Quantum-Chemical Study of the Structure, Aggregation, and NMR Shifts of the Lithium Ester Enolate of Methyl Isobutyrate

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Abstract: *Ab initio* HF-SCF calculations of the equilibrium geometries, energies, and ^{13}C NMR shifts of various monomeric, dimeric, and tetrameric aggregates of the lithium ester enolate of methyl isobutyrate (MIB-Li) were performed. It is shown that an enolate-like nonplanar structure of the MIB-Li monomer, in which a π-interaction between the Li atom and C═C double bond is realized, is more stable than the planar enolate-like structure. The energies of the two MIB-Li dimers consisting of the planar and nonplanar MIB-Li monomers, respectively, were found to be nearly the same. However, the experimental ^{13}C NMR shifts for the MIB-Li dimer in THF agree with those calculated for the planar stereoisomer. For the MIB-Li tetramer, two structures were found, namely, a cubic and a nearly flat eight-membered-ring structure. The calculated ^{13}C NMR shifts for the two tetramers are very similar, but the cubic tetramer is considerably more stable than the flat one at the highest level of theory. Semiempirical MNDO and PM-3 calculations of both specific and nonspecific solvation energies of MIB-Li aggregates solvated by THF were carried out. It was found that the solvation effects decrease in the series monomer > dimer > tetramer. The calculated total solvation energies for MIB-Li aggregates are used to estimate the solvent effects on the *ab initio* relative energies of the aggregates.

Introduction

Ester enolates are important models of the active centers in the anionic polymerization of acrylates and methacrylates. Thus, the knowledge of the structure of these models in polar and nonpolar solvents is important for the understanding of the corresponding polymerizations. ^{13}C and ^{7}Li NMR studies by Wang et al. of the ester enolate of methyl isobutyrate (methyl α-lithioisobutyrate, MIB-Li) in THF solution have revealed an equilibrium between two species, one of them being the dimer of the other.[1] As vapor phase osmometry data have shown that the aggregation degree of MIB-Li in THF at room temperature is about 3.5,[2] it has been concluded[1] that this equilibrium is between the tetramer $(MIB\text{-}Li)_4$ and the dimer $(MIB\text{-}Li)_2$. It has been found that at room temperature the tetramer $(MIB\text{-}Li)_4$ prevails, whereas at low temperature (−78 °C) the tetramer $(MIB\text{-}Li)_4$ and the dimer $(MIB\text{-}Li)_2$ coexist.[1] The ΔH and ΔS values for the reaction of tetramer dissociation into two dimers have been measured:[1] $\Delta H = -8.8$ kJ/mol and $\Delta S = -55$ J/(mol·K).

In a more recent ^{1}H, ^{6}Li, ^{7}Li, and ^{13}C NMR study of MIB-Li in THF,[3] it has been claimed that two different trimers $(MIB\text{-}Li)_3$ exist in the system in an equilibrium with the tetramer $(MIB\text{-}Li)_4$ and the dimer $(MIB\text{-}Li)_2$. For the tetramer to dimer dissociation, the values of $\Delta H = -9.2$ kJ/mol and $\Delta S = -52$ J/(mol·K) have been found[3] in good agreement with Wang's data.[1] These values mean that the dimer is thermodynamically more stable than the tetramer, and the tetramer prevailing at room temperature is due to its higher entropy compared to the dimer. It seems obvious that the only reason for this entropic relationship between the tetramer and the dimer could be a higher degree of specific solvation of the dimer by THF molecules, as compared to the tetramer, causing the decrease in the solvent entropy.

Experimental data for ester enolates in nonpolar solvents like toluene are more scarce than those for THF solution. Only ethyl α-lithioisobutyrate (EIB-Li) shows a good solubility in toluene. However, there are clear indications that the aggregation degree is higher in this solvent than in THF. The suggestion that the lack of the specific solvation by toluene is responsible for this, seems to be reasonable. Thus, a value of degree of aggregation higher than 6 has been obtained by vapor phase osmometry measurements of EIB-Li.[2] Therefore, one should expect the tetramer to be considerably more stable than the dimer in toluene solution and even the formation of hexamers and octamers should be possible.

In order to interpret the NMR data[3] on aggregation of MIB-Li in THF, MNDO[4] calculations of several possible dimeric, trimeric, and tetrameric MIB-Li structures, both nonsolvated and solvated specifically by dimethyl ether (a model for THF), were carried out by Dybal and Kříž.[5] In that paper the dimeric and trimeric MIB-Li structures with ester-like MIB-Li units:

$$(CH_3)_2C(Li){-}COOCH_3$$

have been shown to be more stable than the corresponding aggregates with enolate-like MIB-Li units:

$$(CH_3)_2C{=}C(OLi){-}OCH_3$$

These MNDO results seem to be expectable due to the well-

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known MNDO tendency to considerably overestimate the strength of the C−Li bond.[6] However, they are unlikely from the point of view of known crystal structures of similar compounds.[17]

Ab initio calculations of different MIB-Li aggregates should be helpful in this context. They allow the calculation of the structures and energies of possible aggegrates very accurately. Due to computational costs, so far only Hartree−Fock Self-Consistent Field (HF-SCF or simply SCF) calculations for the monomer have been published.[5] Two slightly different structures of the monomer MIB-Li were found at the 6-31G** level. In one of these structures, the Li atom is situated almost in the plane formed by the carbonyl bond and the C_α atom. In the other one, the Li atom lies above this plane forming a kind of π-complex with the enolate fragment. The latter structure is more stable by ca. 3.6 kcal/mol than the former at the 6-31G** level. Both structures have to be considered as enolate-like, as they are characterized by an almost double C−C bond (the bond lengths are 1.35 and 1.38 Å for these structures) and by a considerably shorter distance between the Li atom and the carbonyl oxygen atom as compared to that between the Li atom and the C_α atom.

