

Ab Initio and Semiempirical Study of the Effect of Ethereal Solvent on Aggregation of a Lithium Enolate

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Abstract: The effect of dimethyl ether solvation on aggregated forms of the lithium enolate of acetaldehyde $(\text{CH}_2=\text{CHOLi})_n(\text{Me}_2\text{O})_x$, $n = 1-4$, $x = 0-4$, was studied theoretically. Density functional theory (DFT) with the B3LYP functional was applied to calculate the energies of PM3 optimized structures (B3LYP//PM3). The accuracy of this method was checked successfully against a representative set of B3LYP//B3LYP computations. The DFT values also were calibrated by comparison with MP4 calculations on solvated methyl lithium. The structures and energies of the aggregates are described, with emphasis on the main factors that control relative stabilities. Common crystal structure motifs are reproduced. Solvation is critical in the equilibria among the aggregated species and in the relative stabilities of the tetrameric isomers but is balanced by π -interactions between lithium and the enolate double bond. A number of tetramer structures were studied, but lithium is tetracoordinated only in the cubic tetramer in the most stable solvated form. Aggregation and successive solvation energies as well as entropy considerations indicate that solution equilibria are dominated by the solvated monomer and tetramer. The desolvated monomer is remarkably stable; addition of a third solvent is far less exothermic than the first two additions and may not suffice to compensate for the corresponding entropy change. Natural population analysis (NPA) suggests that polarization rather than delocalization of charge from oxygen into the enolate double bond is the main mechanism of charge distribution. Previously known experimental aggregation data on lithium enolates are rationalized by the computational results obtained.

Introduction

Lithium enolates are widely used building blocks in modern organic synthesis.¹ A thorough understanding of their structures and reactivities is important, particularly since many of these compounds exist as aggregates in solution and in the solid state.²⁻⁴ A number of fundamental influences are still unknown or not clear quantitatively, but various aspects of reactivity and

regio- and stereoselectivity have been attributed to aggregation.⁵ Structural details of lithium enolates from X-ray crystallographic data show dimers, tetramers, and hexamers, with different types and levels of interaction with solvents and coordinating agents.^{2,6} In solution, Bauer and Seebach obtained average aggregation numbers of several lithium enolates, as well as of lithium azaenolates and alkyl- and aryllithium compounds from freezing-point depression measurements in THF.⁷ Jackman studied aggregation and reactivity of lithium enolates by using ⁶Li and ¹³C NMR spectroscopy.^{2a,2b,8} NMR evidence indicates that the parent lithium enolate of acetaldehyde exists exclusively as a tetramer in THF solution.⁹ We have recently applied a

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combination of UV-vis spectroscopy and coupled ion-pair equilibria¹⁰ to study the aggregation and reactivity of lithium^{3,4} and cesium¹¹ enolates in THF.

We now describe a computational study of the effect of solvent on the structures and aggregation of a lithium enolate. Although high-level ab initio calculations are available for enolate anions and related alkali metal salts,^{12,13} most computational studies have focussed on the isolated species.¹⁴ In order to properly simulate the properties of enolates in solution, it is necessary to account for the solvent. Model solvents used in previous ab initio studies of organic anionic species are relatively unrealistic, such as ammonia, water, or HF. Kahn calculated (RHF/3-21G) aggregation and solvation energies of the lithium enolate of acetaldehyde using HF as the solvent molecule.¹⁵ An extensive study on the structure and energy of aggregates and solvated forms using realistic ligands has been reported only for lithium amides at a semiempirical level (MNDO).¹⁶ MNDO also has been used to investigate aggregation of the lithium salt of methyl isobutyrate.¹⁷ Recent ab initio studies include monomers and dimers of ethynyllithium, LiC≡CH, as well as their solvation by water,¹⁸ and lithium cation-dimethyl ether complexes.¹⁹

To effectively study the role of solvent in aggregation of the lithium enolate of acetaldehyde, CH₂=CHOLi, **1**, it was necessary to use a small ether solvent molecule. Water is not generally suitable because of its tendency to hydrogen bond. Tetrahydrofuran is unnecessarily large. Thus, we chose dimethyl ether as a realistic coordinating solvent. Finally, electron correlation is desirable to properly access the intermolecular interaction energy between solvent molecules and the lithium enolate. The resulting energies are compared with those at the RHF and semiempirical levels. The next section presents the approach used to study the appropriate systems, from the monomer to the tetrasolvated tetramer.

While preparing this paper a theoretical study appeared on aggregation and solvation of the lithium enolate of methyl isobutyrate. Geometry optimizations were carried out at the RHF level (with a basis set comparable to 6-31G*) and the energies of lower aggregates were calculated at MP2. The geometries and energies of THF-solvated systems were computed at a semiempirical level.²⁰

Method of Calculation

We wished to employ a practical but also a reliable method applicable to the largest systems of our study, i.e., the tetrasolvated tetramers of **1**, with chemically realistic solvent molecules and also at

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electron correlational levels. Density functional theory (DFT)²¹ on electrostatic molecular clusters compares well with MP2 results.²² Similarly, B3LYP/6-311+G**²³ DFT calculations on the deprotonation of nitriles with lithium amides agree well with MP2/6-31+G* results.²⁴ Moreover, DFT stabilization energies have relatively small basis set superposition errors.²⁵ Nevertheless, geometry optimization of our largest systems using DFT exceeds our computer capabilities. Hence, we used a combined ab initio and semiempirical approach. Semiempirical energies have larger errors than ab initio, but they have been shown to predict geometries rather successfully. Good agreement between PM3²⁶ calculated structures and MP2 and X-ray data has been obtained for a number of lithium salts of sulfones, sulfoxide, 1,3-dithianes, and nitriles.^{24,27} PM3 is generally superior to MNDO for the calculation of organolithium species.^{24,27} MNDO tends to overestimate C–Li bond strengths.²⁸ Nonetheless, MNDO has been shown to successfully reproduce Li–N, Li–O, and Li–solvent interactions by comparisons with experimental results and ab initio calculations.^{28,29}

The present work uses principally B3LYP energies on PM3 geometries (B3LYP//PM3). Calibrations were made by comparing 6-311+G** and 6-31+G* basis sets for the smaller aggregates and solvates in B3LYP//B3LYP computations. Further calibration was provided by comparison with full fourth order Møller–Plesset theory³⁰ (MP4SDTQ) on monosolvated methylolithium. A selected number of RHF calculations also were compared with the DFT results. Such calibrations showed that B3LYP/6-31+G**//PM3 data gives acceptable geometries and energies.

All ab initio calculations used the GAUSSIAN 94³¹ program package and the standard basis sets 6-31+G* and 6-311+G**. Single-point B3LYP/6-31+G**//PM3 calculations also used five d-orbitals as polarization functions for heavy atoms. Charges were calculated by Natural Population Analysis^{32,33} at the B3LYP/6-31+G**//6-31+G* and B3LYP/6-311+G**//6-31+G* levels. Semiempirical calculations used the VAMP program,³⁴ with the keywords PM3, EF, and GNORM = 0.01. Geometries were fully optimized within the designated symmetry constraints at the ab initio and semiempirical levels. Stationary points were characterized as minima, saddle points, etc., by frequency analysis (number of imaginary frequencies: zero for minima). Zero-point

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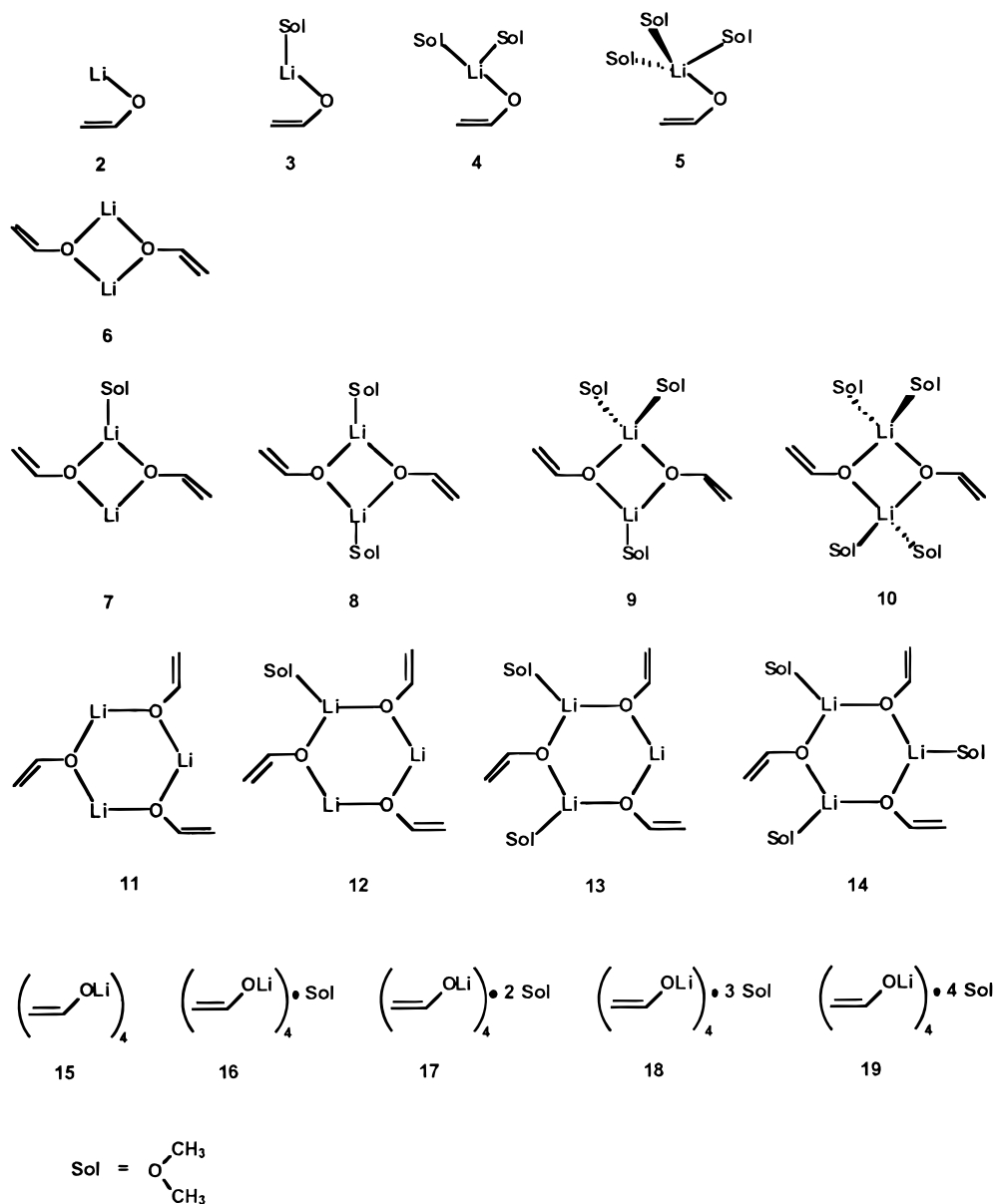
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Chart 1



vibrational energies of Hartree-Fock calculations were scaled by an empirical factor of 0.91.³⁵

