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Structure, Bonding, and Solvation of Dilithiodiamines[†]

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Computational methods were used to determine the structure of dilithiodiamines and the effects of solvation by ethereal solvents. Solvation was examined by the use of microsolvation with explicit dimethyl ether or THF ligands and by the combined use of microsolvation and the IEFPCM continuum solvent model. It was determined that each of the compounds studied exists exclusively as a bridged intramolecular dimer, both in the gas phase and in solution. Thermodynamic properties were calculated at 200 and 298 K to estimate the effect of temperature on the cyclization energies. Infrared spectroscopy was used to confirm the proposed intramolecular dimer structures.

Introduction

Lithium dialkylamides are used extensively in organic synthesis for the formation of enolates. The structure of these bases is of interest because the reactivity and stereoselectivity of enolization is dependent on the lithium amide structure, solvent, and the formation of mixed aggregates.[1−6] Mixed aggregates between the lithium amide and butyllithium are often formed by addition of an excess of butyllithium to the amine to ensure complete deprotonation. Lithium dialkylamide mixed aggregates are also formed with the newly generated lithium enolate in deprotonation reactions, and these mixed aggregates often reduce the enolization stereoselectivity. Dilithiodiamines were initially investigated as potential bases for ketone enolization with high stereoselectivity because it was anticipated that they would resist mixed aggregate formation due to the formation of energetically favorable intramolecular dimers. Although the stereoselectivity of dilithio-*N*,*N*′-dimethyl-1,3-diaminopropane suggests that mixed aggregates are formed even with this system, the structure and bonding in dilithiodiamines remains of interest. In particular, this paper investigates the energy of cyclization of dilithiodiamines in the gas phase and the effects of temperature, solvation, and chain length on the cyclization energy. The cyclic intramolecular dimer gives rise to new vibrational frequencies corresponding to Li−N motions in the bridged structure.

Solvent effects are very important in organolithium chemistry. They dramatically influence the aggregation state and reactivity of alkyllithiums, lithium dialkylamides, and other organolithium compounds.[7−13] Hydrocarbon solvents involve little or no coordination to the lithium atoms, and the associated solvent effects consist primarily of dielectric polarization, dispersion interactions, and cavitation. Hexamethylphosphoramide (HMPA) is at the other extreme, coordinating so strongly to lithium that two-bond NMR spin coupling can be observed between lithium and phosphorus.[14,15] Ethereal solvents such as tetrahydrofuran (THF) are intermediate in their binding affinity for lithium. Rapid exchange of THF ligands prevents the observation of lithium−carbon spin coupling, although coordination of several ethers to lithium dialkylamides has been observed indirectly.[16,17]

A common solvation model for lithium compounds is microsolvation by explicit coordinating ligands such as THF, dimethyl ether, or trimethylamine. The resulting “supermolecules” are presumed to serve as good models for the solution behavior of organolithium compounds. The choice of ligands is often determined by the computational cost and chemical intuition. For example, dimethyl ether is sometimes used in place of THF because of the lower computational cost. Both ligands have similar dielectric constants and have similar steric bulk

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[†] Dedicated to Professor Donald G. Truhlar on the occasion of his 60th birthday.

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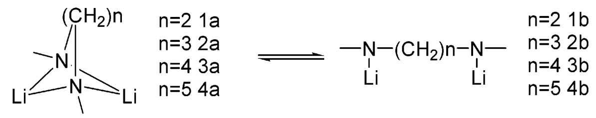
in the vicinity of the coordinated lithium atom. Although water has been occasionally used as a model ligand, it is a poor choice because of the higher dielectric constant and because of computational artifacts resulting from hydrogen bonding. Microsolvation with dimethyl ether instead of THF makes the calculations more tractable with ab initio methods, and microsolvation captures a portion of the solvent dielectric effects. Although several continuum solvation models are available, their use alone (e.g., without microsolvation) is questionable because they may not reproduce the steric effects and specific interactions of coordinated ether ligands. A critical missing element in the use of these solvation models in organolithium chemistry to date is the systematic testing and validation against experiment. Therefore, the dimerization energies were calculated for lithium diisopropylamide (LDA) and lithium tetramethylpiperidide (LiTMP) for comparison to the dilithiodiamines, as the aggregation states for both of those compounds are known experimentally.