No calculations for higher aggregates have been published so far. Recent advances in computational chemistry and computer hardware allow for the *ab initio* treatment of systems with 60−100 atoms without symmetry and even more in cases where symmetry may be exploited.

In this study, we present the results of HF-SCF calculations of the structures, energies, and NMR chemical shifts of the MIB-Li monomer, dimer, and tetramer. The energetics has then been improved through single-point second-order Moller−Plesset perturbation theory (MP2)[7] calculations. These gas phase results should be compared to the data on the MIB-Li or EIB-Li state of aggregation in nonpolar solvents like toluene. To assess the influence of polar solvents like THF, semiempirical calculations which incorporate solvent effects have been performed. Both specific solvation (i.e., the formation of $(\text{MIB-Li})_n{\cdot}x\text{THF}$ complexes with various n and x values) and nonspecific solvation (i.e., the effect caused by the solvent as a dielectric continuum) have been considered. It should be noted that the difference in the nonspecific solvation energies for the tetramer and the dimer may affect the equilibrium between them.

Methods of Computation

Ab Initio Calculations. All *ab initio* SCF geometry optimizations and GIAO-SCF-NMR[8] shielding calculations were performed using the Karlsruhe TURBOMOLE[9] quantum chemistry package on a 6-processor SGI Power Challenge system. For the geometry optimizations, we used the TURBOMOLE split valence (SV) (7s3p)/[3s2p] basis sets[10] augmented with one d-polarization function for carbon (d exponent: 0.8) and oxygen (d exponent: 1.2), a SV (7s)/[3s] basis set for lithium augmented with one p-polarization function with exponent 0.17, and a double-ζ (6s)/[2s] basis set for hydrogen. We refer to this basis set (which is comparable to a 6-31G* basis set) as SVD.

The computation of NMR shifts requires more extended basis sets than structure optimizations. For ^{13}C-SCF-NMR shifts, basis sets of TZP quality are sufficient. In the present calculations, the Karlsruhe TZP basis sets[10] for Li, O, and C have been used. For hydrogen, the same DZ basis set as for the structure optimizations has been used. This basis set is referred to as TZD. The contraction patterns were for Li (10s1p)/[6s1p] and for C and O (10s6p1d)/[6s3p1d]. Typically, the accuracy of ^{13}C-SCF-NMR shift calculations in simple organic molecules is in the range of 1−3 ppm, but deviations up to 7−10 ppm may occur in more complicated cases.[11]

To improve the energetics, single point MP2 calculations with the SVD basis set were performed. Since this basis set is rather small for correlated calculations, the quality of the energetics has been checked by MP2/TZD calculations on the dimers. It is found that the results do not differ significantly as discussed below.

Atomic charges are calculated through the Mulliken population analysis of the HF-SCF wave function.

Semiempirical Calculations. All semiempirical calculations were carried out on an IBM RS-6000 workstation employing a version of the MOPAC 6.0 program specially modified for the inclusion of the nonspecific solvation effects by the solvent continuum.[12] In this program a solute molecule is placed into a cavity of complex shape in the solvent continuum. This cavity is formed by the intersecting van der Waals spheres surrounding the solute atoms. An algorithm for the self-consistent determination of a solvent polarization by a solute charge distribution and reverse polarization of the solute by the polarized solvent is realized.[12]

The MNDO[4] and PM-3[13] parameters were used. Recently published PM-3 parameters for Li[14] have been shown to be much better in describing Li−C interactions than MNDO ones. It seemed interesting to compare the MNDO results and PM-3 results for the systems with strong O−Li interactions.

The geometries of all structures studied, both nonsolvated and solvated specifically, were completely optimized in vacuum using the EF (eigenvector following) procedure. These vacuum-optimized geometries were used further for the calculation of the nonspecific solvation energy, E_{nss}, as the difference between the values of heat of formation, ΔH_f, calculated in the solvent continuum and in vacuum.

For the calculations of E_{nss} the following values of a solvent dielectric, ϵ, constant were used: 7.42 for THF at room temperature and 12.13 for THF at −78 °C.[15]

Results and Discussion

***Ab Initio* Results (Gas Phase).** In order to find the most stable structures of the MIB-Li monomer, dimer, and tetramer, HF-SCF geometry optimizations were performed. No symmetry or other constraints were applied in the calculations of the monomer and the tetramer. For the dimer, C_2 symmetry was assumed. The nature of the minimum was checked by a calculation of the second derivatives of total energy. No negative eigenvalues were found which shows that the dimer really has C_2 symmetry. To allow for direct comparison with available experimental data, NMR chemical shifts of all optimized structures were calculated by means of the GIAO (gauge including atomic orbitals)-SCF-ansatz.[8]

In all systems considered here, we found at least two stable structures for each aggregate. For the monomer and the dimer, the two structures differ by a planar and a nonplanar arrangement of the C═C double bond and the Li−O bond. In the nonplanar structures, there is a direct interaction between the π-system and one lithium atom, whereas this direct (attractive) interaction is missing in the planar systems. However, these structures are very close in energy which shows that the system does not gain much energy through this attractive interaction. All calculated energies (as well as bond distances and angles) are collected in