Results and Discussion

Solvated Methylithium. Calculations on monosolvated monomeric methylithium, $\text{MeLi}(\text{OMe}_2)$, at MP4SDTQ(FC)/6-31+G*/MP2(full)/6-31+G*, B3LYP/B3LYP, and B3LYP/PM3 are compared in Table S1 (Supporting Information). The DFT results on the ab initio-optimized structures agree with the data obtained from the PM3 geometries: the energy difference between monosolvated methylithium and the two reactants ranges from 18.1 to 19.0 kcal mol⁻¹; that is, the difference in solvation energies is less than 1 kcal mol⁻¹. The more extended 6-311+G** basis set does not give any significant difference from the smaller basis. All of the DFT calculations show good agreement with MP4. The MP4 solvation energy is slightly higher (-20.8 kcal mol⁻¹), but the differences are small. The PM3 geometries compare well with

those from the other methods;³⁶ for example, the Li-O(CH₃)₂ bond length is between that of MP2 and B3LYP. Table S2 (Supporting Information) gives the solvation energies for the trisolvated $\text{MeLi}(\text{Me}_2\text{O})_3$, in which the lithium is tetracoordinated, the configuration often the most stable and common for this cation;^{2f} the energy difference between trisolvated methylithium and the four reactants ranges from 35.5 to 36.5 kcal mol⁻¹ by the different methods. Again, agreement among the different calculations is very good and confirms the reliability of PM3 optimized geometries for the present application.³⁷

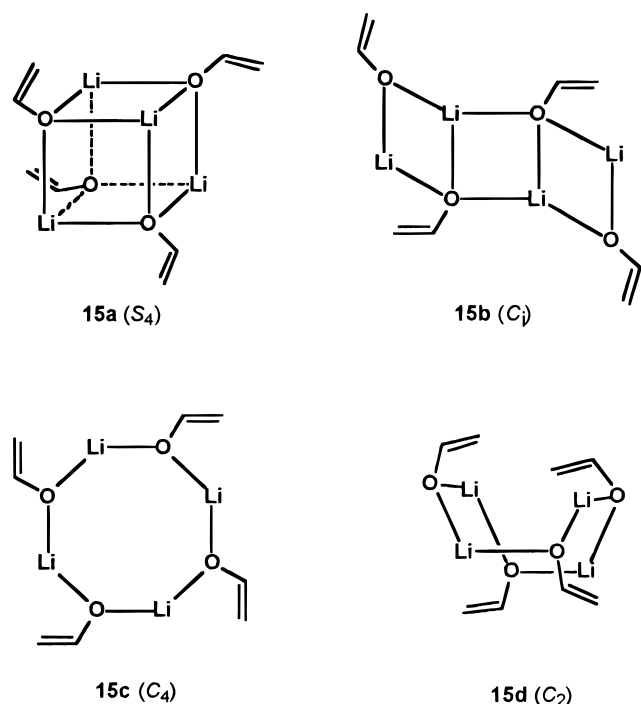
As has been noted before,²⁹ the first solvent molecule is the most effective: the solvation energy of one dimethyl ether is 20 kcal mol⁻¹, while that of three solvent molecules is 36 kcal mol⁻¹. Thus, the second and third solvent molecules together produce less solvation energy than the first solvent.²⁹

(36) Selected bond lengths (in angstroms) for $\text{MeLi}(\text{Me}_2\text{O})$ (C_2) as obtained from MP2/6-31+G*, B3LYP/6-31+G*, and PM3-optimized structures. H₃C-Li: MP2, 2.001; B3LYP, 1.999; PM3, 1.938. Li-O(CH₃)₂: MP2, 1.841; B3LYP, 1.913; PM3, 1.892.

(37) Selected bond lengths (in angstroms) and bond angles (degrees) for $\text{MeLi}(\text{Me}_2\text{O})_3$ (C_3) as obtained from B3LYP/6-31+G* and PM3 optimized structures. H₃C-Li: B3LYP, 2.081; PM3, 2.041. Li-O(CH₃)₂: B3LYP, 2.053; PM3, 2.046. H₃C-Li-O(CH₃)₂: B3LYP, 115.3; PM3, 115.8.

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Chart 2



Isolated and Solvated Aggregates of the Lithium Enolate of Acetaldehyde. The monomers, aggregates, and solvated forms of **1** are shown in Charts 1 and 2. To calibrate the B3LYP/6-31+G**//PM3 method used for all the systems, the energy differences between the monomer **2** and the corresponding complexes with one to three molecules of solvent, **3–5**, respectively, and the unsolvated dimer **6** and trimer **11** were computed at various levels of theory (Scheme 1): PM3, B3LYP/6-31+G**//6-31+G*, B3LYP/6-311+G**//6-31+G*, B3LYP/6-31+G**//PM3, B3LYP/6-311+G**//PM3, RHF/6-31+G**//6-31+G*, and RHF/6-31+G**//PM3. The single-point energies of the PM3 optimized monomers, dimers, trimers, and solvated monomers also were computed at B3LYP/6-311+G**. The geometries of most of these compounds were optimized with B3LYP/6-31+G*, and single-point B3LYP/6-311+G** calculations were performed. As discussed in more detail below, all of the DFT based approaches gave similar results. In particular, the B3LYP/6-31+G**//PM3 results for the larger systems are comparable to those using B3LYP/6-31+G*-optimized geometries. On the other hand the PM3//PM3 data deviate strongly; energy changes typically are about 5 kcal mol⁻¹ too positive.

Scheme 2 shows only the B3LYP/6-31+G**//PM3 and PM3//PM3 results. This scheme includes the dimer and its corresponding complexes with one to four molecules of solvent, **7–10**, respectively; trimer **11** and the corresponding complexes with one to three molecules of solvent, **12–14**, respectively; tetramer **15** and the corresponding complexes with one to four molecules of solvent, **16–19**, respectively. These structures are summarized in Chart 1. Scheme 3 summarizes the energy changes among different isomers of the unsolvated and solvated tetramers.

Different point group symmetries were considered for all of the systems. With the exception of the trimers, the aggregates with the largest number of solvent molecules have tetracoordinated lithium. Higher solvated forms were not examined. This choice is justified by the small or negligible stabilization afforded by addition of the last ligand.²⁹

All PM3 and DFT energies are reported in Table S3 (Supporting Information), together with frequency analysis and

zero-point vibrational energies. Table 1 contains relative energies of isomers with different symmetries. Selected systems also were studied at the Hartree–Fock level (RHF/6-31+G*) (Table S5 (Supporting Information)). Finally, values of selected bond lengths of DFT- and PM3-optimized structures are reported in Table 2. Full structural details of all of these species are given as Cartesian coordinates in the Supporting Information.

Structures. The optimized structures of isolated and solvated **1** monomers are presented in Figures 1 and 2. As was noted previously,^{13a} the isolated bridged lithium enolate structure with C₁ symmetry, **2a**, in which the lithium cation is stabilized by a π -interaction with the enolate anion, is the most stable minimum in the B3LYP//B3LYP computations. For convenience, the structure of the monomer without π -bonding, **2b**, is also shown in Figure 1 although, as shown below, π -interaction is a significant stabilizing factor in determining the most stable isomeric structure even in the higher aggregates. This interaction is maintained in the mono- and disolvated species but is lost when a third molecule of solvent is introduced (Figure 2). The lithium coordination requirements are satisfied by the three solvent molecules of solvent, and interaction with the enolate π -system is no longer necessary. Solvation increases the bond lengths between the enolate oxygen atom and the lithium in the mono- and disolvated enolates. Correspondingly, the distance between lithium and the solvent also increases. The trend ends with the trisolvated **5b**, where the Li–O (enolate) distance is even less than in the isolated species. Due to steric hindrance, the Me₂O solvent molecules are almost 0.2 Å farther from the lithium center relative to the monosolvated **3**. The larger lithium–dimethyl ether distances and the absence of coordination to the double bond strengthens the predominantly ionic interaction with the enolate oxygen, as is shown by the almost linear C–O–Li enolate bond angle. However, as we will comment later, when entropy is also taken into account, this stronger interaction does not compensate for the loss of bond energy that comes from the lack of interaction with the double bond and from the loosening of solvent coordination. That is, the third molecule of solvent provides little net stabilization. Lithium often does not reach tetracoordination with external ligands;^{6g–i,29} the same may be true for lithium enolates. The lithium coordination needs are better satisfied in the disolvated species, where the fourth ligand is the double bond together with the two molecules of solvent and the negatively charged enolate oxygen. In most cases where such coordination is possible, as in benzyllithium,³⁸ cyclopentadienyllithium,³⁹ and lithium derivatives of indenenes, fluorenes, carbazole, etc.,^{6g–i} tetracoordination of lithium by “external” ligands is unimportant.⁴⁰ No external ligands are present in the crystal structure of hexameric lithium pinacolate.⁴¹ In this structure each lithium center is formally tricoordinated but is also relatively close to the enolate double bonds.

Comparison of geometries obtained from B3LYP and PM3 optimizations (Table 2) shows excellent agreement for the O–C and C–C bond lengths; in general, PM3 distances to Li are almost 0.1 Å longer, although apparently this makes little difference in the relative energies.