Computational Methods

All geometry optimizations and frequency calculations were performed using Gaussian 98 or Gaussian 03.[18] Solvation was modeled by microsolvation with explicit dimethyl ether or THF ligands on the lithium atoms and by single-point IEFPCM[19] continuum solvation energy calculations on the gas phase or microsolvation-optimized structures. In this model, as with other continuum solvation models, the dielectric polarization effects are approximated by a cavity model in a continuous dielectric medium. Gas- and solution-phase free energies were obtained by adding the thermal correction to the free energy, obtained from the frequency calculations, to the gas-phase or solution-phase internal energies, respectively. While the CPM models have been parametrized for a temperature of 298 K, it is instructive to see how they perform at other temperatures as well. The only user adjustable parameter that is related to temperature is the dielectric constant, and other work currently in progress showed that small changes in the dielectric constant have a minimal effect on aggregation energies. Therefore, the default parameters for IEFPCM were used throughout this paper.

All frequency calculations in this paper were carried out for a temperature of 200 and 298 K. The standard-state molar free energy of a solute in the liquid phase at these temperatures are given by $G°_T(\text{liq}) = G°_T(\text{gas}) + \Delta G°_S$ ($T = 200$ or 298 K) where liq denotes a solute in the liquid phase and $\Delta G°_S$ is the standard-state free energy of solvation. Furthermore, $G°_T(\text{gas}) = E_{en} + E^{vib}_0 + G^{trans,o}_T + G^{rot}_T + G^{vib}_T + R\text{T}$ where R is the gas constant. The individual terms were calculated as follows:

SCHEME 1. Cyclization of Dilithiodiamines



E_{en}, the electronic energy plus nuclear repulsion, by the B3LYP hybrid density functional method[20,21] with the 6-31+G(d) basis set.[22,23]

E^{vib}_0, the y = unscaled zero point energy, by B3LYP calculations with the MIDI![24] basis set.

$G^{trans,o}_T$, the standard-state thermal translational energy for a standard state of 1 mol/L (not 1 atm) from the masses.

G^{rot}_T, the thermal rotational free energy, from B3LYP/MIDI! geometries.

G^{vib}_T, the thermal vibrational free energy, from unscaled B3LYP/MIDI! vibrational frequencies.

$\Delta G°_S$, from B3LYP/6-31+G(d)/IEFPCM calculations, with a gas-phase standard state as specified above and a liquid-phase standard state of 1 mol/L.

The formulas given above are correct for solutes and will be applied to $(RLi)_n$ (liq) and $(RLi)_n \cdot mE(liq)$, where R is an alkyl group and E is an ether molecule. However, for E(liq), since E is the solvent we must use a standard state of the pure liquid. This requires an extra term:[25] $G°_S(\text{solvent}) = G°_S(\text{liq}) + RT \ln M°_{liq}/M°_{solvent}$ where $M°_{liq}$ is the standard-state molarity of liquid solutes (taken as 1 M in this work), and $M°_{solvent}$ is the molarity of the pure THF solvent, which was calculated in each case from its tabulated density at 200 or 298 K. This term is numerically equal to −1.0273 kcal/mol per THF at 200 K and −1.4884 kcal/mol at 298 K.

Experimental Methods

The dilithiodiamines were prepared from *N*,*N'*-dimethylethylenediamine and *N*,*N'*-dimethyl-1,3-propanediamine, respectively, and butyllithium. Butyllithium (1.6 M in hexanes, 2.1 mmol) was added to a solution of 1.0 mmol of the diamine in 8.6 mL of THF at −80 °C. The dilithio-*N*,*N'*-dimethylethylenediamine precipitated as a white solid. The THF solution of dilithio-*N*,*N'*-dimethyl-1,3-propanediamine was used for infrared spectroscopic studies. Infrared spectra were acquired on a Bomen MB 102 model spectrometer with a polyethylene liquid cell which is transparent in the spectral region of interest, 200−700 cm^{-1}. One hundred scans were co-added to obtain each spectrum with a 4 cm^{-1} resolution.