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Table 1. Stabilization Energies per Monomer, ΔE, of MIB-Li Aggregates at Various Levels of Theory

	ΔE, kJ/mol					
	monomer		dimer		tetramer	
	planar	nonplanar	planar	nonplanar	planar	cubic
SCF/SVD//SCF/SVD	2.1	0	−121.1	−117.3	−168.4	−174.1
SCF/TZD//SCF/SVD	1.6	0	−115.3	−110.2	−159.8	−161.5
MP2/SVD//SCF/SVD	12.5	0	−117.1	−120.4	−176.3	−186.2

Table 2. Comparison of Important Bond Lengths (Å) for the SCF/SVD Optimized Geometries of MIB-Li Aggregates

	monomer		dimer		tetramer	
	planar	nonplanar	planar	nonplanar	planar	cubic
C═C	1.356	1.387	1.342	1.362	1.335	1.335
C═O	1.279	1.262	1.298	1.284	1.297	1.312
Li−O	1.721	1.802	1.804	1.943	1.80/1.90	1.91/1.94
L−C$^{\alpha}$	2.964	2.246	3.119	2.458	3.606	3.241

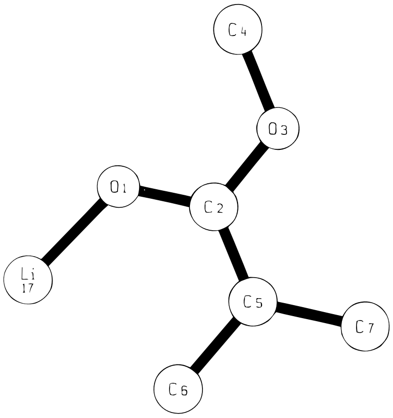

Figure 1. Optimized geometry of the planar MiBLi monomer at the SCF level with SVD basis as described in Methods of Computation. Hydrogens are omitted for clarity. Bond distances and angles are given as supporting information.

the supporting information. For all considered structures the stabilization energies per monomer,

$$\Delta E = E[(\text{MIB-Li})_n]/n - E(\text{MIB-Li})$$

reflecting the relative stabilities of the structures, are presented in Table 1.

In the tetrameric aggregates, the coordination number of the Li atoms is enlarged. Consequently, no interaction between any C═C bond and Li atoms is found. The bond distances (C═C and C═O, Table 2) found in all structures are more typical of enolate-like rather than of ester-like compounds.

We now discuss the various kinds of aggregates in more detail.

(a) Monomer. Dybal and Křiž[5] already presented HF-SCF calculations for the planar (Figure 1) and the nonplanar (Figure 2) monomer. Since our results are very similar, we refer to their work for a discussion of structural details etc. In addition to their work, we performed MP2/SVD//MP2/SVD (MP2 energies at the completely MP2 optimized geometries with SVD basis) and single point MP2 energy calculations at the SCF geometry (MP2/SVD//SCF/SVD) to improve the assessment of the relative stability of the structures. It turned out that the nonplanar structure is the more stable one (by 13.6 kJ/mol) at the MP2/SVD//MP2/SVD level. This energy gap is too small to allow for predictions concerning the stability at ambient temperatures and in polar solvents.

Table 3. Comparison of Calculated (SCF/TZD//SCF/SVD Level of Theory) and Experimental ^{13}C NMR Chemical Shifts (in ppm with Respect to TMS) of MIB-Li Aggregates

monomer

	planar	nonplanar
C═O	169.6	176.7
C$_{\alpha}$	50.8	44.5

dimer

	planar	EIB-Li,[a] planar for comparison	nonplanar	expt: −80 °C, THF[1]
C═O	164.1	163.9	164.5	158.9
C$_{\alpha}$	66.8	67.2	58.3	65.8

tetramer

	planar	cubic	expt: EIB-Li,[a] −60 °C, toluene[19]	expt: −80 °C, THF[1]
C═O	161.9	162.3/162.4	158.5/159.2	160.5
C$_{\alpha}$	78.8	77.9/78.1	76.5/78.5	72.5/73.5

[a] Ethyl α-lithioisobutyrate.

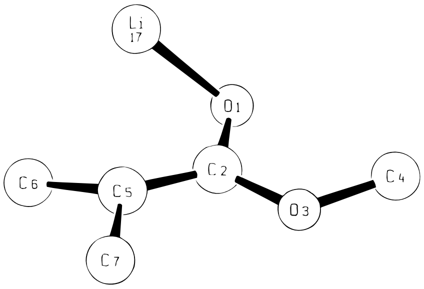

Figure 2. Optimized geometry of the nonplanar MiBLi monomer at the SCF level.

More pronounced differences can be found in the calculated ^{13}C-NMR shifts (Table 3). We find a high-field shift of the α-carbon (50.8 ppm) with a Mulliken charge of −0.49 for the planar structure compared to 44.5 ppm and a charge of −0.66 for the nonplanar one. It should be noted that the MIB-Li monomer itself is rather hypothetical and perhaps only stable in the gas phase. However, its structure may serve as a model for the structure of the living ends of non-aggregated PMMA-Li chains, the existence of the latter ones during the polymerization of MMA being very probable on the basis of kinetic and viscosity studies.[16] This may be due to the steric hindrance exerted by the polymer chain. Moreover, the results obtained here for the MIB-Li monomer may be transferred to the higher aggregates. It is shown by these results that the α-carbon of the nonplanar monomer has a stronger carbanion character than that of the planar one and is thus assumed to have a higher activity in anionic polymerization. This carbanion character is reflected in both the charges and the calculated NMR shifts. To make this point clear, we consider the shifts of an olefinic double bond. The olefinic carbons are electrophilic and usually show shifts at $\delta \approx 130-140$ ppm. The closer to the olefinic region the shift is, the less carbanion character the α-carbon has. Here, in the case of the planar structure, we find shifts of the α-carbon at $\delta \approx 50.8$ ppm and, for the nonplanar structure, 44.5 ppm (less olefinic than the planar one). This means that the nonplanar structure has more carbanion character than the planar one, it is more nucleophilic.