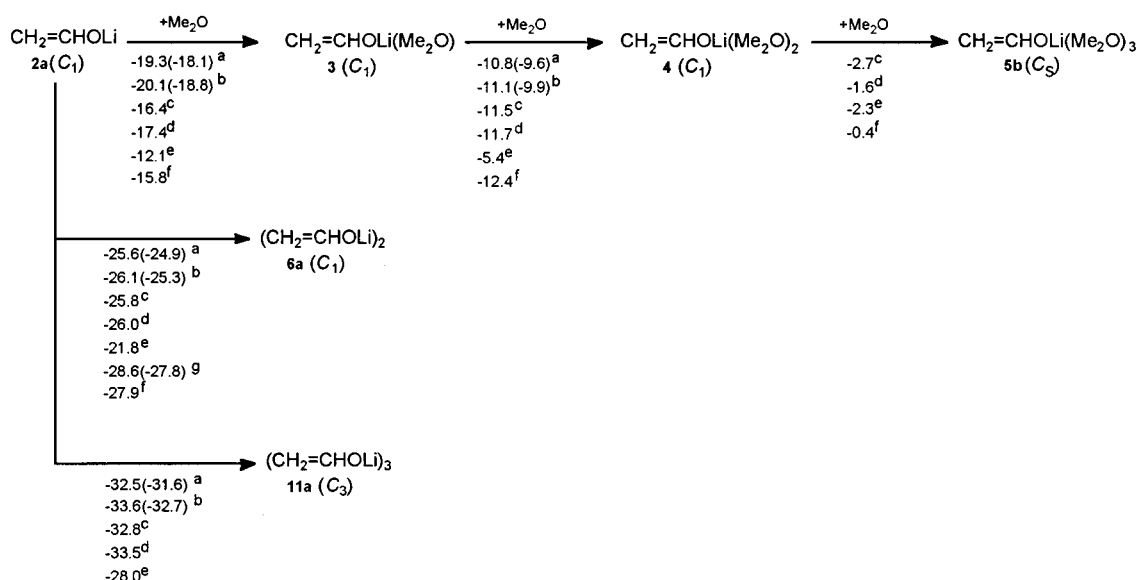
The geometries of six dimer isomers **6a** (C₁), **6b** (C₁), **6c** (C_i), **6d** (C_s), **6e** (C_{2h}) and **6f** (C_{2h}) were optimized at the B3LYP level (the most representative optimized structures are reported

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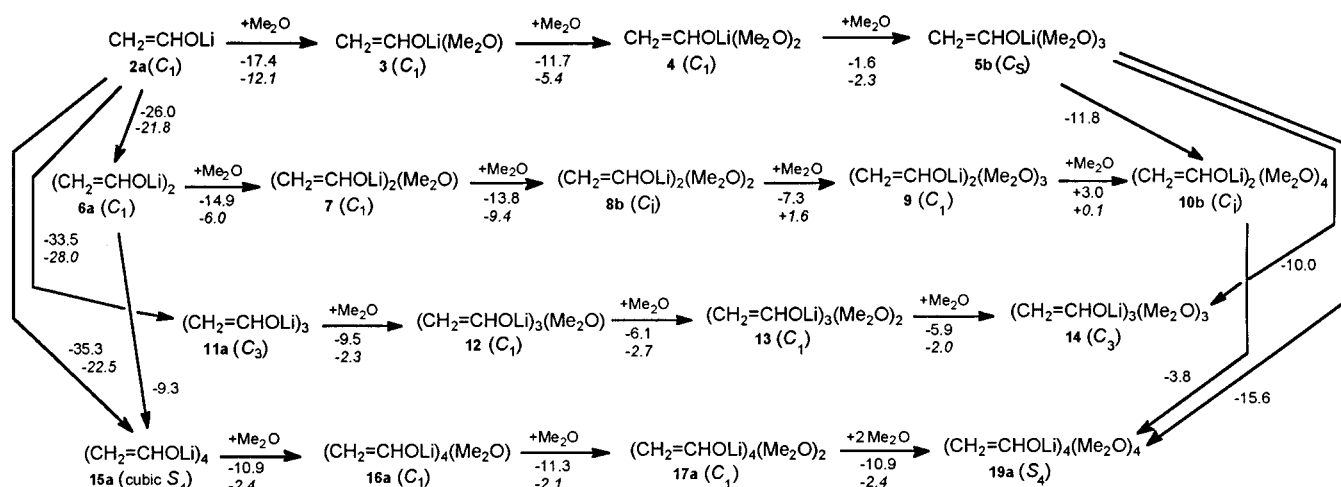
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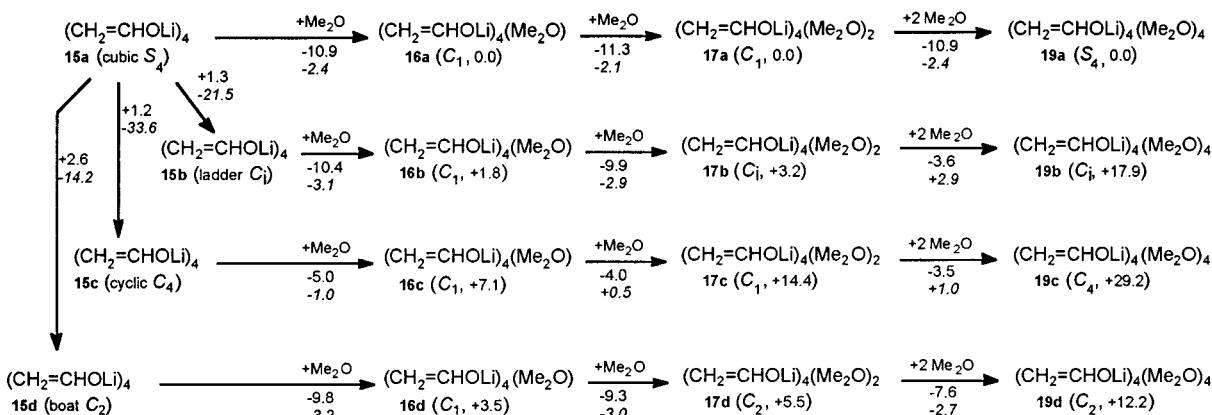
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Scheme 1. Solvation and Aggregation Energies of Lithium Vinylide^b

^a B3LYP/6-311+G**//B3LYP/6-31+G*. ^b B3LYP/6-31+G**//B3LYP/6-31+G*. ^c B3LYP/6-311+G**//PM3. ^d B3LYP/6-31+G**//PM3. ^e PM3. ^f RHF/6-31+G*/6-31+G*. ^g RHF/6-31+G*/PM3. ^h Aggregation energies in kcal mol⁻¹/mol of monomer. Solvation energies per mole of solvent. Values in parentheses are corrected for zero-point energies.

Scheme 2. Energy Changes for Aggregation and Solvation of Lithium Vinylide^a

^a Numbers are B3LYP/6-31+G**//PM3, kcal mol⁻¹. Numbers in italics are PM3//PM3. Energy changes are given per Me₂O molecule added.

Scheme 3. Relative Energies and Solvation of Lithium Vinylide Tetramers^a

^a Numbers are B3LYP/6-31+G**//PM3, kcal mol⁻¹. Numbers in italics are PM3//PM3. Energy changes are given per Me₂O molecule added.

in Figure 3). Systems **6a,b** differ in the transoid and cisoid, respectively, arrangement of the enolate units. The whole **6e** system (not shown) is planar, while in **6f** the plane formed by the central Li–O–Li–O moiety is perpendicular to that defined

by the carbon atoms of the enolate. The two lithium and the two oxygen atoms form four-member rings in all of the dimers. Only **6a**, **6b**, and **6d** are minima, whereas the other stationary points have one or two imaginary frequencies. Although the

Table 1. PM3 and Becke3LYP (B3LYP) Relative Energies^a of Monomeric and Aggregated Structures of CH₂=CHOLi and Corresponding Solvated (Me₂O) Forms

species	PM3	B3LYP/ 6-311+G**//PM3	B3LYP/ 6-31+G**//PM3	B3LYP/ 6-311+G**//6-31+G** ^b	B3LYP/ 6-31+G**//6-31+G** ^b
2a	CH ₂ =CHOLi (C ₁)	+1.9	+0.4	0.0	0.0
2b	CH ₂ =CHOLi (C _s)	0.0	0.0	+1.0	+2.6 (+2.4)
5a	CH ₂ =CHOLi(Me ₂ O) ₃ (C ₁)	+0.1	+0.4	+0.2	
5b	CH ₂ =CHOLi(Me ₂ O) ₃ (C _s)	0.0	0.0	0.0	
6a	(CH ₂ =CHOLi) ₂ (C ₁) ^c	0.0	+0.2	+0.1	0.0
6b	(CH ₂ =CHOLi) ₂ (C ₁) ^d	+0.1	0.0	0.0	+0.2 (+0.2)
6c	(CH ₂ =CHOLi) ₂ (C _i) ^e	e			+0.5 (+0.3)
6d	(CH ₂ =CHOLi) ₂ (C _s) ^e	e			+0.5 (+0.3)
6e	(CH ₂ =CHOLi) ₂ (C _{2h}) ^f	0.0	+1.2	+1.4	+0.5 (+0.3)
6f	(CH ₂ =CHOLi) ₂ (C _{2h}) ^g	+3.9			+1.2 (+1.0)
8a	(CH ₂ =CHOLi) ₂ (Me ₂ O) ₂ (C ₁)	0.0			
8b	(CH ₂ =CHOLi) ₂ (Me ₂ O) ₂ (C _i)	+0.2			
8c	(CH ₂ =CHOLi) ₂ (Me ₂ O) ₂ (C _{2h})	+1.6			
10a	(CH ₂ =CHOLi) ₂ (Me ₂ O) ₄ (C ₁)	+1.2			
10b	(CH ₂ =CHOLi) ₂ (Me ₂ O) ₄ (C _i)	0.0			
10c	(CH ₂ =CHOLi) ₂ (Me ₂ O) ₄ (C _{2h})	+3.0			
11a	(CH ₂ =CHOLi) ₃ (C ₃)	0.0	0.0		0.0
11b	(CH ₂ =CHOLi) ₃ (C _{3h})	+2.0	+4.9		+4.8
15a	(CH ₂ =CHOLi) ₄ (S ₄) ^h	+33.6		0.0	
15b	(CH ₂ =CHOLi) ₄ (C _i) ⁱ	+12.1		+1.3	
15c	(CH ₂ =CHOLi) ₄ (C ₄) ^j	0.0		+1.2	
15d	(CH ₂ =CHOLi) ₄ (C ₂) ^k	+19.4		+2.6	
16a	(CH ₂ =CHOLi) ₄ (Me ₂ O) (C ₁) ^h	+32.2		0.0	
16b	(CH ₂ =CHOLi) ₄ (Me ₂ O) (C ₁) ⁱ	+10.0		+1.8	
16c	(CH ₂ =CHOLi) ₄ (Me ₂ O) (C ₁) ^j	0.0		+7.1	
16d	(CH ₂ =CHOLi) ₄ (Me ₂ O) (C ₁) ^k	+17.2		+3.5	
17a	(CH ₂ =CHOLi) ₄ (Me ₂ O) ₂ (C ₁) ^h	+29.6		0.0	
17b	(CH ₂ =CHOLi) ₄ (Me ₂ O) ₂ (C _i) ⁱ	+6.6		+3.2	
17c	(CH ₂ =CHOLi) ₄ (Me ₂ O) ₂ (C ₁) ^j	0.0		+14.4	
17d	(CH ₂ =CHOLi) ₄ (Me ₂ O) ₂ (C ₂) ^k	+13.6		+5.5	
18a	(CH ₂ =CHOLi) ₄ (Me ₂ O) ₃ (C ₁) ^h	+26.5			
18b	(CH ₂ =CHOLi) ₄ (Me ₂ O) ₃ (C ₁) ⁱ	+8.4			
18c	(CH ₂ =CHOLi) ₄ (Me ₂ O) ₃ (C ₁) ^j	0.0			
18d	(CH ₂ =CHOLi) ₄ (Me ₂ O) ₃ (C ₁) ^k	+9.9			
19a	(CH ₂ =CHOLi) ₄ (Me ₂ O) ₄ (S ₄) ^h	+22.8		0.0	
19b	(CH ₂ =CHOLi) ₄ (Me ₂ O) ₄ (C _i) ⁱ	+10.4		+17.9	
19c	(CH ₂ =CHOLi) ₄ (Me ₂ O) ₄ (C ₄) ^j	0.0		+29.2	
19d	(CH ₂ =CHOLi) ₄ (Me ₂ O) ₄ (C ₂) ^k	+6.3		+12.2	