Results and Discussion

The gas-phase cyclization of the dilithiodiamines is illustrated in Scheme 1, and the cyclization energies are listed in Table 1. The optimized geometries of the cyclic form are shown in Figure 1. The calculations predict that at both 200 and 298 K each dilithiodiamine will exist exclusively as a bridged intramolecular dimer. The free energies are more exergonic at 200 K, as would be expected from the loss of translational entropy upon cyclization. The temperature effect increases as the number of methylene groups in the chain increases from

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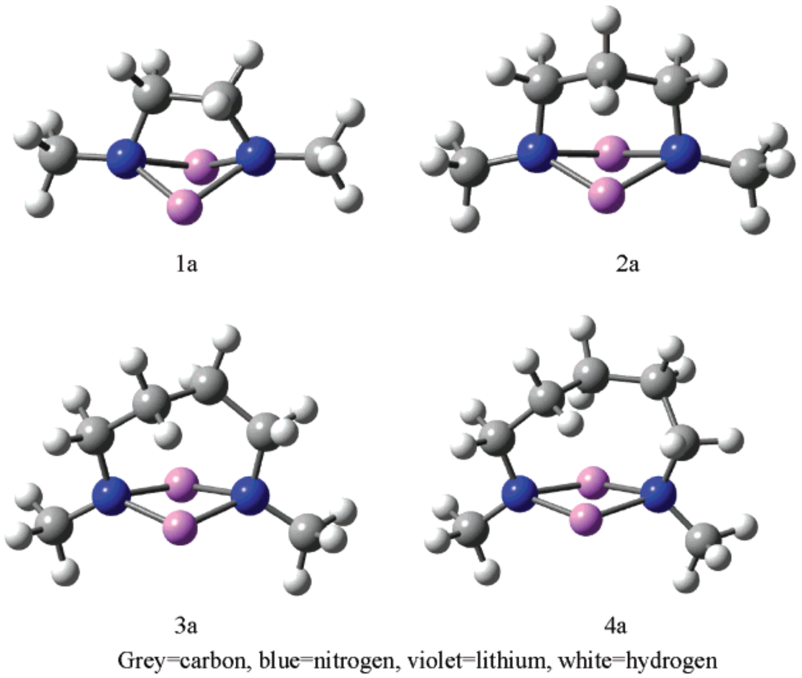

FIGURE 1. Optimized geometry of gas-phase dilithiodiamines.

SCHEME 2. Third and Fourth Solvation of Dilithiodiamine Intramolecular Cyclic Dimers

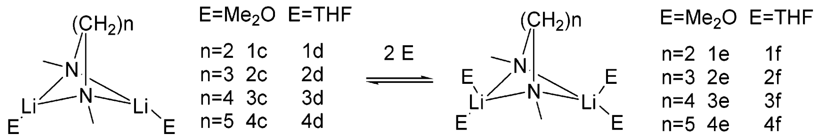

TABLE 1. Gas-Phase Cyclization Free Energies of Dilithiodiamines (kcal/mol)

molecule	200 K	298 K	mean N−Li length (Å)
$CH_3NLi(CH_2)_2NLiCH_3$	−30.8	−30.1	1.913
$CH_3NLi(CH_2)_3NLiCH_3$	−43.3	−42.0	1.919
$CH_3NLi(CH_2)_4NLiCH_3$	−41.1	−39.0	1.921
$CH_3NLi(CH_2)_5NLiCH_3$	−38.7	−36.9	1.930

2 to 4 and then drops slightly as the chain length increases to 5 carbons. The cyclization free energy is least exergonic in compound **1a**, apparently as a result of ring strain in the bridged system. This free energy is at a minimum in compound **2a**, and then increases with the strain in the larger rings of compounds **3a** and **4a**. The mean N−Li bond lengths increase with the size of the bicyclic ring from 1.913 Å in **1a** to 1.930 Å in **4a**.

The third and fourth solvations of the dilithiodiamines are shown in Scheme 2, and the corresponding free energies are shown in Table 2. Coordination of two additional dimethyl ether or THF ligands is energetically unfavorable in each case. At 298 K, the free energies are more endergonic, in part, as a result of a loss of translational entropy as free ethereal molecules become coordinated to lithium. Although the trend is what would be expected from entropy considerations, the numerical values should not be taken too literally because of a shortcoming in the model. Ethereal molecules in the vicinity of the lithium atoms are not completely "free" or completely "bonded" to the lithium but have an intermediate degree of translational freedom.

