Pergamon

Tetrahedron Vol. 51, No. 21, pp. 5955-5970, 1995

0040-4020/95 $9.50+0.00

0040-4020(95)00276-6

A Computational Study of Lithio Azaallylic Systems

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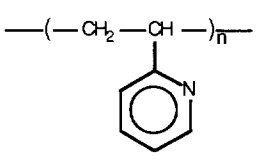
Abstract: Ab initio and semiempirical PM3 calculations were performed on lithioimines as a model system for molecules in which lithium is $^3\eta$ bound to the aza-π-allylic system, such as the growing poly (2-vinylpyridine) chain end. Comparison to the ab initio calculations and published x-ray crystal data showed that the semiempirical calculations performed reasonably well for these systems. The PM3 calculations overestimate the lithium bond distances to the atoms in the allylic system by about 0.1 A, and underestimate the dimerization energies of lithioimines by about 7 kcal/mole, compared to the ab initio results. The solution structure of these molecules is largely determined by steric hindrance and the solvation state. Lithioimines have been found to aggregate into dimers, and in some cases two or more aggregated species coexist in equilibrium with the monomer.

Introduction

Our recent work with poly(2-vinylpyridine) (P2VP, **1**) has shown some interesting solvation effects on the polymerization stereochemistry.[2] A largely isotactic polymer is formed in THF, while polymerization in tetramethylethylenediamine (TMEDA) yields an atactic material. Both ab initio and semiempirical molecular orbital calculations indicate that the growing chain end exists not as a simple carbanion, but as a lithio aza-π-allylic system (**2**), in which the azaallylic orbital rather than the aromatic ring dominates the chemistry of this system.



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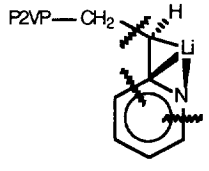

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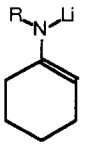
Lithiated imines are the simplest molecules containing this interesting functional group, and have been chosen as model compounds for our study. These compounds are also worthy of study in their own right, due to their reported use as enolate equivalents. Numerous examples of lithiated azaallylic systems have appeared in the organic chemistry literature. Lithiated imines (**3**), hydrazones (**4**), and oximino ethers (**5**) have all been used as enolate equivalents for the purpose of improving the stereoselectivity and regioselectivity of enolate alkylations. This goal has been met with varying degrees of success. Hosomi and coworkers[3] have demonstrated the

regioselectivity of 2-methylcyclohexanone imine alkylations, where the more substituted position is preferentially alkylated, while the product ratios were shown to be solvent dependent. Several examples of regioselective and stereoselective alkylations of conformationally rigid lithiated imines and oximino ethers have been reported by Fraser et al.[4,5] Ketimines are quite unstable to hydrolysis, and it is not known if the relatively low alkylation stereoselectivity is due, in part, to epimerization during the hydrolysis to the alkylated ketone. The ratios of syn versus anti alkylation of aldimines and ketimines have also been reported.[6,7]



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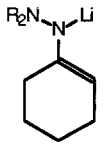

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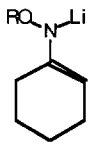

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In spite of the importance of lithiated azaallylic system, very little work has been published concerning the solution structure and bonding of these molecules. It has long been known that most organolithium compounds exist as one or more aggregated species, and that the aggregation state is often dependent on concentration, temperature, and solvents. Lithium NMR, although very useful in determining the Li-C and Li-N bonding in isotopically labeled alkyllithiums[8-10] and lithium amides,[11,12] respectively, is of limited usefulness in π-allylic systems due to the fact that coupling to the π systems is not normally observable, as was demonstrated by Seebach and coworkers with benzylic lithium compounds.[13] In contrast, these investigators observed large ^{6}Li-^{13}C coupling constants of 17 Hz in halolithium carbenoids, which have much more s character in the carbon-lithium bonding orbital than simple alkyllithiums, which show coupling constants of about 7 Hz.[10] The coupling constants are proportional to the s character of the bonding orbitals of the coupled atoms, and therefore show little or no coupling via atomic orbitals which have predominantly π character.[14] Clardy, Collum, and coworkers have reported an x-ray crystal structure of lithio-cyclohexanone dimethylhydrazone, which exists as a polymeric species in the solid state, with each lithium $^{4}\eta$ coordinated to the π system of the hydrazone, as well as to a nitrogen atom of the adjacent hydrazone unit.[15] They also reported two unusual crystal structures in which the π-allylic bonding is disrupted, by coordination to a strong donor ligand in lithiated 2-carbomethoxycyclohexanone dimethylhydrazone, and by steric effects in the bis(diisopropylamine) solvate of lithiated cyclohexanone phenyl imine.[16] The solid state structures are subject to crystal packing forces, however, and are not necessarily the same as the solution structures of the same compounds. In the case of the lithiated cyclohexanone phenylimine, the $^{3}\eta$ lithium bonding was sufficiently disrupted as to allow the observation of a small amount of ^{6}Li-^{15}N coupling.[17] In recent years computational methods have become increasingly important in the study of organolithium compounds. Although ab initio methods are limited to the study of relatively small model systems, reliable semiempirical methods have been developed which are able to calculate the properties and structures of large solvated organolithium systems. MNDO calculations have been used to accurately predict the structure and bonding in lithium dialkylamides.[18] Unfortunately, the MNDO parameterization significantly overestimates the lithium-carbon strength[19] and gives incorrect geometries and energies for many systems containing lithium-carbon bonds, although the error in geometry is relatively small in some simple, sterically unhindered π-allylic systems.[20] Our preliminary studies with MNDO generated highly distorted geometries for lithioimine dimers which were far from either the ab initio or published experimental geometries. Recently reliable parameters have been developed for the semiempirical PM3 Hamiltonian, which