^a Energies in kcal/mol. ^b Values in parentheses are zero-point energy (B3LYP/6-31+G**//6-31+G*) corrected. ^c Transoid arrangement of the enolate units. ^d Cisoid arrangement of the enolate units. ^e Optimized geometries and corresponding energies are the same as those in the C_{2h} structure, with all atoms in the same plane. ^f All atoms are in the same plane. ^g The plane corresponding to the moiety Li–O–Li–O is perpendicular to the plane of the carbon atoms. ^h Cubic geometry. ⁱ Ladder geometry. ^j Cyclic geometry. ^k Boat geometry.

Table 2. Selected Bond Lengths (Å) in Optimized Monomeric and Aggregated Structures of CH₂=CHOLi and Corresponding Solvated Forms

species (point group)	method	O–Li	O–C _α	C _α –C _β	Li···S ^a	
2a	CH ₂ =CHOLi (C ₁)	B3LYP ^b	1.76	1.30	1.38	
		PM3	1.85	1.31	1.38	
3	CH ₂ =CHOLi(Me ₂ O) (C ₁)	B3LYP ^b	1.80	1.30	1.38	1.89
		PM3	1.88	1.30	1.39	2.02
4	CH ₂ =CHOLi(Me ₂ O) ₂ (C ₁)	B3LYP ^b	1.82	1.30	1.38	1.95, 1.98
		PM3	1.90	1.30	1.38	2.04, 2.06
5a	CH ₂ =CHOLi(Me ₂ O) ₃ (C _s)	PM3	1.69	1.30	1.35	2.16, 2.16, 2.19
6a	(CH ₂ =CHOLi) ₂ (C ₁)	B3LYP ^b	1.76, 1.80, 1.80, 1.92	1.32, 1.33	1.35, 1.36	
		PM3	1.78, 1.79, 1.94, 2.05	1.32, 1.33	1.35, 1.36	
10b	(CH ₂ =CHOLi) ₂ (Me ₂ O) ₄ (C _i)	PM3	1.91, 1.91	1.32	1.35	2.10, 2.16
11a	(CH ₂ =CHOLi) ₃ (C ₃)	B3LYP ^b	1.76, 1.86	1.32	1.36	
		PM3	1.80, 1.98	1.33	1.36	
14	(CH ₂ =CHOLi) ₃ (Me ₂ O) ₃ (C ₃)	PM3	1.89, 1.90	1.33	1.35	2.10
15a	(CH ₂ =CHOLi) ₄ (S ₄)	PM3	1.99, 2.00, 2.15	1.34	1.35	
19a	(CH ₂ =CHOLi) ₄ (Me ₂ O) ₄ (S ₄)	PM3	2.05, 2.06, 2.07	1.34	1.35	2.09

^a In angstroms. ^b Bond length between Li and O of Me₂O. ^c B3LYP/6-31+G*.

C₁ geometry with a transoid arrangement of the enolate units is the most stable, all of the structures differ but little in energy (from 0.2 to 1.2 kcal mol⁻¹, relative to the cisoid C₁ dimer). Hartree–Fock calculations give somewhat different results. In addition to the DFT minima, **6c** (C_i) is also a minimum with no imaginary frequencies. All of the RHF structures also have comparable energies. However, the RHF global minimum is

not the C₁ system, which is actually computed to be the highest energy minimum. Other differences also suggest that RHF may be less accurate than B3LYP for these systems, although the differences in energies are small.

PM3 optimization results in only four geometries: two C₁ structures computed to be the most stable (**6a** is shown in Figure 3), a C_{2h} conformational isomer (**6c** = **6d** = **6e**), and a C_{2h}

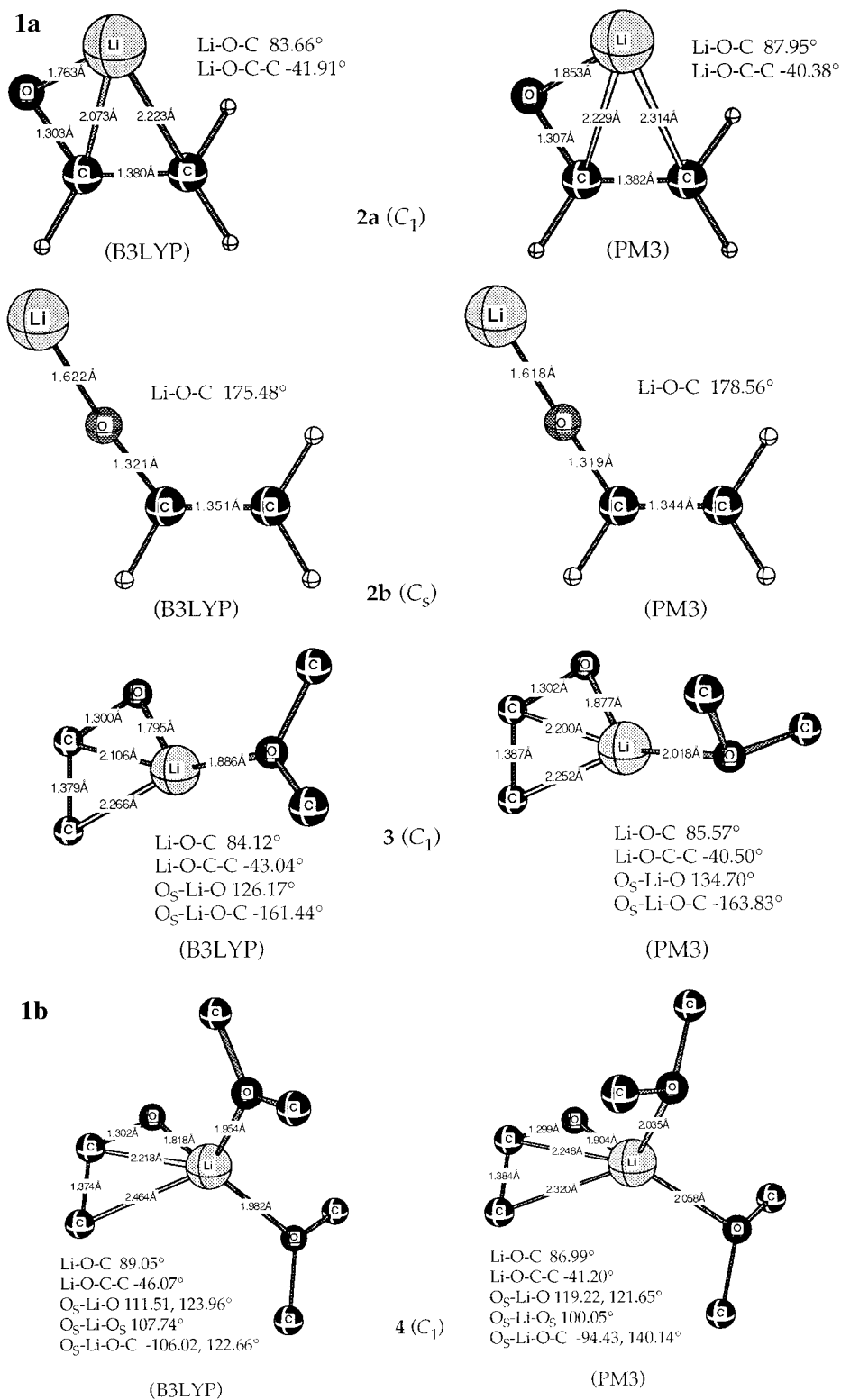


Figure 1. Optimized structures of monomer $\text{CH}_2=\text{CHOLi}$, **2a** and **2b**, and its complexes with one and two molecules of Me_2O (**3** and **4**, respectively), as obtained from B3LYP/6-31+G* and PM3 calculations (hydrogen atoms are omitted from some pictures for sake of clarity).

dimer **6f**, the highest energy minimum. The relative stability of the C_1 dimers undoubtedly is due to the stabilizing interaction between lithium cation and the enolate double bond. There is no significant energy difference between transoid and cisoid enolate moieties. Interestingly, only one of the enolate units both in DFT and PM3 coordinates strongly with lithium; this behavior clearly is found only when all symmetry constraints are released.

