having about the same charge-to-radius ratio as lithium (both ~1.7). From NMR measurements of $T_{1\rho}$ relaxation data for protons of the PEO chain (MW = 4 × 10$^6$) of $Sr[N(CF_3SO_2)_2]_2PEO_9$, an activation energy of 61 kJ mol$^{-1}$ in the amorphous phase was evaluated.[25] In that system, the glass transition temperature ($T_g$) has been determined to be 0 °C,[26] and the correlation times calculated from the relaxation measurements follow an Arrhenius behavior in the temperature interval investigated (25−120 °C). The experimentally determined activation energy, 61 kJ mol$^{-1}$, can be compared with our calculated one of 80 kJ mol$^{-1}$ for a change from a tetra- to tridentate coordination in the lithium−triglyme complex. The experimental result is an average over all types of conformational changes, and some of these do not necessarily involve metal ion coordinated ether oxygens. This probably explains the main difference between our calculated and the experimentally determined activation energies. Furthermore, in the experiments, ion-pairing with the imide anions must be

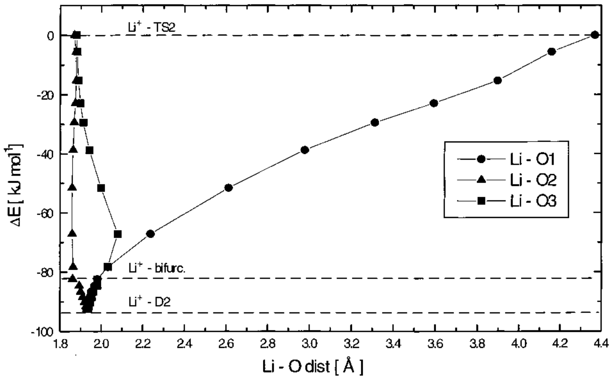

**Figure 8.** Relative energy as a function of the Li$^+$−O distances for the IRC path of Li$^+$−TS2.

considered possible, which also should lower the probability of conformational changes involving a completely ether oxygen coordinated cation.

**Possible Lithium Ion Transport Mechanism**. A mechanism based on the local coordination around the lithium cation in a polyether system will be discussed, and it will be based on the above-mentioned quantum mechanical calculations of the reaction paths 1 and 2 for conformational changes in the lithium−glyme systems. For the first type of path calculated, where a rather simple change in only one dihedral angle occurs, there is no obvious way for making lithium move along the chain. The second type of path calculated does offer, on the other hand, an interesting possibility for lithium ion transport. The occurrence of a bifurcation point in the reaction path, which is only 6 kJ mol$^{-1}$ above the Li$^+$−D2 structure, is certainly an interesting feature. Following the lithium−oxygen distances along the reaction path shows the possibility of a lithium ion transport of 0.15 Å by a change from Li$^+$−D2 to a point somewhat higher in energy than the bifurcation point (Figure 8). This change can be accomplished with little energy cost, and furthermore, the system can choose any one of the two symmetry-related paths starting from the bifurcation point. In a real polymer or longer oligomer this results in two nonequivalent positions of lithium in a local Li$^+$−D2 structure sequence (in the diglyme case they are truly equivalent). By a cooperative change for several consecutive O−C−C−O units, one can imagine a "channel" for lithium ion transport being formed.

**TABLE 4: Oligomer Backbone Geometry Changes for the Constructed Lithium Migration Path**[a]

| structure | d(O1−C2−C3−O2) | d(C2−C3−O2−C4) | d(C3−O2−C4−C5) | d(O2−C4−C5−O3) | d(O3−C6−C7−O4) |
|---|---|---|---|---|---|
| A1 | 45.0 | 90.0 | 195.0 | 50.0 | 180.0 |
| A2 | 45.0 | 90.0 | 190.0 | 50.0 | 100.0 |
| A3 | 44.0 | 95.0 | 188.0 | 48.0 | 92.0 |
| A4 | 44.0 | 100.0 | 184.0 | 47.0 | 85.0 |
| A5 | 43.0 | 110.0 | 181.0 | 46.0 | 79.0 |
| A6 | 43.0 | 115.0 | 177.0 | 45.0 | 72.0 |
| A7 | 42.0 | 120.0 | 174.0 | 44.0 | 66.0 |
| A8 | 42.0 | 130.0 | 170.0 | 43.0 | 59.0 |
| A9 | 41.0 | 140.0 | 167.0 | 42.0 | 53.0 |
| A10 | 41.0 | 150.0 | 163.0 | 41.0 | 46.0 |
| A11 | 40.0 | 165.0 | 160.0 | 40.0 | 40.0 |

| structure | d(O1−C2−C3−O2) | d(O2−C4−C5−O3) | d(C4−C5−O3−C6) | d(C5−O3−C6−C7) | d(O3−C6−C7−O4) |
|---|---|---|---|---|---|
| A11 | 40.0 | 40.0 | 160.0 | 165.0 | 40.0 |
| A12 | 46.0 | 41.0 | 163.0 | 150.0 | 41.0 |
| A13 | 53.0 | 42.0 | 167.0 | 140.0 | 41.0 |
| A14 | 59.0 | 43.0 | 170.0 | 130.0 | 42.0 |
| A15 | 66.0 | 44.0 | 174.0 | 120.0 | 42.0 |
| A16 | 72.0 | 45.0 | 177.0 | 115.0 | 43.0 |
| A17 | 79.0 | 46.0 | 181.0 | 110.0 | 43.0 |
| A18 | 85.0 | 47.0 | 184.0 | 100.0 | 44.0 |
| A19 | 92.0 | 48.0 | 188.0 | 95.0 | 44.0 |
| A20 | 100.0 | 50.0 | 190.0 | 90.0 | 45.0 |
| A21 | 180.0 | 50.0 | 195.0 | 90.0 | 45.0 |

[a] Dihedral bond angles (*d*) in degrees.