have corrected most of the deficiencies in the MNDO parameterization.[21] Thus, it is now possible to explore this interesting and important area of organolithium chemistry via reliable computational methods which were previously unavailable. The purposes of this work are to demonstrate the reliability of the new PM3 parameterization for the systems of interest by comparison to ab initio, and where available, experimental data; and to explore the structure, bonding, aggregation, and solvation of lithiated azaallylic molecules.

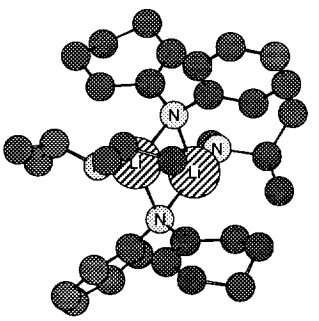
Computational methods

Semiempirical PM3[22] calculations were performed with the MOPAC[23] program and the Insight II graphical interface, produced by Biosym[24] on a Silicon Graphics Indigo 2 workstation. All PM3 geometry optimizations were performed in Cartesian coordinates without symmetry constraints, using the PRECISE keyword, which improves the convergence criteria by a factor of one hundred. The PM3 parameters of Anders[21] were used as an external parameter set. Ab initio geometry optimizations were performed with the Gaussian 92[25] program at the Hartree Fock level of theory, using the 6-311G* and 6-311+G* basis sets, on either an IBM SP1 processor run in single node mode, or an IBM 590 workstation. Vibrational frequency calculations were performed at the Hartree-Fock level of theory and, where applicable, with both the ^{6}Li and ^{7}Li isotopes. All calculated frequencies were scaled by a factor of 0.89.

Results and discussion

In order to determine the reliability of the PM3 parameters for the systems of interest, calculations were performed on lithiated azaallylic and chelating systems for which x-ray structures have been published. One such system is the lithiated phenyl imine of cyclohexanone, solvated by 2 diisopropylamine molecules[16] (**6**). The calculated structure was similar to the published crystal structure, but the calculated average lithium-nitrogen bond distance was 2.120 A, compared to 2.031 A in the crystal structure. The calculated structure showed no bonding to the cyclohexanone carbons, while the x-ray structure showed a very distorted azaayllic system, with a lithium-terminal carbon distance of 2.971 A. Since any bonding interactions would be quite small at this distance, the difference between the calculated and x-ray structures may be due, at least in part, to crystal packing forces.

The x-ray structure of the lithiated dimethylhydrazone of cyclohexanone showed a nitrogen bridged polymeric structure.[15] A PM3 geometry optimization was performed on the asymmetric unit of this polymer (**7**), and the results were in reasonable agreement with the experimental data. The major difference was the position of the lithium atom above the $^{4}\eta$ π system, with the calculated lithium distances to the inner carbon and



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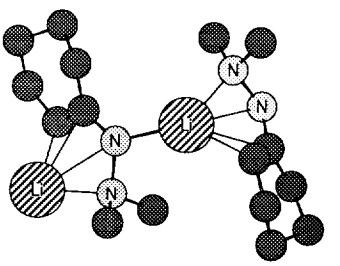

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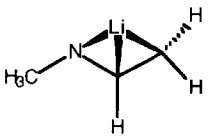
nitrogen atom exceeding the experimental values by about 0.4 A. Due to the relatively large amount of ionic character in the lithium-π system bond, such discrepancies are not surprising, as the crystal packing forces could easily distort such a polar bond.



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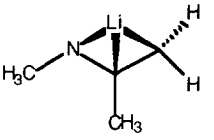

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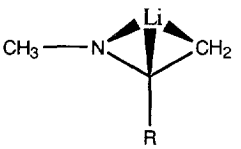
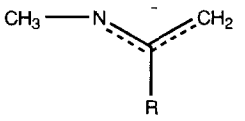
The performance of the PM3 parameters was further evaluated by comparison to high level calculations on the lithiated methyl imines of acetaldehyde (**8**) and acetone (**9**), as well as the corresponding anions. The calculated geometries of the lithioimine monomers are shown in Table 1, and the corresponding anions in Table 2. In the case of both the lithioaldimine and ketimine, the PM3 calculation overestimated the C-N bond length by about 0.06 A, and the Li-N and Li-C bond lengths by 0.1 A or more, relative to the best ab initio results. The overestimation of the Li-N and Li-C bonds is not a serious problem, however, due to the large ionic character of these bonds. The addition of diffuse functions to the 6-311G* basis set had only a small effect on the optimized geometry, with the Li-C bond lengths increasing by about 0.01 A. The imine anions also showed longer PM3 calculated C-N bond lengths, and the diffuse functions had a larger effect on bond lengths, with the C-N bond length decreasing in both the aldimine and ketimine anions. The longer C-C and C-N bond lengths in the lithioimine ion pairs may arise from the interaction of the nearly empty lithium s orbital with the bonding π orbital of the azaayllic fragment, thereby removing a small amount of electron density from the C-C-N bond.