TABLE 2. Energies of Addition of a Third and Fourth Ethereal Ligand to Dilithiodiamine Disolvated Intramolecular Dimer (kcal/mol)

molecule	micro, 200 K	IEFPCM, 200 K	micro, 298 K	IEFPCM, 298 K
1c→1e	13.6	11.0	22.7	20.1
2c→2e	14.1	9.9	23.1	19.0
3c→3e	15.2	8.8	24.0	17.6
4c→4e	18.2	13.0	27.0	21.8
1d→1f	7.1	12.5	16.3	21.8
2d→2f	6.0	10.4	14.3	18.8
3d→3f	9.3	11.9	18.5	21.1
4d→4f	12.8	14.8	22.5	24.5

Use of the IEFPCM model in conjunction with microsolvation caused a significant change in the calculated free energies associated with the coordination of the two additional ethereal ligands. When dimethyl ether was used for microsolvation, IEFPCM caused the free energies to become less endergonic, while the opposite was true when THF ligands were used. In each case, however, the free energy of coordination of the two additional ligands was endergonic, leading to the conclusion that the bridged intramolecular dimers exist primarily as the disolvates. The THF disolvated structures are shown in Figure 2.

The cyclization of the tetrasolvated open chain form of the dilithiodiamines to the disolvated cyclic form is shown in Scheme 3, and the energies are listed in Table 3. Contrary to the gas-phase cyclizations, the free energies at 298 K were more exergonic than at 200 K, apparently as a result of the increase in entropy from

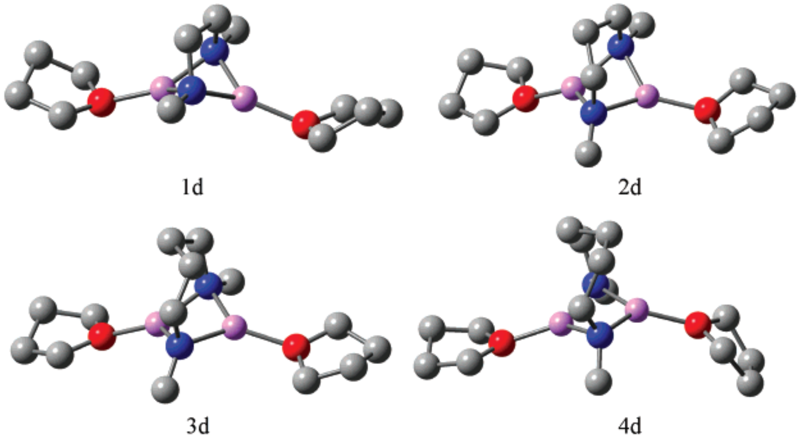

FIGURE 2. Optimized geometry of THF disolvated dilithiodiamines. Hydrogens omitted for clarity.

SCHEME 3. Cyclization of Solvated Dilithiodiamines

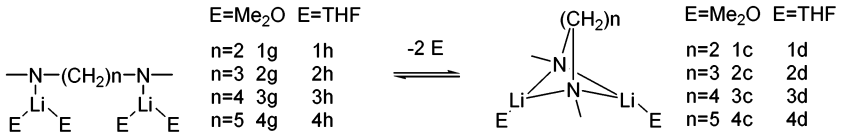

TABLE 3. Cyclization Energies of Dilithiodiamines in Solution (kcal/mol)

molecule	micro, 200 K	IEFPCM, 200 K	micro, 298 K	IEFPCM, 298 K
1g→1c	−26.8	−28.1	−34.7	−36.0
2g→2c	−35.8	−35.8	−44.5	−44.6
3g→3c	−30.1	−28.8	−36.6	−35.3
4g→4c	−25.5	a	−32.2	a
1h→1d	−19.6	−27.9	−28.2	−36.6
2h→2d	−25.6	−32.5	−34.3	−41.1
3h→3d	−24.2	−30.7	−32.8	−39.2
4h→4d	−20.0	−27.6	−28.0	−35.6

[a] IEFPCM failed to converge for this compound in solution.