(b) Dimer. The SCF geometry optimizations of the dimeric systems yield similar results. Two dimer structures were found, namely a planar structure (Figure 3) and a nonplanar one (Figure

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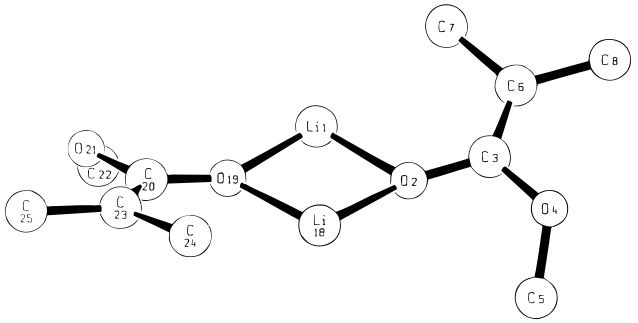

Figure 3. Optimized geometry of the planar MiBLi dimer at the SCF level.

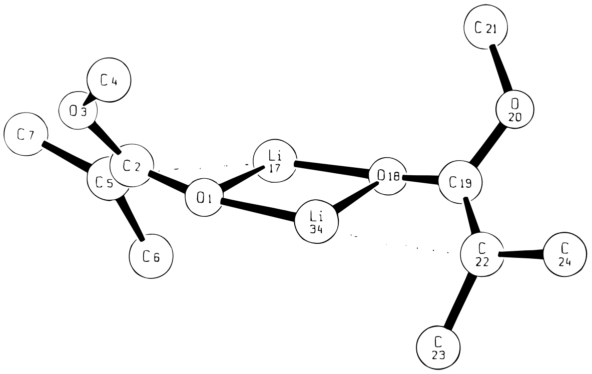

Figure 4. Optimized geometry of the nonplanar MiBLi dimer at the SCF level.

4). On the best level of theory (MP2/TZD//SCF/SVP), the two structures are almost isoenergetic; the difference is about 4 kJ/mol (Table 1), the nonplanar structure being more stable at the correlated level. This difference is smaller than our expected errors (roughly 10 kJ/mol). It should be noted also that the solvent effects, which cannot be accounted for in *ab initio* calculations, may readily change the sign of the difference. The stabilization energy for the dimer is $\Delta E \approx -120$ kJ/mol in the gas phase. This estimate has to be corrected by taking into account solvent effects which we consider in the next section by means of semiempirical techniques.

Similarly to the monomeric structures, the carbanionic character of the α-carbon is stronger in the nonplanar structure (charge: -0.57) than in the planar one (charge: -0.47). The corresponding calculated shifts lie at 66.8 (planar) and 58.3 ppm (nonplanar) (see Table 3).

The agreement between the calculated shift for the planar structure and the experimental one (65.8 ppm) found by Wang et al.[1] is convincing. Thus, it appears that the shift of the dimer measured in THF solution belongs to the planar structure.

(c) Tetramer. In the case of the possible tetrameric structures, the concept of filling up the coordination sphere of the electron-deficient Li through electron-richer parts of MIB-Li becomes more flexible. We now find as the most stable aggregates a cubic structure (Figure 5) and a nearly flat eight-membered-ring structure (Figure 6).

At the best level of theory (MP2/SVD//SCF/SVD), the cubic structure is significantly (ca. 40 kJ/mol) more stable than the planar one. This finding is in agreement with the X-ray data for crystalline ester enolates[17] and *ab initio* calculations[18] of comparable systems (LiX_4, X = OH, F), where cubic structures were found to be most stable. It is interesting to note that the stabilization energies for the tetramers are $\Delta E \approx -180/-190$ kJ/mol (see Table 1), which means that at least in the gas phase or in nonpolar solvents, like toluene, the tetramers are more stable than the dimers and the monomers. This stabilization of higher aggregates is in accord with experimental data obtained through vapor phase osmometry,[2] where higher degrees of aggregation (e.g. hexamers) have been shown to be possible in toluene. In THF, however, the dimer has been found to be the most stable aggregate due to solvent effects which are discussed below.

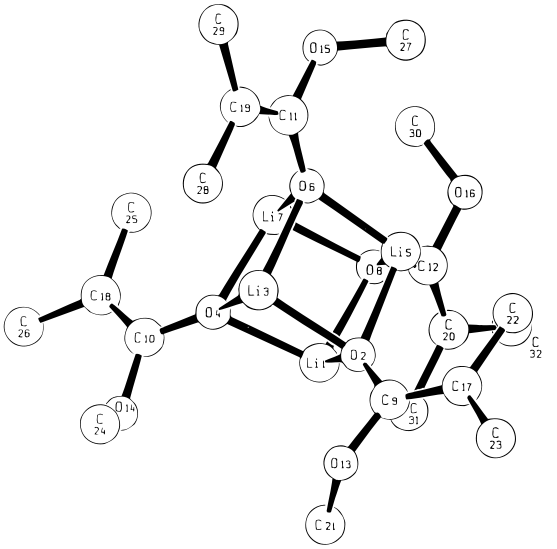

Figure 5. Optimized geometry of the cubic MiBLi tetramer at the SCF level.