Table 1. Calculated bond distances (A) in the lithioimine monomers



R	Method	C-N	C-C	N-Li	C1-Li	C2-Li
H	PM3	1.3826	1.3843	1.9468	2.2506	2.2811
H	6-311G*	1.3179	1.3844	1.8448	2.1348	2.0946
H	6-311+G*	1.3192	1.3841	1.8448	2.1466	2.1053
Methyl	PM3	1.3884	1.3918	1.9529	2.2405	2.3083
Methyl	6-311G*	1.3260	1.3945	1.8420	2.1008	2.1256
Methyl	6-311+G*	1.3281	1.3931	1.8416	2.1146	2.1338

Table 2. Calculated bond distances in the imine anions



R	Method	C-N	C-C
H	PM3	1.3625	1.3612
H	6-311G*	1.3117	1.3721
H	6-311+G*	1.3096	1.3791
Methyl	PM3	1.3688	1.3672
Methyl	6-311G*	1.3690	1.3670
Methyl	6-311+G*	1.3223	1.3812

Ab initio calculations on all lithioimine monomers showed a strong infrared active N-C-C stretching frequency at 1470-1520 cm^{-1}. The effect of basis sets, isotopes, and molecular structure are summarized in Table 3. In each case the addition of diffuse functions to the basis set resulted in a lower calculated vibrational frequency, with the largest effect seen in the free anions, which showed higher frequencies than the lithium

Table 3. C-N-N stretching frequencies (cm^{-1})in the lithioimines and imine anions

R	Isotope	6-311G*	6-311+G*
H	^{6}Li	1516.6	1511.1
H	^{7}Li	1516.4	1510.9
H	Anion	1555.0	1526.4
Methyl	^{6}Li	1476.7	1474.5
Methyl	^{7}Li	1476.6	1474.4
Methyl	Anion	1505.3	1476.7

Table 4. Calculated (6-311+G*) IR active vibrational frequencies and relative IR intensities involving substantial lithium movement

R	Isotope	Frequency (cm^{-1}) /IR Intensity (KM/mole)					
H	^{6}Li	561.3	126.9	617.1	175.5	662.5	186.0
H	^{7}Li	553.2	44.4	606.5	256.7	658.3	142.8
Methyl	^{6}Li	576.7	19.0	627.4	43.2	649.4	250.0
Methyl	^{7}Li	558.2	39.9	624.2	92.1	643.2	199.2

containing molecules. The ^{6}Li--^{7}Li vibrational isotope effect was only about 0.2 cm^{-1} for this stretching mode. In contrast, the 3 modes between 550 and 660 cm^{-1} involved considerable motion of the lithium atom, and showed large ^{6}Li--^{7}Li isotope effects in both the frequencies and infrared intensities, as shown in Table 4. In each case the vibrational frequency increased upon isotopic substitution with ^{6}Li. The infrared intensity of the highest vibration (640-665 cm^{-1}) increased, and that of the middle vibration (605-630 cm^{-1}) decreased with the lighter isotope. Isotopic substitution of the lowest energy mode (550-565 cm^{-1}) greatly increased the intensity in the case of the aldimine, but caused a slight decrease in intensity in the ketimine.

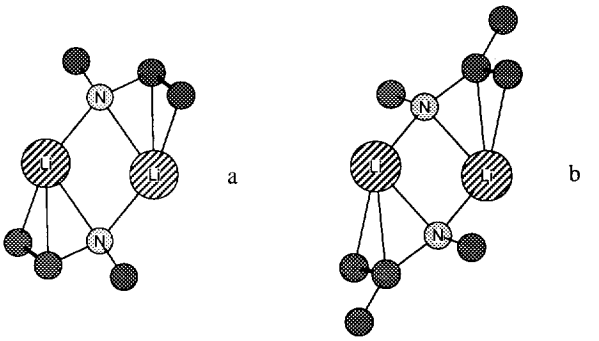


Figure 1. Lowest energy dimeric isomer (Dimer 1) of the lithiated methyl imine of acetaldehyde (**a**) and acetone (**b**).

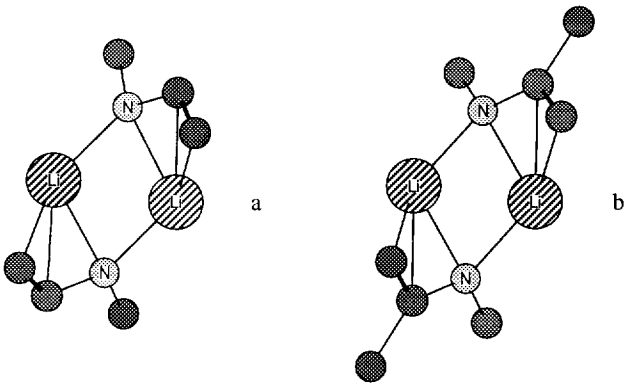


Figure 2. Second isomeric dimer (Dimer 2) of the lithiated methyl imine of acetaldehyde (**a**) and acetone (**b**).