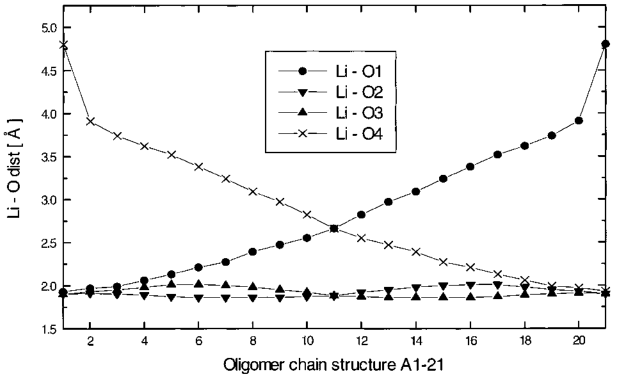

**Figure 9.** Modeled reaction path using Table 4 values of dihedral angles.

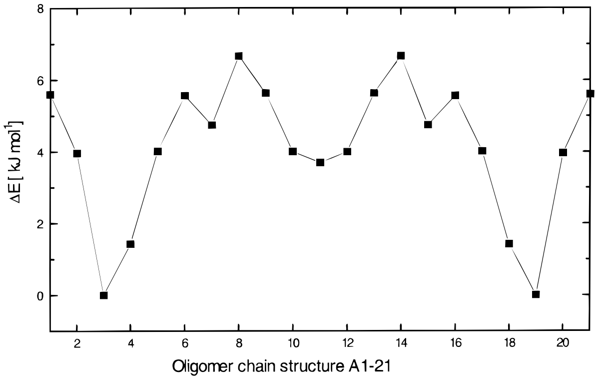

**Figure 10.** Relative energy as a function of the modeled reaction path.

To evaluate a possible detailed mechanism along the suggested lines, calculations were performed for lithium−triglyme complexes with different oligomer backbone dihedral angles as listed in Table 4. In these model calculations of our suggested transport path, A1, is a tricoordinated structure (∼Li$^+$−D2) of lithium−triglyme with a C6−C7 dihedral angle of 180° for the uncoordinated ether part. In the following sequences we mainly turn the C3−O2 and the C4−O2 dihedrals of the coordinated part and the C6−C7 dihedral of the uncoordinated part in a cooperative manner to reach a structure with all C−C dihedrals equal (40°) and all C−O dihedrals within 160−165° (A11). These values make the chain conformation resemble the bifurcation point structure as obtained for lithium−diglyme (Li$^+$−bifurc). With all three C−C dihedral angles equal, this structure has $C_2$ symmetry just as in the vicinity of the bifurcation point structure of diglyme. By letting the C5−O3 and O3−C6 dihedral angles move toward the value for the Li$^+$−D2 structure (195° and 95°) and the C1−C2 dihedral toward 180°, we will be back in a conformation equivalent to the initial one (A21) but with the big difference that lithium has moved along the chain (Figure 9). The energy changes along this path are below 10 kJ mol$^{-1}$ (Figure 10), and a further optimization would most likely result in even smaller changes. The suggested path for lithium transport thus involves successive coordination changes from tri- to "tetra-" to tridentate coordination, and each step results in a lithium ion transfer of ∼0.15 Å. This can be compared with MD results[3] stating the Li$^+$ transport being performed by consecutive oxygens with coordination changes from penta- to tetra- to pentadentate coordination along one polymer strand as one of the possible mechanisms. In the MD work, however, no detailed information on the energy required for such a transport is given and there is also a suggestion that an anion or a oxygen from another strand can be present around the lithium ion during an intermediate state. The above suggested model does, however, not exclude any of these involvements. There is certainly space available at a tri- or tetracoordinated lithium ion for further coordination.

## Conclusions

The use of transition-state calculations for analyzing the complexation of a lithium ion to two different highly flexible oligomers and a possible mechanism for lithium ion transport in PEO has been demonstrated. The calculations on complexes between a lithium ion and diglyme result in different possibilities of complexation and also suggest a bidentate structure as an intermediate between the two tridentate complexes. The calculations on the longer glyme, triglyme, prove that geometry and energy barriers for one of the obtained transition states are stable toward changes in the oligomer size. Clearly, calculations on even longer glymes with higher coordination numbers for lithium would be of use to verify this proposal.

The vibrational calculations verify the validity of the transition states, and the IRC calculations show the connection of the transition states to the reactants and products, and furthermore, one of the transition states and its associated IRC calculation reveal a possibility of a conformational change and associated lithium ion transport via a bifurcation point. A possible low-energy transport path for $Li^+$ has been traced involving coordination changes from tri- to "tetra-" to tridentate coordination between $Li^+$ and triglyme.

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