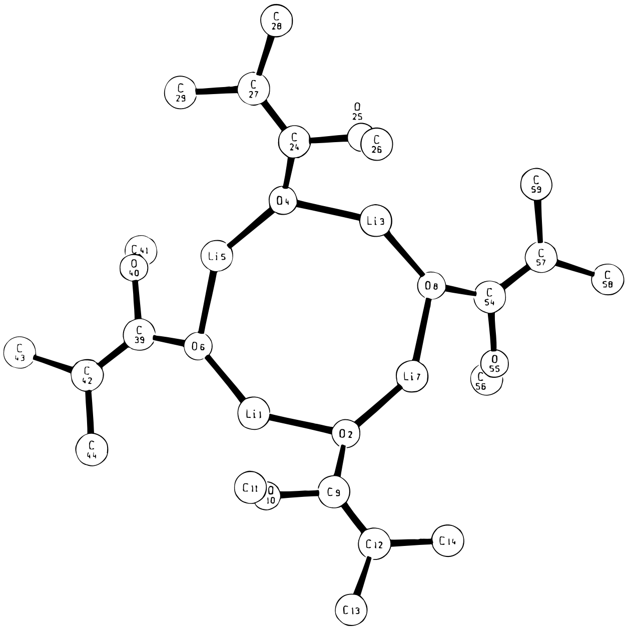

Figure 6. Optimized geometry of the cyclic MiBLi tetramer at the SCF level.

The tetramers have shifts at $\delta \approx 78$ ppm and Mulliken charges of -0.41 and -0.42, respectively. It is quite interesting to note that the cubic structure and the eight-membered-ring structure of the tetramer have the same shifts and charges. The calculated NMR shifts agree well with those measured by Schlaad et al.[19] for EIB-Li in toluene. The effect of the alkyl group of the ester on the calculated shifts of the planar MIB-Li

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Table 4. Correlation between C_α-NMR Shifts, Mulliken Charges, and the C═C Bond Lengths Calculated for the SCF/SVD//SCF/SVD Geometries of MIB-Li Aggregates

	monomer		dimer		tetramer	
	planar	nonplanar	planar	nonplanar	planar	cubic
shift (ppm)	50.8	44.5	66.8	58.3	∼78	∼78
charge	−0.49	−0.66	−0.47	−0.57	−0.41	−0.42
bond length (Å)	1.356	1.387	1.342	1.36	1.335	1.335

Table 5. MNDO Calculated Values of Heats of Formation, ΔH_f, Energies of Nonspecific and Specific Solvation, E_{nss} and E_{ss}, and Averaged Energies per MIB-Li Molecule, $\bar{E}$, for the Complexes $(MIB\text{-}Li)_n\cdot x$THF

complex	ϵ	ΔH_f, kJ/mol	E_{nss}, kJ/mol	E_{ss}, kJ/mol	$\bar{E}$, kJ/mol
MIB-Li, enolate-like	1	−460.9	0.0	0.0	−460.9
	7.42	−502.7	−41.8	0.0	−502.7
	12.13	−506.9	−46.0	0.0	−506.9
MIB-Li, ester-like	1	−472.6	0.0	0.0	−472.6
	7.42	−498.1	−25.5	0.0	−498.1
	12.13	−500.6	−28.0	0.0	−500.6
(MIB-Li)•2THF	1	−1051.8	0.0	−94.9	−555.8
	7.42	−1098.2	−46.4	−89.5	−592.2
	12.13	−1102.4	−50.6	−88.7	−595.6
(MIB-Li)•3THF	1	−1282.6	0.0	−77.7	−538.6
	7.42	−1338.2	−55.6	−76.5	−579.2
	12.13	−1343.7	−61.1	−76.6	−583.5
$(MIB\text{-}Li)_2$	1	−1095.7	0.0	0.0	−547.9
	7.42	−1126.2	−15.3	0.0	−563.1
	12.13	−1130.0	−17.2	0.0	−565.0
$(MIB\text{-}Li)_2$•2THF	1	−1628.5	0.0	−18.4	−566.3
	7.42	−1672.8	−22.2	−20.3	−583.4
	12.13	−1677.0	−24.3	−20.1	−585.1
$(MIB\text{-}Li)_2$•4THF	1	−2078.9	0.0	4.4	−543.5
	7.42	−2129.9	−25.5	4.1	−559.0
	12.13	−2135.7	−28.4	3.9	−561.1
$(MIB\text{-}Li)_4$, cubic	1	−2170.5	0.0	0.0	−542.6
	7.42	−2206.8	−9.1	0.0	−551.7
	12.13	−2210.6	−10.1	0.0	−552.7
$(MIB\text{-}Li)_4$, planar	1	−2311.0	0.0	0.0	−577.8
	7.42	−2338.6	−6.9	0.0	−584.7
	12.13	−2341.9	−7.7	0.0	−585.5
$(MIB\text{-}Li)_4$•4THF, cubic	1	−3069.2	0.0	23.3	−519.3
	7.42	−3116.0	−11.7	25.7	−526.0
	12.13	−3121.0	−13.0	25.9	−526.9
$(MIB\text{-}Li)_4$•4THF, planar	1	−3256.9	0.0	11.6	−566.2
	7.42	−3319.7	−15.7	7.8	−576.9
	12.13	−3326.8	−17.5	7.2	−578.3
THF	1	−248.0	0.0		
	7.42	−253.0	−5.0		
	12.13	−253.4	−5.4		

and EIB-Li dimers is shown to be negligible. The charges on the α-carbon and the NMR shifts (Table 4) clearly show that the carbanion (or nucleophilic) character of the α-carbon decreases due to aggregation. This trend, which is consistent going from the monomer through the dimer to the tetramer, is also reflected in the reactivity in anionic polymerization.