Two isomeric lithio methylimine cyclic dimers of acetaldehyde and acetone were found by both ab initio and semiempirical PM3 calculations. The lowest energy structure, dimer 1 (Figure 1), is of approximately C_i

symmetry. The other cyclic structure, dimer 2 (Figure 2), is of approximately C_2 symmetry, and was generated by inversion of one nitrogen atom of the symmetrical dimer, followed by full geometry optimization. In the cyclohexanone imine, which will be discussed later, the PM3 optimized geometry of this second cyclic dimer is distorted by steric hindrance, so that no symmetry elements are present. (Figure 3) The addition of diffuse functions to the 6-311G* basis set caused only very small changes in the optimized geometry. As in the case of the monomer, the PM3 calculations overestimated the lithium bond distances to the π system by about 0.1 A.

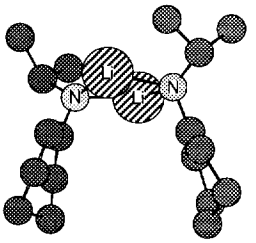


Figure 3. PM3 optimized geometry of the second dimeric isomer (Dimer 2) of the lithiated N-isopropyl cyclohexanone imine.

Table 5 shows the calculated dimerization energies of the lithioimines and the equilibrium constants for the interconversion of the 2 isomers. The PM3 calculations underestimated the dimerization energies by about 7 kcal/mole relative to the 6-311+G ab initio results, and also overestimated the stability of the less stable dimer

Table 5. Dimerization energies (kcal/mole) of lithioimines

R	Method	Dimer 1	Dimer 2	k^{298} 1 ⇌ 2
H	PM3	-38.03	-37.31	0.29
H	6-311G*	-46.09	-44.16	0.038
H	6-311+G*	-45.12	-43.27	0.043
Methyl	PM3	-35.61	-35.94	1.75
Methyl	6-311G*	-43.07	-42.11	0.20
Methyl	6-311+G*	-42.86	-41.34	0.076

isomer. A third isomeric open dimer was also found by PM3 (Figure 4), which was similar to the published lithio cyclohexanone dimethylhydrazone x-ray asymmetric unit described earlier. Several attempts failed to find a corresponding isomer by ab initio calculations in the unsolvated state, as the structure collapsed to the cyclic dimer 2 upon geometry optimization. We therefore conclude that the unsolvated open dimer is either an artifact of the PM3 method, or is a shallow minimum on the potential energy surface. The solvated open dimer geometry could not be optimized by ab initio calculations due to the size of the system, but may be a true local minimum due to the similarity to the x-ray structure, and may be an important species in lithioimine reactions.

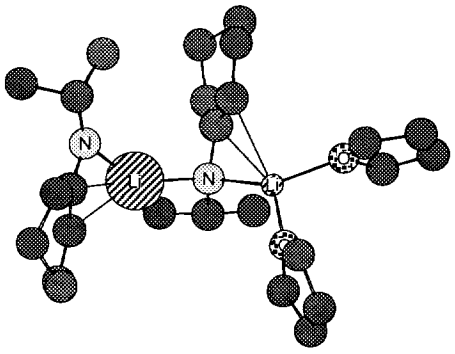


Figure 4. Open dimeric form (Dimer 3) of the lithiated N-isopropyl cyclohexanone imine.

The N-C-C coupled out of phase stretching frequencies of the two unsolvated lithioimine dimer isomers are listed in Table 6. Due to the size of the molecules, the frequencies were calculated using the 6-311G* basis set at the HF/6-311G* optimized geometry. As in the case of the monomer, the ketimine dimers showed a lower stretching frequency than the aldimine by about 30 cm^{-1}. The ^{6}Li--^{7}Li isotope effect was a negligible 0.1 cm^{-1}. The stretching frequency of dimer 1 was higher than that of dimer 2 by only about 2.5 cm^{-1}, which would make it difficult to distinguish the two isomers by vibrational spectroscopy. The frequency of the dimers is higher than that of the monomer by 35-45 cm^{-1}, which would allow the two species to be distinguished, although the magnitude of this may be different in solution. The higher frequency of the dimeric form is suggestive of a larger ionic character of the lithium-π-system bond in the aggregated species. A literature search revealed surprisingly little published data concerning the vibrational spectra of organolithium compounds, although several studies were performed on methylmagnesium haildes, and the vibrational modes assigned with the aid of x-ray crystal structures. [26-29] The few studies reported for alkyllithiums were performed before the aggregation behavior of these materials was fully understood.[30-31] The vibrational spectra of monomeric methyllithium were observed in an argon matrix, along with a second species of unknown structure. As the aggregation behavior is better understood, vibrational analysis may become a more important tool for structure determination of organolithiums.