The same considerations extend to the stable hexagonal cyclic trimer $(\text{CH}_2=\text{CHOLi})_3$ **11a** (C_3), with the difference that

π -coordination is exhibited by all of the enolate units (Figure 5). For this reason, the C_{3h} isomer **11b**, where interaction of lithium with the double bond is not present, is less stable by $4.8 \text{ kcal mol}^{-1}$ (B3LYP/6-31+G*/B3LYP/6-31+G*). A comparison of monomer, dimer, and trimer systems, with or without π -coordination, (**2a** vs **2b**, **6a** vs **6c**, and **11a** vs **11b**), shows the π -coordination energy to be $0.5\text{--}2.6 \text{ kcal mol}^{-1}$. For the trisolvated monomer (and for other aggregates, see below) π -coordination energy is lost on solvation; this energy effect must be considered when studying the stability of solvated

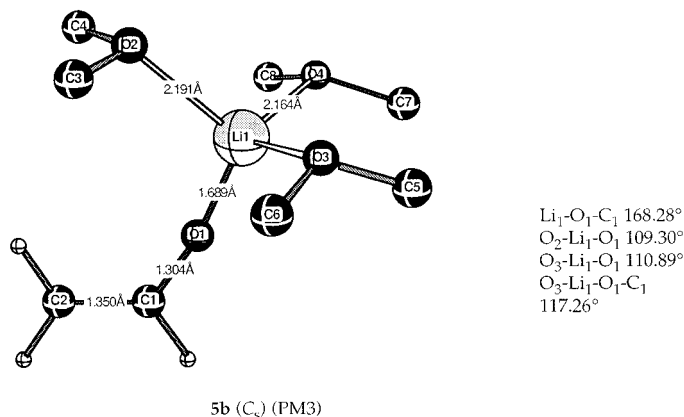


Figure 2. Optimized structure of $\text{CH}_2=\text{CHOLi}(\text{Me}_2\text{O})_3$, **5b**, as obtained from PM3 calculations (hydrogen atoms are omitted from the molecules of solvent).

lithium enolates and may be a decisive factor in determining the most stable degree of solvation.

Other starting structures of the trimer all converged to one of these two minima. In particular, no stable three-rung ladders were found in which one lithium is bonded to three enolate oxygens. In contrast, four-rung ladder minima are found for the tetramer (see below).

The following solvated dimers were optimized at the semiempirical level: $(\text{CH}_2=\text{CHOLi})_2(\text{Me}_2\text{O})$ **7** (C_1); $(\text{CH}_2=\text{CHOLi})_2(\text{Me}_2\text{O})_2$ **8a** (C_1), **8b** (C_i), and **8c** (C_{2h}); $(\text{CH}_2=\text{CHOLi})_2(\text{Me}_2\text{O})_3$ **9** (C_1); $(\text{CH}_2=\text{CHOLi})_2(\text{Me}_2\text{O})_4$ **10a** (C_1), **10b** (C_i), and **10c** (C_{2h}) (principal structures are reported in Figure 4). The energies among the different isomers of **8** and **10** do not differ significantly, but generally the C_i geometries are the most stable. These were chosen for the B3LYP single-point calculations.

In contrast to monomeric **1**, π -coordination between lithium and the enolate is already broken after the first association with the solvent. Although steric factors may be important, this behavior is quite unexpected because one lithium atom could achieve tetracoordination by interaction with the π -system. Similar behavior is observed in the solvated trimers $(\text{CH}_2=\text{CHOLi})_3(\text{Me}_2\text{O})$ **12** (C_1), $(\text{CH}_2=\text{CHOLi})_3(\text{Me}_2\text{O})_2$ **13** (C_1), and $(\text{CH}_2=\text{CHOLi})_3(\text{Me}_2\text{O})_3$ **14** (C_3) (Figure 5). After each addition of a molecule of Me_2O , one π -coordination is lost, until none is left after the third Me_2O solvation in **14**.

A few crystal structures of lithium enolate dimers are known.^{6h} Particularly interesting is the comparison with the crystal structure of a lithium amide enolate dimer that crystallizes with four molecules of THF.^{6b} In this structure the enolate fragments range about a four-membered ring formed by the lithium and oxygen atoms. The π -system does not participate in the lithium complexation. Each lithium center is solvated by two molecules of THF, and the geometry around lithium is slightly pyramidal. Measured bond lengths for $\text{Li-O}(\text{enolate})$ were 1.88 and 1.92 Å, and for $\text{Li-O}(\text{THF})$, 1.99 Å. Overall agreement with the PM3 calculated species **10b** is good, except that the lithium-solvent oxygen distance is computed to be longer by about 0.1 Å (as already noted above by comparison with DFT results for the solvated monomers). However, such overestimation of the bond distance to the solvent does not significantly affect the solvation energies. Comparison with the X-ray data shows that the DFT geometries reproduce the lithium-solvent distances accurately.

Known crystal structures and previous computational studies on aggregated metal enolates, metal amides, and organoalkali species have suggested four structural types of tetramers $(\text{CH}_2=\text{CHOLi})_4$, as well as their corresponding solvated

forms: cubic **15a** (S_4), ladder **15b** (C_i),^{42,43} octagonal cyclic **15c** (C_4), and boatlike **15d** (C_2) (Chart 2). Optimization of other starting geometries, including those without symmetry constraints, only gave one of these isomers. Optimized structures of the isolated tetramers and of the most stable solvated species are shown in Figures 6 and 7. X-ray analysis reveals the tendency of tetrameric lithium enolates to assume a distorted cubic arrangement.^{2f,6a,c,f} The cubic crystal structures of the lithium enolate of pinacolone, either complexed with four molecules of THF^{6a} or with four or three molecules of pyridine^{6f} are particularly interesting. To our knowledge, the latter represents the only known crystal structure of a lithium enolate complex where at least one lithium center is neither tetracoordinated nor exhibits π -interaction with the enolate double bond. Stabilization may be provided by a stronger interaction with the enolate oxygens, as indicated by comparison of the average Li-O bond lengths in the tetrapyridine and tripyridine adducts, 1.97 and 1.89 Å, respectively. Similar bond lengths to the tetrapyridine adduct were found for the tetra-THF adduct, where the average $\text{Li-O}(\text{enolate})$ bond distances are 1.94, 1.99, and 1.99 Å, while the distance between lithium and the solvent oxygen is 1.97 Å.⁴⁴

Among the computed unsolvated tetramers, the cubic structure **15a** is the only one in which each lithium is tricoordinated with three enolate oxygens. Coordination of lithium is lower than that in the other topologies, although in some cases interaction with the enolate double bond is evident. This is particularly so for the cyclic isomer **15c**, where interaction is present for each lithium, but is found to a lesser extent in the remaining isomers. For example, only the "external" lithium atoms, coordinated to two oxygens (instead of three), are involved in dative bonding with the enolate double bond in the ladder **15b**.

(42) For a number of ladder-shaped structures are known for lithium amides, see: (a) Armstrong, D. R.; Barr, D.; Clegg, W.; Hodgson, S. M.; Mulvey, R. E.; Reed, D.; Snaith, R.; Wright, D. S. *J. Am. Chem. Soc.* **1989**, *111*, 4719. (b) Barr, D.; Clegg, W.; Hodgson, S. M.; Lamming, G. R.; Mulvey, R. E.; Scott, A. J.; Snaith, R.; Wright, D. S. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1241–1243. (c) Gregory, K.; Schleyer, P. v. R.; Snaith, R. *Adv. Inorg. Chem.* **1991**, *37*, 47. (d) Mulvey, R. E. *Chem. Soc. Rev.* **1991**, *20*, 167. (e) Clegg, W.; Horsburgh, L.; Mackenzie, F. M.; Mulvey, R. E. *J. Chem. Soc., Chem. Commun.* **1995**, 2011–2012. (f) For a review, see: Pauer, F.; Power, P. P. In *Lithium Chemistry: A Theoretical and Experimental Overview*; Sapse, A.-M., Schleyer, P. v. R., Eds.; John Wiley and Sons: New York, 1995; p 295.

(43) To our knowledge, only one ladder structure is known for an organoalkali. See: Sorger, K.; Schleyer, P. v. R.; Stalke, D. *J. Chem. Soc., Chem. Commun.* **1995**, 2279–2280.

(44) For other bond lengths, see: $\text{O-C} = 1.35$ Å, $\text{C-C} = 1.34$ Å (ref 6a).

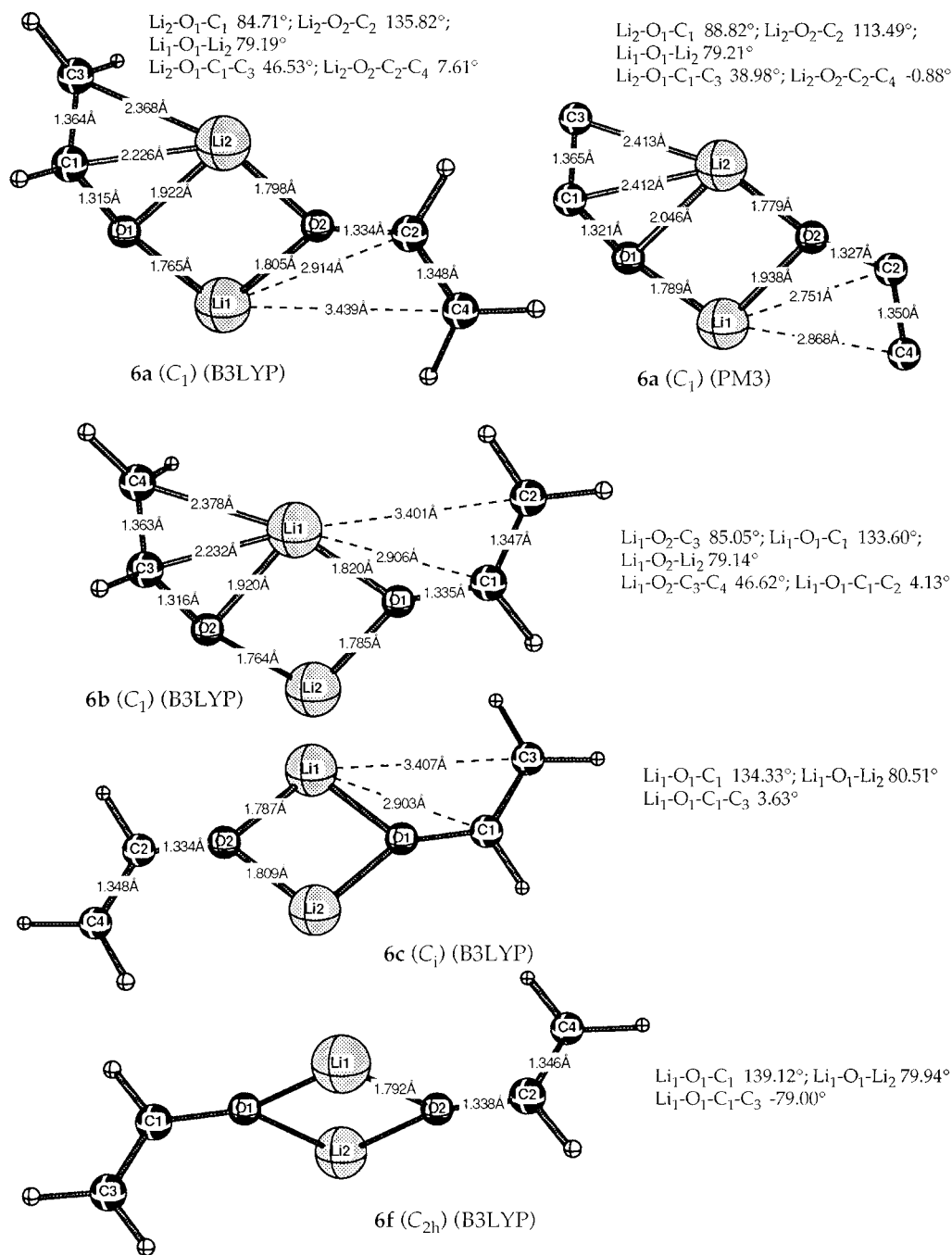


Figure 3. Selected optimized structures of dimers $(\text{CH}_2=\text{CHOLi})_2$ as obtained from B3LYP/6-31+G* and PM3 calculations (hydrogen atoms are omitted from PM3 picture).