Semiempirical Results: Effect of Specific and Nonspecific Solvations by THF. In order to estimate the solvent effect on the stability of the dimer with respect to both monomer and tetramer, complete geometry optimizations for several monomeric, dimeric, and tetrameric structures, both nonsolvated and solvated specifically with different numbers of THF molecules, were carried out. For all considered structures, the values of a single stability parameter were calculated, which makes an easy direct estimation of their relative stabilities possible. It is an averaged energy of one MIB-Li molecule in a complex $(MIB\text{-}Li)_n\cdot x$THF (the systems with $n = 1, 2, 4$ and $x = 2, 3, 4$ were calculated):

Table 6. PM-3 Calculated Values of Heats of Formation, ΔH_f, Energies of Nonspecific and Specific Solvation, E_{nss} and E_{ss}, and Averaged Energies per MIB-Li molecule, $\bar{E}$, for the complexes $(MIB\text{-}Li)_n\cdot x$THF

complex	ϵ	ΔH_f, kJ/mol	E_{nss}, kJ/mol	E_{ss}, kJ/mol	$\bar{E}$, kJ/mol
MIB-Li, enolate-like	1	−376.8	0.0	0.0	−376.8
	7.42	−416.5	−39.7	0.0	−416.5
	12.13	−421.1	−44.3	0.0	−421.1
(MIB-Li)•2THF	1	−871.5	0.0	−65.7	−442.5
	7.42	−912.1	−40.6	−55.6	−472.1
	12.13	−916.3	−44.8	−53.6	−474.7
(MIB-Li)•3THF	1	−1101.1	0.0	−80.8	−457.6
	7.42	−1145.4	−44.3	−68.9	−485.4
	12.13	−1150.9	−49.8	−67.4	−488.5
$(MIB\text{-}Li)_2$	1	−925.5	0.0	0.0	−462.8
	7.42	−946.8	−10.6	0.0	−473.4
	12.13	−949.3	−11.9	0.0	−474.7
$(MIB\text{-}Li)_2$•2THF	1	−1373.8	0.0	−9.6	−472.4
	7.42	−1409.8	−18.0	−11.5	−484.9
	12.13	−1413.9	−20.1	−11.5	−486.2
$(MIB\text{-}Li)_2$•4THF	1	−1800.4	0.0	−8.4	−471.2
	7.42	−1849.7	−24.7	−11.5	−484.9
	12.13	−1858.9	−29.3	−13.2	−487.9
$(MIB\text{-}Li)_4$, cubic	1	−1743.9	0.0	0.0	−436.0
	7.42	−1774.4	−7.6	0.0	−443.6
	12.13	−1777.8	−8.4	0.0	−444.4
$(MIB\text{-}Li)_4$, planar	1	−1982.7	0.0	0.0	−495.7
	7.42	−2012.4	−7.4	0.0	−503.1
	12.13	−2016.6	−8.4	0.0	−504.1
$(MIB\text{-}Li)_4$•4THF, cubic	1	−2559.0	0.0	10.7	−425.3
	7.42	−2602.9	−11.0	12.9	−430.7
	12.13	−2609.1	−12.5	12.9	−431.5
$(MIB\text{-}Li)_4$•4THF, planar	1	−2764.3	0.0	19.1	−476.6
	7.42	−2835.8	−17.9	14.1	−489.0
	12.13	−2851.7	−21.9	12.0	−492.1
THF	1	−214.5	0.0		
	7.42	−220.0	−5.5		
	12.13	-220.8	-6.3		

$$\bar{E} = \{\Delta H_f[(\text{MIB-Li})_n\cdot x\text{THF}] - x\Delta H_f(\text{THF})\}/n$$

Also, the energies of specific solvation, E_{ss}, and nonspecific solvation, E_{nss}, per one MIB-Li molecule were determined:

$$E_{ss} = \{\Delta H_f[(\text{MIB-Li})_n\cdot x\text{THF}] - \Delta H_f[(\text{MIB-Li})_n] - x\Delta H_f(\text{THF})\}/n$$

$$E_{nss} = \{\Delta H_f[(\text{MIB-Li})_n\cdot x\text{THF, solvent}] - \Delta H_f[(\text{MIB-Li})_n\cdot x\text{THF, vacuum}]\}/n$$

The results obtained by using the MNDO and PM-3 methods are compared in Tables 5 and 6. Generally, it can be seen that nonspecific solvation has a significant stabilizing effect on the energies of all structures, whereas the effect of changing the temperature from 20 ($\epsilon = 7.42$) to −78 °C ($\epsilon = 12.13$) is small. Therefore, in the following we will only discuss the data for −78 °C ($\epsilon = 12.13$).