Table 6. Calculated (6-311G*) C-C-N stretching frequencies of lithioimine dimers

R	Isotope	Isomer 1	Isomer 2
H	^{6}Li	1551.1	1548.6
H	^{7}Li	1551.0	1548.5
Methyl	^{6}Li	1519.8	1517.4
Methyl	^{7}Li	1519.7	1517.3

Solvation effects

Comparison of the semiempirical and published x-ray structures shows that the lithium PM3 parameters are sufficiently accurate to give good semiquantitative geometries and energies for lithio aza-π-allylic systems.

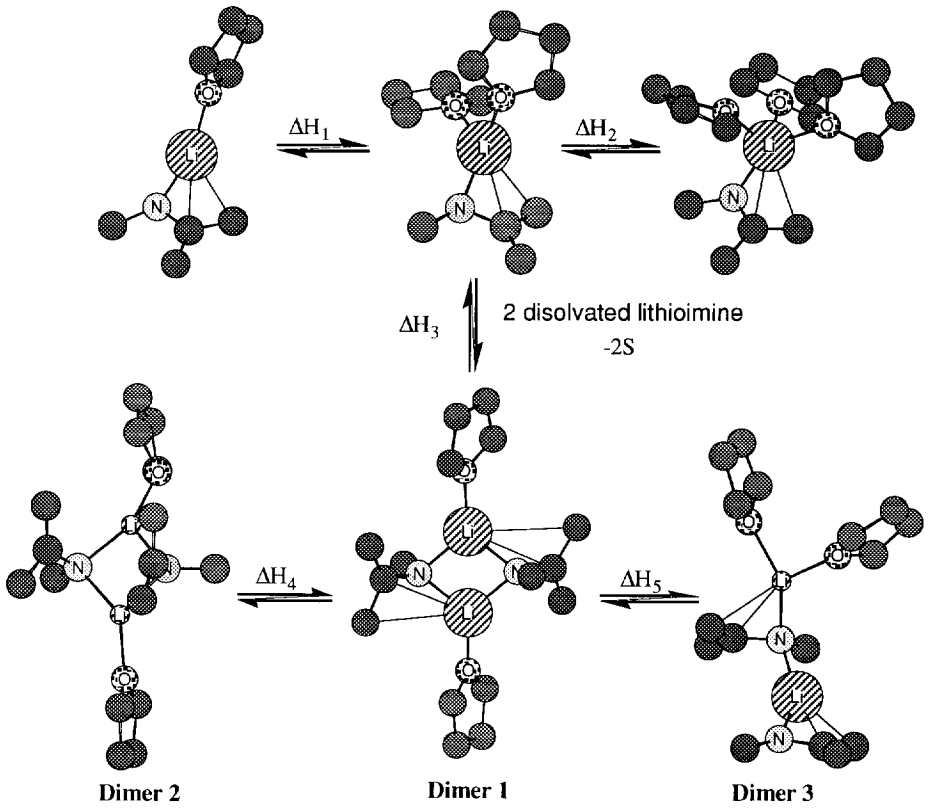
Therefore, the PM3 method was used to explore the effects of solvation and steric factors on the aggregation state of these molecules. The methyl lithioimine of acetone (**10**), and the lithio methyl (**11**), isopropyl (**12**), t-butyl (**13**), and cyclohexyl (**14**) imines of cyclohexanone were chosen for this study.

Table 7 shows the successive heats of solvation of the monomeric lithioimines **10-14** with THF, HMPA, and TMEDA. The THF solvation enthalpy was nearly independent of the imine studied for the first two solvations. The third solvation was endothermic for each of the imines. Addition of the third THF ligand resulted in a weakening of the $^3\eta$ bonding, resulting in an increase in the terminal C-Li bond length from about 2.4 A to about 2.7 A. In the case of the acetone imine, the trisolvated lithium was $^1\eta$ coordinated to the imine nitrogen. A similar pattern was seen with HMPA solvation, except that the $^3\eta$ bonding was weakened by the second HMPA ligand. The third solvation occurred only with the acetone imine, and resulted in $^1\eta$ coordination of the lithium via the imine nitrogen atom. TMEDA coordinated to the lithioimines in an $^2\eta$ fashion and did not disrupt the $^3\eta$ coordination to the π system. The second and third THF and HMPA solvation enthalpies reflect a competition between the solvent and π system for coordination to the lithium atom.

Table 7. PM3 calculated solvation enthalpies (kcal/mole) of lithioimine monomers

		THF			HMPA		TMEDA
Imine	$\Delta H\ S_1$	$\Delta H\ S_2$	$\Delta H\ S_3$	$\Delta H\ S_1$	$\Delta H\ S_2$	$\Delta H\ S_3$	$\Delta H\ S$
10	-12.4	-4.0	+2.1	-22.8	-4.1	+2.6	-21.5
11	-11.2	-5.3	+1.5	-23.8	-12.8	N/A	-23.4
12	-10.8	-5.9	+0.4	-23.4	-12.3	N/A	-21.3
13	-10.8	-5.6	+0.3	-23.0	-9.9	N/A	-23.1
14	-11.1	-5.6	+0.8	-23.4	-13.7	N/A	-22.6