Solvation with one, two, three, and four molecules of solvent were computed for each of the four tetrameric isomers, giving the optimized structures **16a–d**, **17a–d**, **18a–d**, and **19a–d**, respectively. The letter following the number is the same as that for the corresponding unsolvated tetramer from which they were obtained by sequential inclusion of solvent molecules. Symmetry point groups of the solvated tetramers are reported in Tables S3 (Supporting Information) and 4. The relative stabilities of the solvated isomers (Scheme 3 and Table 1) reveal the dramatic role played by solvation. Whereas the various unsolvated tetramers differ little in energy (B3LYP), the tetrasolvated cubic tetramer is the most stable by far. The tetrasolvated cubic tetramer is the only structure in which each lithium reaches tetracoordination. In the remaining isomers, the higher stability of **19a** is not due to the cubic arrangement intrinsically, but rather to the solvent effect. The solvation

energies for the cubic tetramer are high (about 10 kcal mol^{-1} /solvent); this is the only tetramer where sequential solvation steps do not decrease the complexation energy, since each successive solvent molecule coordinates with a different lithium. The four solvent molecules do not interact mutually and their spatial arrangement (without steric hindrance) is optimal. An analysis of the Li–O (enolate) and Li–O (solvent) bond lengths reveals that the higher degree of coordination of the cubic tetramer lithiums is not achieved at the expense of lower bond strengths. Average distances for the Li–O (enolate) bond are 2.06, 2.00, 1.92, and 2.04 Å for **19a**, **19b**, **19c**, and **19d**, respectively. Lithium–solvent lengths are 2.09, 2.12, 2.17, and 2.08 Å for **19a**, **19b**, **19c**, and **19d**, respectively. Comparison with the crystal structure of the tetrameric lithium pinacolate complexed with four THF molecules, whose geometric parameters were given above, confirms that PM3 Li–O (solvent) bond

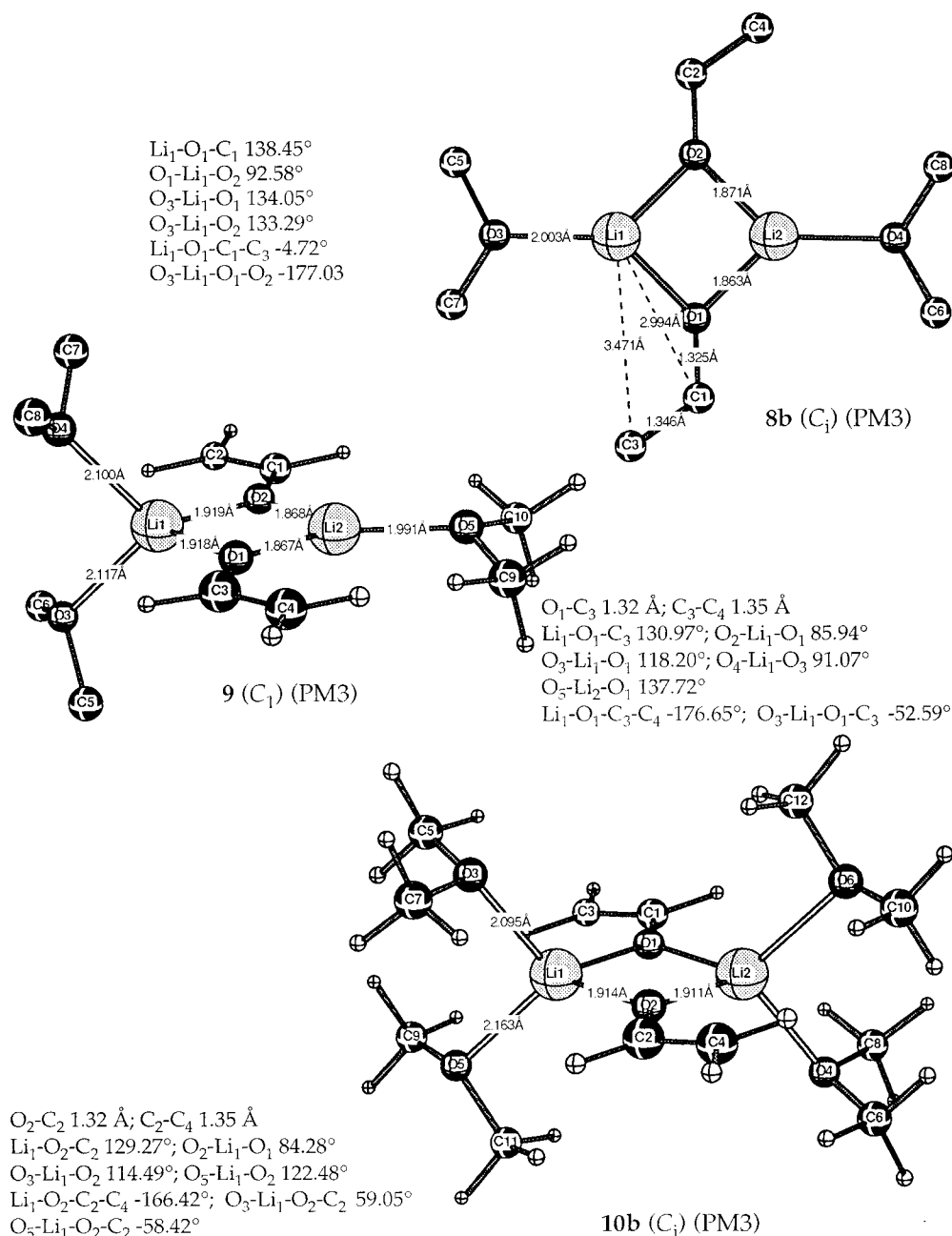


Figure 4. Optimized structures of the complexes of the dimer $(\text{CH}_2=\text{CHOLi})_2$ with two, three, and four molecules of Me_2O , **8b**, **9**, and **10b**, respectively, as obtained from PM3 calculations (hydrogen atoms are omitted from some pictures).

lengths are overestimated by 0.1 Å (see Table 2), although the agreement for the O–C and C–C distances is excellent (± 0.01 Å).

A low degree of coordination of lithium and weak interaction with solvent, a consequence of the steric demands of introducing of the four ether molecules (bond lengths are almost 0.1 Å longer than in **19a**) renders cyclic **19c** the least stable solvated tetramer, almost 30 kcal mol⁻¹ less stable than the cubic **19a**. In the ladder and boatlike structures, interaction with the double bond of the enolate fragment is partially retained even at the fourth degree of solvation. The bond lengths between the central lithium atoms and the opposite-facing enolate oxygens of the ladder are computed to be quite long (2.20 Å vs a typical value of ca. 2.0 Å) and it is likely that this additional coordination does not stabilize the structure much. In addition, the introduction of four molecules of solvent is more sterically demanding in the ladder, as reflected by the longer bond lengths between lithium and dimethyl ether.

Aggregation and Solvation Energies. Schemes 1 and 2 summarize the heats of solvation and aggregation of the monomer, dimer, trimer, and tetramer of **1**. B3LYP/6-31+G*/PM3 energies for the first, second, and third solvation of the monomer are -17.4, -11.7, and -1.6 kcal mol⁻¹, respectively. These values compare well with results of higher level calculations. The first and second coordination energies obtained from B3LYP/6-311+G**//B3LYP/6-31+G*, the highest level of theory used here, are -19.3 and -10.8 kcal mol⁻¹, respectively. Hartree–Fock binding energies are less accurate; deviations from the highest level computations are 3.5 and 1.6 kcal mol⁻¹, for the first and second solvations, respectively. Whereas PM3 geometries of solvated lithium enolate are reasonably accurate, PM3 energies are incorrect. Monomer solvation energies are highly underestimated and are only about half of the DFT values. The same trend is observed for all of the remaining calculated solvation and aggregation energies. In some cases, these even have the opposite sign compared to the DFT data. In conclu-