(a) Monomer. Two monomeric structures of MIB-Li were calculated by the MNDO method, namely, an enolate-like and an ester-like one, the latter being more stable by ca. 12 kJ/mol in vacuum than the former (see Table 5). However, only an enolate-like structure corresponds to a local energy minimum on the PM-3 potential surface, in agreement with *ab initio* results. It already has been mentioned in the Introduction that this difference between the MNDO and PM-3 potential surfaces is due to an overestimation of the relative strength of the Li−C bond with respect to the Li−O bond by the MNDO method. For example, the difference between the ΔH_f values of methyl lithium and lithium methoxide is ca. 113 and 46 kJ/mol, in

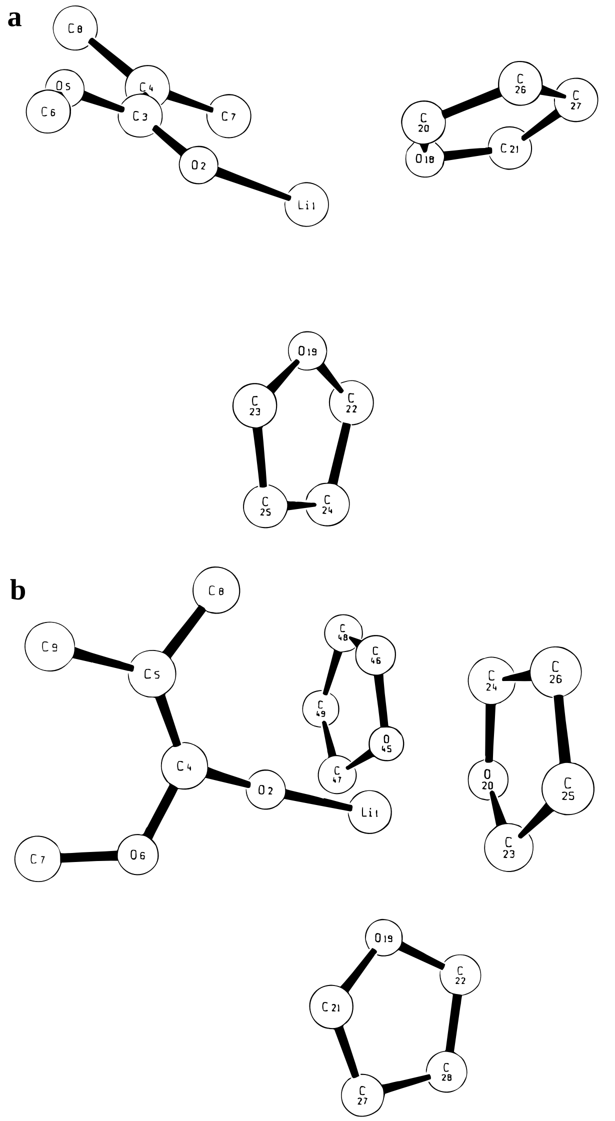

Figure 7. (a) Completely optimized MNDO geometry of the (MIB-Li)·2THF complex. (b) Completely optimized PM-3 geometry of the (MIB-Li)·3THF complex.

MNDO and PM-3 methods, respectively. Thus, PM-3 reduces the difference between the strengths of Li—C and Li—O bonds by ca. 67 kJ/mol, which results in the disappearance of the ester-like local minimum. However, it is worthwhile to note that taking into account nonspecific solvation effect makes—even in the MNDO method—the enolate-like structure more stable than the ester-like one (see Table 5). Therefore, the ester-like structure was not used in all subsequent calculations.

According to MNDO data (Table 5), the most preferable structure of the monomer in THF solution is the enolate-like structure specifically solvated by two THF molecules (Figure 7a). In this structure, the Li atom is coordinated with the carbonyl oxygen, two THF oxygens, and one of the two methyl carbons attached to the C═C double bond. This result is consistent with the MNDO data by Dybal and Kříž using dimethyl ether as the solvent.[5] The most favorable PM-3 monomeric structure (see Table 6) is a (MIB-Li)·3THF complex (Figure 7b), in which the Li atom is situated almost on the line of the carbonyl bond and is coordinated with the carbonyl oxygen and the three THF oxygens. Again, this difference between the MNDO and PM-3 most stable monomeric structures is due to overestimation of the Li—C attraction by the MNDO method.