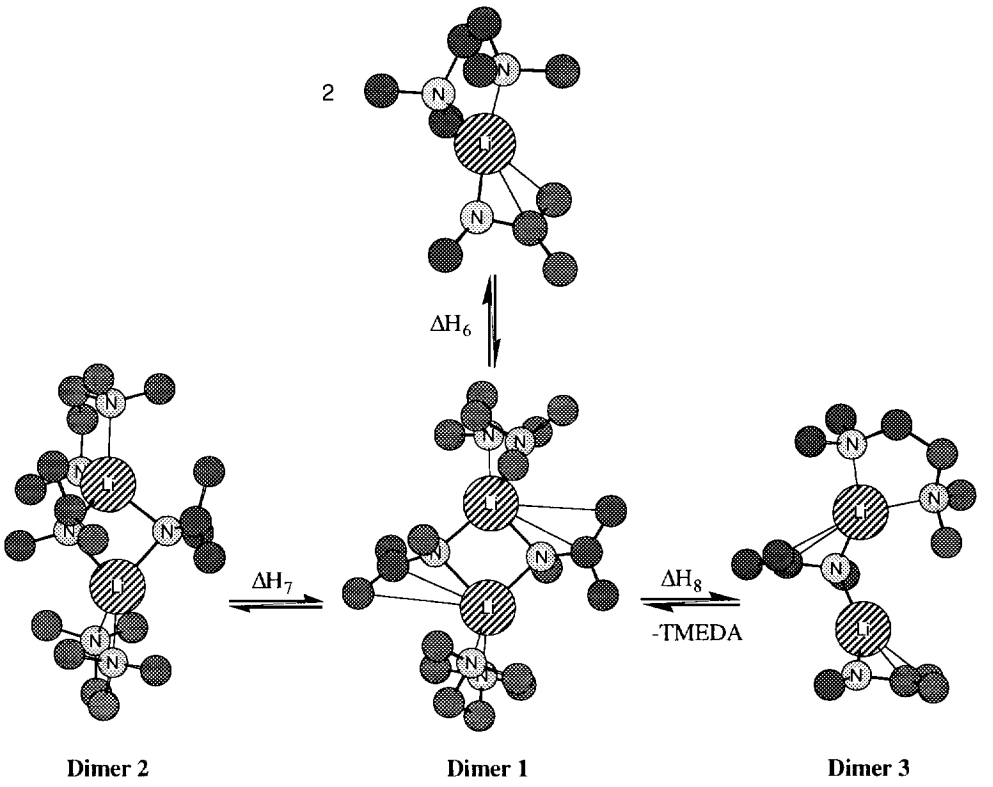
Scheme 1 illustrates the equilibrium between the aggregates of lithioimines **10-14** in THF and HMPA. The enthalpy differences, calculated from the differences in heats of formation of each species, are listed in Table 8. The corresponding equilibria in TMEDA are illustrated in Scheme 2, and the enthalpy values listed in Table 9. In THF each of the lithioimines exists as an equilibrium mixture of 2 cyclic dimers (dimers 1 and 2), with a negligible concentration of the monomer or open dimer. It should be noted that the π system is distorted or broken in the C_1 form (dimer 2) of the solvated cyclohexanone imines, with the lithium bonded primarily to the imine nitrogen atoms. The equilibrium mixture is much different in HMPA, where the aggregation appears to be dominated by steric hindrance. The acetone methyl lithioimine exists mostly in dimeric form, with dimer 2 predominating. At 298 K the concentration of the open dimer (dimer 3) is about 1.5×10^{-4}, which is comparable to the enol form concentration in many common aldehydes and ketones. Each of the cyclohexanone lithioimines appears to exist mostly as the disolvated monomer, although the cyclohexyl imine has a small but substantial concentration of the two cyclic dimers. The dimer concentration will probably be somewhat higher than calculated due to the tendency of PM3 to underestimate the dimerization energy, relative to the ab initio calculations. A similar situation was found in TMEDA, where the methyl lithioimines of acetone and cyclohexanone exist as a mixture of the two cyclic dimers. As the steric hindrance is increased by bulkier N-alkyl groups, the monosolvated monomer, the disolvated cyclic dimers, and the monosolvated open dimer



Scheme 1 Equilibria between solvated lithioimine species in THF or HMPA. THF solvate shown. Hydrogens and cyclohexanone ring atoms (where applicable) omitted for clarity.

Table 8. Isomerization enthalpies of THF and HMPA solvated lithioimines

	ΔH_1		ΔH_2		ΔH_3		ΔH_4		ΔH_5	
Imine	THF	HMPA	THF	HMPA	THF	HMPA	THF	HMPA	THF	HMPA
10	-4.0	-4.1	+2.1	+2.6	-14.1	-9.2	+0.20	-1.8	+10.3	+3.4
11	-5.3	-12.6	+1.5	N/A	-14.8	+7.6	+0.16	+2.3	+12.9	+8.76
12	-5.9	-12.3	+0.4	N/A	-14.9	+8.1	+3.5	+1.0	+12.3	+4.5
13	-5.6	-9.9	+0.3	N/A	-9.8	+2.8	-2.6	+1.7	+12.5	+9.2
14	-5.6	-13.7	+0.8	N/A	-9.6	+15.8	-0.64	-1.8	+9.2	+1.2



Scheme 2 Equilibria between solvated lithioimine species in TMEDA.