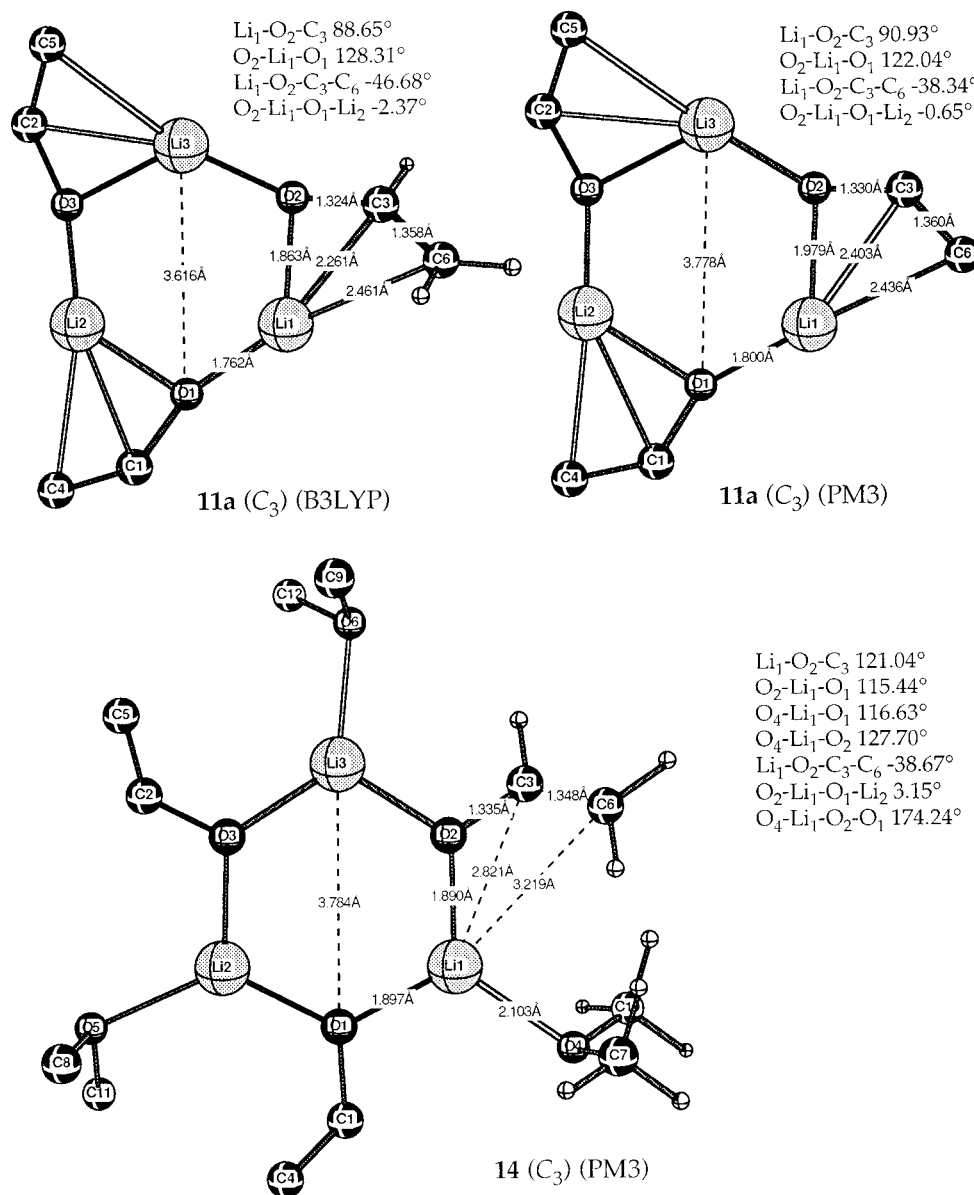


Figure 5. Optimized structures of trimer $(\text{CH}_2=\text{CHOLi})_3$, **11a**, and its complex with three molecules of Me_2O **14** as obtained from B3LYP/6-31+G* and PM3 calculations (some hydrogen atoms are omitted for sake of clarity).

sion, semiempirical energies cannot be considered to be useful in a study of solvated and aggregated lithium enolates.

The binding energy decreases strongly from the first solvation to the second and the third. This behavior is consistent with data reported in the literature for the solvation of lithium cation, methyl lithium and lithium amides. Solvation energies in the gas phase have been measured recently for the clusters $\text{Li}(\text{Me}_2\text{O})_n^+$ ($n = 1-4$): -39.9 , -29.5 , -20.8 , and -15.8 kcal mol⁻¹ for the first, second, third, and fourth solvent, respectively.¹⁹ First and second coordination enthalpies of MeLi with ammonia were computed (ab initio) to be -21.3 and -12.4 kcal mol⁻¹.^{29c} Similar results were obtained in a computational study of the reaction between lithium amide and methane.⁴⁵ Solvation energies of a series of lithium compounds LiX ($X =$ hydrogen and first-row groups) with water and ammonia were found (MP2) to be constant at -18.0 ± 1.2 and -21.5 ± 1.3 kcal mol⁻¹, respectively.⁴⁶ Since the series LiX included such compounds as LiF and LiOH , our first solvation energy for **1**

suggests a high ionic character for the bond between lithium and the enolate oxygen.

The binding energy of the third molecule of solvent is small (-1.6 kcal mol⁻¹). We have already interpreted this result in terms of a combination of saturated coordination capacity of the lithium center, steric effects, and of the lost π -interaction with the enolate double bond. An important further factor is undoubtedly ligand-ligand repulsion as shown in computations of hydrated sodium cation.⁴⁷

Each solvation process is also unfavorable entropically because of the reduced freedom of motion. Seebach⁴⁸ and McGarrity⁴⁹ have measured, through ¹³C NMR and ⁷Li NMR investigations, respectively, the thermodynamic parameters of the equilibrium between $(\text{BuLi})_2(\text{THF})_4$ and $(\text{BuLi})_4(\text{THF})_4$. The experimental ΔS value for the reaction dimer \rightleftharpoons tetramer, where

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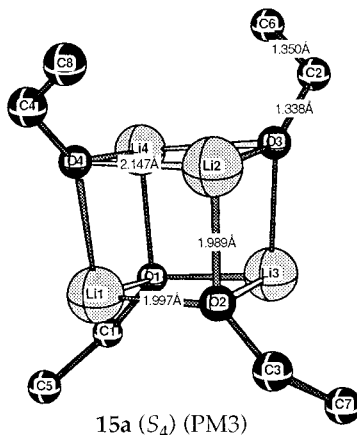
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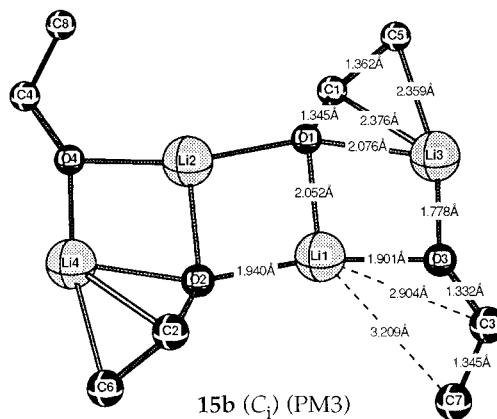
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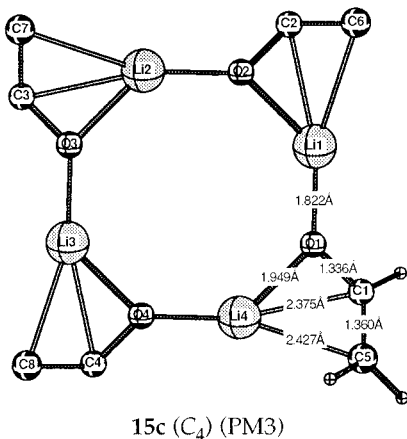
Li₃-O₂-C₃ 105.03°; O₂-Li₃-O₃ 92.47°
 O₁-Li₃-O₂ 95.57°
 Li₃-O₂-C₃-C₇ -1.33°
 O₁-Li₁-O₂-Li₃ 3.92°; O₂-Li₂-O₃-Li₃ 6.10°



Li₃-O₁-C₁ 85.09°; Li₁-O₃-C₃ 126.94°
 O₁-Li₃-O₃ 102.46°; O₁-Li₁-O₃ 99.14°; O₁-Li₁-O₂ 96°
 Li₃-O₁-C₁-C₅ -42.03°
 Li₁-O₃-C₃-C₇ 3.44°; O₂-Li₁-O₁-O₃ 173.07°



Li₄-O₁-C₁ 90.61°; O₂-Li₁-O₁ 134.64°
 Li₄-O₁-C₁-C₅ -39.40°; O₂-Li₁-O₁-Li₄ 1.53°



Li₃-O₄ 2.00 Å; O₁-Li₂ 3.22 Å; Li₃-O₁-C₁ 115.38°
 Li₂-O₄-C₆ 115.48°; O₁-Li₃-O₄ 115.23°
 O₁-Li₁-O₃ 115.21°

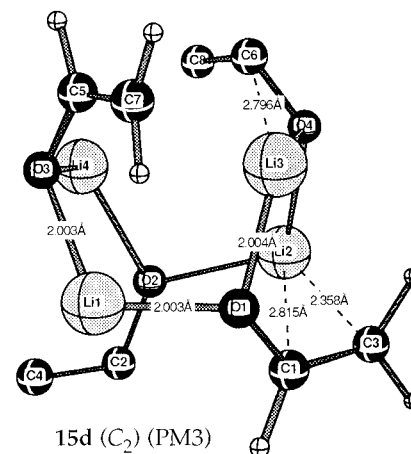


Figure 6. Optimized structures of tetramers (CH₂=CHOLi)₄, **15a–d**, as obtained from PM3 calculations (some hydrogen atoms are omitted for sake of clarity).

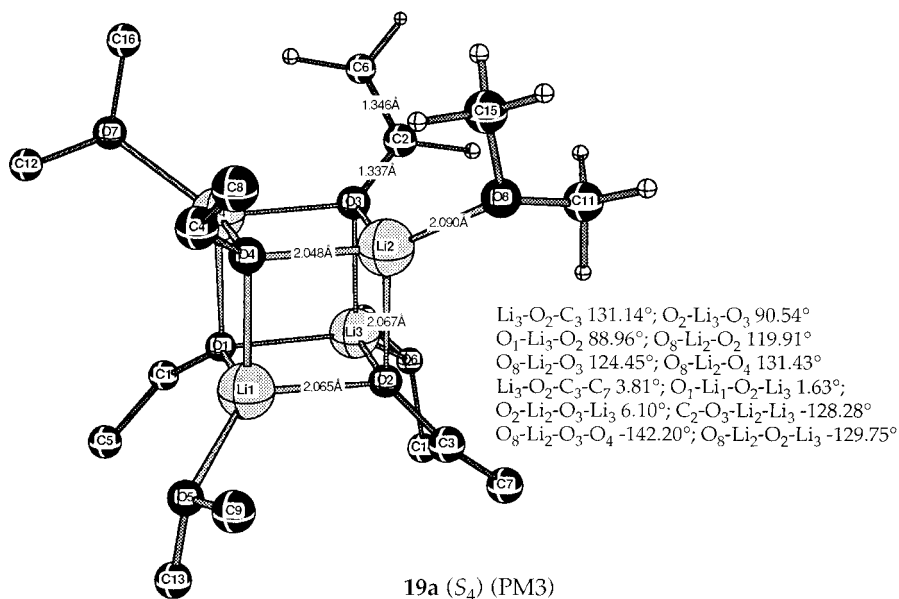


Figure 7. Optimized structure of cubic tetrasolvated tetramer (CH₂=CHOLi)₄(Me₂O)₄, **19a**, as obtained from PM3 calculations.