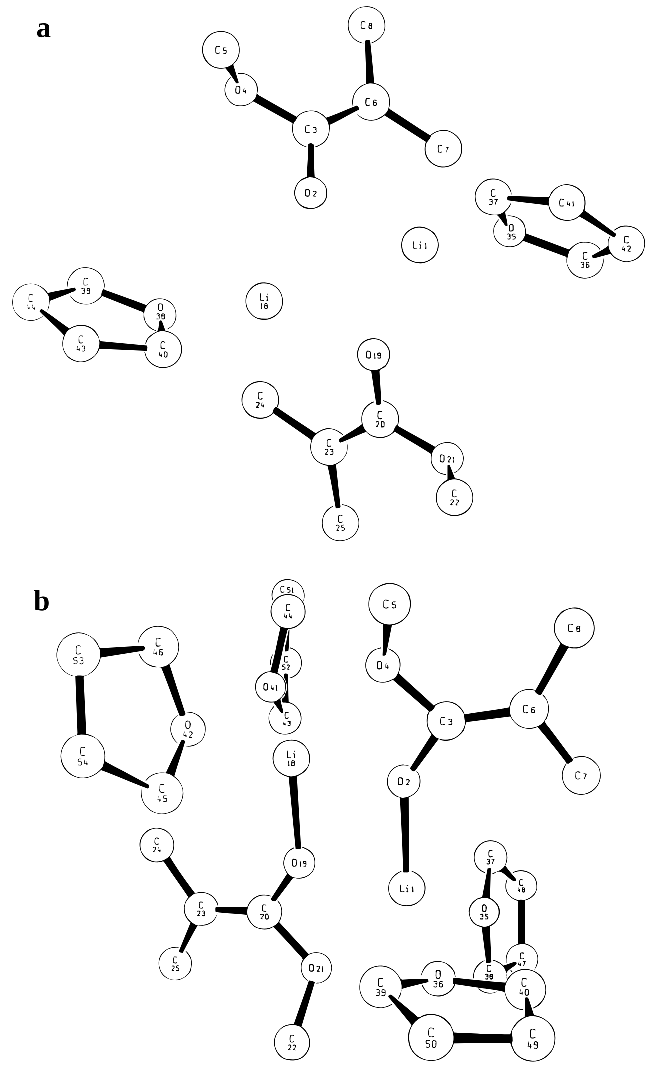

Figure 8. (a) Completely optimized MNDO geometry of the (MIB-Li)$_2$·2THF complex. (b) Completely optimized PM-3 geometry of the (MIB-Li)$_2$·4THF complex.

(b) Dimer. The completely optimized geometries of the dimeric structure with enolate-like MIB-Li moieties (similar to the *ab initio* planar dimeric structure), specifically solvated with two and four THF molecules, were found. The former, (MIB-Li)$_2$·2THF shown in Figure 8a, is predicted by the MNDO method as the most stable form (see $\bar{E}$ values in Table 5), while the two structures are almost equally stable according to the PM-3 data (see Table 6). The MNDO data are in agreement with the results by Dybal and Kříž[5] obtained for the complexes of (MIB-Li)$_2$ with dimethyl ether.

As seen from Tables 5 and 6, both the MNDO and PM-3 methods erroneously predict that the monomeric MIB-Li structure is more stable in THF solution than the dimeric one (compare the lowest $\bar{E}$ values for the monomer and dimer in Table 5). However, the difference E_{ts}(dimer) − E_{ts}(monomer) between the total solvation energy values per monomer, $E_{ts} = E_{ss} + E_{nss}$, for the most stable monomeric and dimeric structures characterizes the solvent effect on the dimer $\leftrightarrows$ monomer equilibrium. As the data in Tables 5 and 6 show, the monomer is much more stabilized by the solvent than the dimer, according to both MNDO and PM-3 predictions. However, the difference E_{ts}(dimer) − E_{ts}(monomer) for the most stable dimeric and monomeric structures is ca. 105 and 75 kJ/mol, according to MNDO and PM-3 data, respectively. Thus, the specific and nonspecific solvation effects lead to an increase in the ΔE value for the dimer (ca. −120 kJ/mol, Table 1) by 75/105 kJ/mol. The resultant ΔE value for the dimer is, however, still negative (−15/−45 kJ/mol), which is in agreement with the absence of the monomer among experimentally found MIB-Li structures.[1,3]

(c) Tetramer. Two different tetrameric structures of MIB-Li were found by both MNDO and PM-3 methods, namely, a slightly distorted cubic and an eight-membered ring structure, which are analogous to the corresponding structures found by *ab initio* calculations. Both MNDO and PM-3 methods predict the eight-membered-ring structure to be much more stable than the cubic one, which contradicts *ab initio* results. As seen from a comparison of the $\bar{E}$ values for the bare and specifically solvated tetramers (see Tables 5 and 6), the specific solvation of both tetrameric structures is unfavorable, both in the MNDO and PM-3 methods, which agrees with experimental findings that the entropy of the dimer is lower than that of the tetramer.[1,3]

As to the solvent effect on the dimer ⇆ cubic tetramer equilibrium, the dimer is stabilized by the solvent to a higher extent than the tetramer. However, the difference E_{ts}(cubic tetramer) − E_{ts}(dimer) is only ca. 34 kJ/mol, according to both MNDO and PM-3 data. According to *ab initio* results, the difference ΔE(cubic tetramer) − ΔE(dimer) is ca. −60/−70 kJ/mol (Table 1). Thus, if *ab initio* data for the energies of the dimer and cubic tetramer are used in combination with the semiempirical results for their E_{ts} values, the tetramer is still more stable than the dimer, in disagreement with the experimental results.[1,3] It is interesting to note in this context that both semiempirical methods predict the dimer to be more stable than the cubic tetramer (see the corresponding $\bar{E}$ values in Tables 5 and 6).

Conclusions

Ab initio calculations, carried out in the present study, made it possible to determine the preferrable geometries of different MIB-Li aggregates. The chemical shifts found for these structures are in very good agreement with the experimental data.[1,3,19] Semiempirical calculations were found to be helpful for estimating the polar solvent effect on the relative stability of the aggregates. Comparing the MNDO and PM-3 calculated nonspecific and specific solvation energies (Tables 5 and 6), one can see that for the MIB-Li aggregates the results are very similar (the differences are ca. 10 kJ/mol). For the nonaggregated and thus highly charged MIB-Li monomer, the differences between the MNDO and PM-3 results are more pronounced, up to ca. 35 kJ/mol. This value may be considered as an approximate estimation for the error bar which has to be expected from these semiempirical calculations.

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Supporting Information Available: Tables containing detailed geometries and energies of the compounds studied (24 pages). See any current masthead page for ordering and Internet access instructions.

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