Table 9. Isomerization enthalpies of TMEDA solvated lithioimines

Imine	ΔH_6	ΔH_7	ΔH_8
10	-13.4	-0.65	+10.4
11	-10.4	+5.4	+15.5
12	-5.3	+0.068	+5.7
13	+4.3	-3.3	+0.94
14	+0.11	-3.5	+4.9

become comparable in energy, and the lithioimines exist as equilibrium mixtures of all four species.

PM3 calculations were performed on unsolvated and THF and TMEDA solvated 2(1-lithioethyl)pyridine, as a model for the growing P2VP chain end. The optimized geometries are shown in Figure 5. Although the third THF solvation enthalpy was endothermic by 5.5 kcal/mole, the lithium retained the $^3\eta$ bonding to the aza-π-allylic system, in contrast to many of the simple lithioimine molecules, in which the $^3\eta$

bonding was destroyed or severely distorted by the third solvent molecule. This may result from both the aromaticity of the system, as well as the reduced steric demands of the flat pyridine ring.

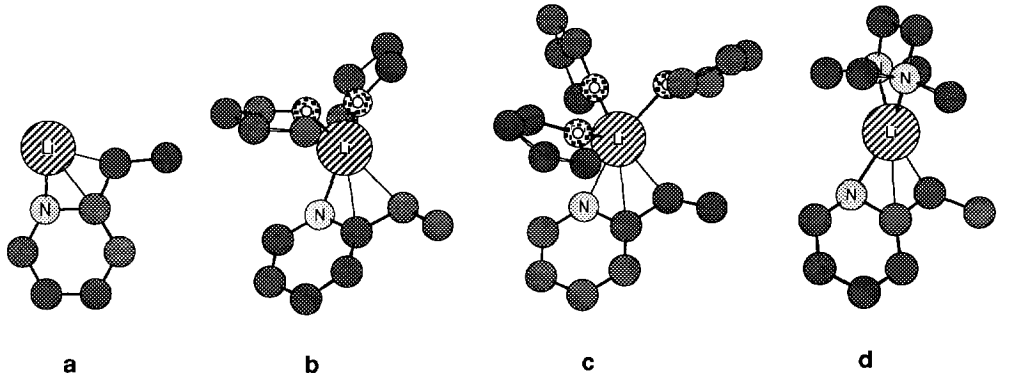


Figure 5. PM3 calculated geometries of 2(1-lithioethyl)pyridine. (a) unsolvated (b) THF disolvate (c) THF trisolvate (d) TMEDA solvate

Calculations were performed on the least sterically hindered dimeric form of 2(1-lithioethyl)pyridine. Although the unsolvated dimer is a stable molecule, solvation by either THF or TMEDA causes the dimer to dissociate into two loosely bound monomeric units. These results are illustrated in Figure 6. We therefore

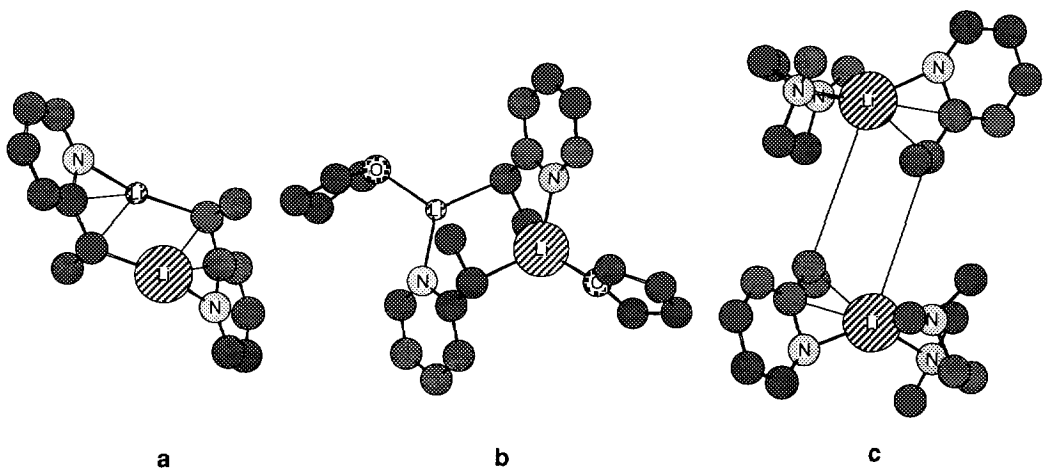


Figure 6. PM3 calculated dimers of 2(1-lithioethyl)pyridine. (a) unsolvated (b) THF solvate (c) TMEDA solvate

conclude that 2-vinylpyridine polymerizes via an unaggregated chain end, at least in polar solvents. Indirect evidence has suggested that the stereochemistry of 2-vinylpyridine is determined by the coordination of the lithium atom by the penultimate pyridine ring, as well as to solvent ligands.[32-34] These effects are currently being studied, and will be presented in a later work.