Table 3. Natural Charge Population in Monomeric and Aggregated Structures of CH₂=CHOLi and Corresponding Solvated Forms

species (point group)		method ^a	Li	O	C _α (CH)	C _β (CH ₂)	LiOCH=CH ₂
2a	CH ₂ =CHOLi (C ₁)	A	+0.926	-0.887	+0.158 (0.336)	-0.820 (-0.375)	0
		B	+0.923	-0.884	+0.192 (0.330)	-0.758 (-0.369)	0
3	CH ₂ =CHOLi(Me ₂ O) (C ₁)	A	+0.889	-0.882	+0.161 (0.331)	-0.803 (-0.367)	-0.029
		B	+0.888	-0.881	+0.194 (0.324)	-0.742 (-0.360)	-0.029
4	CH ₂ =CHOLi(Me ₂ O) ₂ (C ₁)	A	+0.873	-0.891	+0.159 (0.318)	-0.765 (-0.346)	-0.046
		B	+0.868	-0.891	+0.192 (0.313)	-0.706 (-0.340)	-0.050
6a	(CH ₂ =CHOLi) ₂ (C ₁)	unit 1 ^b					
		A	+0.913	-0.998	+0.160 (0.348)	-0.725 (-0.273)	0
		unit 1 ^c					
		B	+0.913	-1.002	+0.195 (0.343)	-0.660 (-0.267)	0
		unit 2 ^b					
		A	+0.943	-1.059	+0.160 (0.330)	-0.625 (-0.203)	0
		unit 2 ^c					
		B	+0.950	-1.068	+0.196 (0.327)	-0.564 (-0.199)	0
6f	(CH ₂ =CHOLi) ₂ (C _{2h}) ^d	A	+0.948	-1.087	+0.148 (0.322)	-0.615 (-0.182)	0
11a	(CH ₂ =CHOLi) ₃ (C ₃)	A	+0.921	-1.015	+0.145 (0.332)	-0.688 (-0.238)	0
		B	+0.921	-1.019	+0.181 (0.329)	-0.624 (-0.233)	0

^a Method A: B3LYP/6-31+G*/6-31+G* calculations. Method B: B3LYP/6-311+G**/6-31+G* calculations. ^b Bridged (Li- π -interaction) unit of the dimer. ^c Not bridged unit of the dimer. ^d Plane corresponding to the moiety Li-O-Li-O is perpendicular to the plane of the carbon atoms.

four molecules of THF are released, is +18.8⁴⁸ or +13.8⁴⁹ eu, a contribution of about +5 eu/molecule of solvent. Fraenkel et al. investigated with ¹³C and ⁷Li NMR the equilibrium in THF between monomeric neopentyl lithium, assumed to be coordinated with three molecules of ether, and the dimer, tetracoordinated with the solvent, giving the value of $\Delta S = +11.4$ eu (corresponding to the release of two molecules of THF).⁵⁰ A further example is the ΔS value of about -11 eu for the equilibrium between solvent separated and contact ion-paired fluorenyllithium,⁵¹ a change that must involve one or two solvent molecules. In conclusion, if we assume that the negative entropic contribution relative to the third solvation process of monomeric **1** is about 5-10 eu, the small negative enthalpy suggests that this step has a positive ΔG at room temperature. Thus, tetracoordination of the lithium center is not necessarily a thermodynamically favored process and less solvated species with coordinatively unsaturated lithium may well be more stable. A similar conclusion is reached for the trimer, where the first coordination energy of the bare lithium center of the disolvated aggregate is already low (-6 kcal mol⁻¹). In the dimer the fourth solvation step is even endothermic, probably because of its higher steric requirements in addition to ligand-ligand repulsion. The situation is different for the case of the cubic tetramer. The first coordination energy is lower than in the monomer, as expected since each lithium is already bound to three oxygens in the unsolvated species, but it remains constant in the subsequent solvation steps. This result is probably a consequence of the optimal spatial arrangement of the cubic form, which minimizes steric effects and reduces ligand-ligand repulsion. Each unsolvated lithium is not perturbed by the presence of the molecules of solvent already coordinated to other lithium centers, and it binds the solvent with the same energy found for the unsolvated tetramer.

Schemes 1 and 2 emphasize the large role of solvation on the aggregation energies. All of the enthalpies involving equilibria between unsolvated monomer and higher aggregates are greatly decreased for the solvated forms. If we consider, based on the solvation enthalpies and entropies, that the most stable solvated species are the disolvated monomer **4**, the trisolvated dimer **9**, the trisolvated trimer **14**, and the tetrasolvated tetramer **19a**, the association energies among these solvated species are: monomer/dimer -14.9, monomer/trimer -11.6, and monomer/tetramer -17.2 kcal mol⁻¹ (per mole of monomeric unit). These values should be compared to the corresponding energies without solvation of -26.0, -33.5, and -35.3 kcal mol⁻¹, respectively. The association energies in the absence of solvent increase in the order: monomer/dimer < monomer/trimer < monomer/tetramer, but a different order is found when solvation is included, with the monomer/trimer

equilibrium being the least favored. Moreover, aggregation enthalpies from monomer to dimer and from monomer to tetramer are similar, with the latter being slightly more favored. This result rationalizes the known tendency of lithium enolates (and some other organoalkali compounds) to exist in solution and in the solid state as monomers, dimers, and tetramers, but not as trimers. Solvation stabilizes the monomer preferentially with respect to the aggregated species. Coordination with solvent stabilizes each unit in the monomer, dimer, and tetramer by about 30, 18, and 11 kcal mol⁻¹, respectively. Moreover, for larger enolates, steric factors may further destabilize the aggregates with respect to monomer. Thus, these conclusions complement experimental data on the lithium enolate of *p*-phenylisobutylphenone, where the dominant equilibrium is monomer-tetramer.³ Note that the reaction of two moles of disolvated monomer to give trisolvated dimer (2 **4** → **9**) plus one mole of solvent has $\Delta E = -30$ kcal mol⁻¹ and ΔS of about 0. By comparison, the tetramerization of disolvated monomer to tetrasolvated tetramer (4 **4** → **19a**) plus four moles of solvent is more exothermic ($\Delta E = -69$ kcal mol⁻¹) and has a large positive entropy change.

This role of entropy in aggregation of alkali ion pairs is not new. Chabanel in particular has shown how dimerization of lithium thiocyanate in ether solutions is driven by the entropy of desolvation.⁵²

Charges. Table 3 summarizes the natural charge populations calculated for a number of selected B3LYP/6-31+G*-optimized structures, using two different basis sets, 6-31+G* and 6-311+G**. Group charges, where the populations on the hydrogens are included, are also reported. The difference in the population of the carbons between the two methods is due to the inclusion of extra polarization functions in the more extended basis set, which assigns more electron population to the hydrogens.⁵³ In fact, the group charges do not show any significant differences.

The negative charge increases on the oxygens on aggregation and decreases on the carbons while no significant variation is observed for the remaining sites. These results are readily rationalized. With respect to the monomer, each oxygen of the dimer is close to two positively charged lithium centers and, as a consequence of its higher effective electronegativity, removes more charge from the double bond. Indeed, the increase of the

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oxygen charge is about the same as the decrease in the C_β charge. The effect of cations on polarization in enolates and phenoxides has been computed previously.^{13b,d}

In the dimer **6a** the lithium cation coordinated to the enolate double bond is less positively charged than the lithium of the second unit, where such coordination is absent, as a result of the π -donation from the double bond to the lithium. As a consequence, the oxygen of the bridged unit is effectively less electronegative and less charge is withdrawn from the α -carbon. Therefore π -coordination between the enolate double bond and the lithium cation increases the negative charge (by about 0.1 electrons) at the β -position.

It is interesting to compare the C_1 dimer **6a** with the C_{2h} dimer **6f**, where the Li–O–Li plane is perpendicular to the C–C–O plane of the enolate moiety. In the latter, the appropriate electron pair of the oxygen does not have the correct symmetry to interact with the double bond. As a consequence, less negative charge should be delocalized onto the β -position. On the contrary, no significant difference is observed between the carbon of the “unbridged” unit of **6a** (unit 2: see Table 3) and the corresponding position of the C_{2h} isomer. This result suggests that π -delocalization from oxygen to the double bond is not important and that polarization mechanism controls charge redistribution in lithium enolates.⁵⁴ This conclusion is confirmed by the fact that the O–C and C–C distances in the unbridged enolate unit of the C_1 isomer and in the C_{2h} isomer (see Figure 3), are nearly identical in the two structures. In view of these conclusions, the small difference in energy (about 1 kcal mol⁻¹) between the most stable C_1 dimer and the C_{2h} isomer **6f** is explained, since the geometries and the charge distributions are similar. The same conclusions are reached by the comparison between **6f** and the remaining dimers **6c–e**, where the free electron pair on the oxygen atom would have the right symmetry to be delocalized effectively onto the carbons.

Since the negative charge on C_β decreases on going from monomer to higher aggregates, one would expect the opposite behavior in the solvated monomers, where each lithium is bonded to more oxygens than in the free monomeric species. Actually the reverse is observed, although the differences in charge populations are small between the free monomer and

the solvated species. Upon coordination with the solvent, the effective positive charge on Li decreases, but there is no significant change for the oxygens, and a small charge redistribution occurs between (CH) and (CH₂), with electrons shifting from the latter to the former. Solvation limits its effect on charge redistribution primarily to the lithium cation, and the populations on the enolate moiety are relatively unaffected by solvent coordination.

Conclusions

A theoretical study of the aggregation and solvation effects of a lithium enolate has been performed using a realistic solvent, dimethyl ether. The B3LYP//PM3 approach gives apparently reliable aggregation and coordination energies and allows molecules as large as the tetrasolvated tetramers of the lithium enolate of acetaldehyde to be studied at uniform levels. B3LYP energies are superior to RHF calculations and comparable to MP4 values, at least for the types of systems considered here; PM3 energies are clearly inadequate but geometries are well described by this semiempirical method.

Solvation has a critical role in determining the relative energies of the aggregated species. π -Interaction between Li and the enolate double bond is another factor that helps to determine the relative stabilities of isomers and the degree of solvation. The cubic tetramer is stable because of the electrostatic stabilization of aggregation, but the monomeric species is important in the equilibrium because of its high solvation energies. In contrast, the dimer, and to a greater extent, the trimer, are less important. The tendency of lithium cation to reach tetracoordination is shown to be less significant than is commonly believed.

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Supporting Information Available: Tables of energies (Tables S1, S2, S3 and S5) and coordinates of all structures (25 pages). See any current masthead page for ordering and Internet access instructions.

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