Based on the results of the geometry calculations it is possible to predict the type of information which can be obtained by lithium NMR on these systems. ^{6}Li--^{13}C coupling will not be observed in any of these molecules as the lithium is bound to carbon exclusively in an aza-π-allylic manner. In nonpolar or weakly polar solvents no ^{6}Li--^{15}N coupling will be observed in the monomeric form, or in the cyclic dimers of unhindered lithioimines, for the same reason. In strongly coordinating solvents such as HMPA, ^{6}Li--^{15}N coupling will likely be observable in some disolvated or trisolvated monomers, due to the disruption of the aza-π-allylic system and the resulting σ bonding of the lithium to the imine nitrogen. The coupling constants in the cyclic dimers will be highly dependent on both the structure and solvation state of the species. Sterically hindered imines, such as those derived from cyclohexanone, are more likely to show coupling due to the larger σ character of the Li-N bond as the π system is disrupted by the steric hindrance. This was, in fact, observed in the dimeric lithiated phenyl imine of cyclohexanone, with a ^{6}Li--^{15}N coupling constant of 3.4 Hz[17], compared to a value of 4.8-5.1 Hz typically found in lithium dialkyl amides.[12] In general, more coupling will likely be observed in the C_1 (dimer 2) form in nonpolar solvents, as the hindrance between the two cyclohexanone rings do not allow the lithium to bind in an $^{3}\eta$ manner. The x-ray structure[16] suggests that the phenyl imine may be an exceptional case, as the cyclohexyl and phenyl groups are similar in size. In principle, ^{6}Li--^{15}N coupling information could be used to study the bonding in the growing P2VP chain end, although the expense of synthesizing ^{15}N labeled material would be prohibitive. In general, the coupling constants will depend on the relative affinities of the solvent ligands and the aza-π-allylic system for the lithium atom. Thus, relatively small steric effects may have a large effect on the NMR coupling in these systems.

Conclusions

The semiempirical PM3 method has been applied to the study of lithio aza-π-allylic molecules. Comparison of the semiempirical results to large basis set ab initio calculations and published x-ray crystal structures show that PM3 is sufficiently accurate to generated reasonably good geometries and relative energies of the various aggregated species. PM3 does appear to underestimate the bonding between the lithium atom and the aza-π-allylic orbital of the imine. Due to the large degree of ionic character in this bond, this does not present a serious problem, although it may result in slightly distorted structures in sterically hindered aggregated species. In contrast, a few preliminary MNDO calculations generated very poor geometries for lithioimines, especially the dimeric forms. Thus, PM3 is the semiempirical method of choice for the study of lithioimine chemistry and 2-vinylpyridine polymerization.

Lithioimines and structurally similar molecules exhibit bonding in which the lithium atom resides above the aza-π-allylic orbital and is bonded in an $^{3}\eta$ manner. In weakly polar solvents the molecule exists as an equilibrium mixture of two cyclic dimers of similar energy. Substantial changes in structure and bonding occur upon addition of strongly coordinating solvents. A third open dimer, similar to the asymmetric unit of lithiohydrazones in the solid state, may occur as a minor species in the presence of strongly coordinating or chelating solvents. Steric hindrance also affects the structure and bonding of these compounds, and in polar solvents, hindered lithioimines may exist as an equilibrium mixture of solvated monomers and dimers. This may account for the relatively low alkylation stereoselectivity of lithioimines reported in the literature. Although living anionic polymerization is a synthetic method of major importance, the structure and bonding between the growing chain end and the lithium "counterion" has been poorly understood. As in lithioimines, the

"counterion" forms an integral part of the structure. The structure of the growing P2VP chain end is similar to those of the simple lithioimine momoners. The calculated structures of solvated 2-(1-lithioethyl)pyridine, chosen as a convenient model system for the polymer chain end, indicate that the $^{3}\eta$ bonding in this system is disrupted by coordinated solvent molecules less than simple lithioimines. Although the dimeric form is stable in the absence of coordinating solvent molecules, the THF and TMEDA solvated dimers dissociate into a pair of weakly bound solvated monomers.

The $^{3}\eta$ bonding in unsolvated and sterically unhindered lithioimine species prevents the observation of lithium-carbon or lithium-nitrogen NMR coupling, thus limiting the structural data which can be obtained by this method. In some solvated systems, the $^{3}\eta$ bonding is disrupted, however, and lithium-nitrogen coupling may be observed. Due to the weak character of the lithium-π-system bond, small changes in the structure or solvation of the molecule may cause large changes in the character of the lithium-nitrogen bond, and thus in the type of ^{6}Li--^{15}N coupling information which can be obtained. Both the monomer and dimer show a strong infrared C-C-N stretching frequency, with the monomer frequency lower than that of the dimer by about 35-50 cm^{-1}. Therefore, a combination of infrared and NMR spectroscopy may be useful to determine the solution structure of lithioimines and similar molecules.

Acknowledgments

This work was supported by NSF grant #RII-9005196 and NIH grant #GM 08247-07. Computer and software resources were provided by the Center for Theoretical Studies of Physical Systems (CTSPS), the Army Center for Excellence in Information Sciences, and the High Performance Polymers and Ceramics (HiPPAC) Center at Clark Atlanta University.

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(*Received in USA* 15 *January* 1995; *accepted* 31 *March* 1995)