SCHEME 4. Dimerization of THF-Solvated LDA and LiTMP

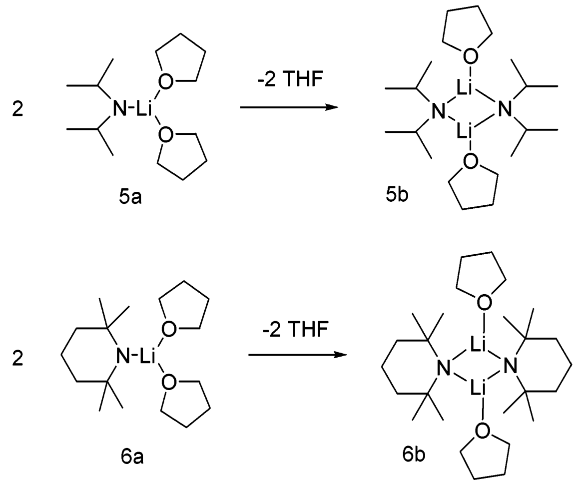

TABLE 4. Calculated Dimerization Free Energies of Lithium Dialkylamides

molecule	micro, 200 K	IEFPCM, 200 K	micro, 298 K	IEFPCM, 298 K
LDA	−16.7	−20.5	−21.7	−25.8
LiTMP	−1.8	−8.3	−5.6	−12.4

the change in solvation state between the open and cyclic forms. Once again, the entropy change is likely to be overestimated by the calculations because of the model which assumes that the ethereal ligands are either completely "free" or completely "bonded" to the lithium atoms. With both dimethyl ether and THF as the solvent ligands, the use of the IEFPCM model predicted the free energy of cyclization to be more exergonic. When dimethyl ether was used, this effect was only about 1−2 kcal/mol, and about 6−7 kcal/mol with THF. In all cases, the calculated free energies indicate that each of the dilithiodiamines will exist exclusively in the cyclic form in THF solution. As with the gas-phase calculations, the cyclization of dilithio-*N*,*N*′-dimethyl-1,3-propanediamine was the most energetically favorable.

The IEFPCM model has not yet been extensively tested with lithium compounds, and the accuracy of predicting aggregation states with this model is unknown. We therefore performed calculations on the dimerization of lithium diisopropylamide (LDA) and lithium tetramethylpiperidide (LiTMP), whose aggregation states in THF are known. NMR studies in THF at low temperature (−90 to −115 °C) showed that LDA exists entirely as dimer,[26] while LiTMP is about 90% dimer and 10% monomer.[27] The calculations were performed on the THF disolvated monomers and disolvated dimers of LDA and LiTMP, as outlined in Scheme 4. The results are listed in Table 4. Both models correctly predict LDA to be essentially 100% dimer in THF. A 1.0 M solution of LiTMP will contain approximately 0.9 M dimer and 0.1 M monomer at 200 K, for an equilibrium constant of about 90, which is close to the value of 93 predicted by

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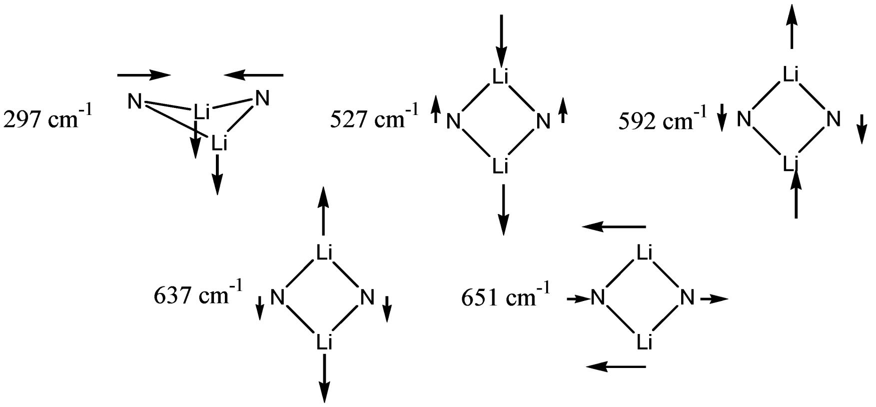

FIGURE 3. Calculated Li−N vibrations of gas-phase cyclic dilithio-*N*,*N*′-dimethyl-1,3-propanediamine.

TABLE 5. IEFPCM-Calculated Cyclization and Dimerization Energies without Microsolvation

molecule	200 K	298 K
$CH_3NLi(CH_2)_2NLiCH_3$	−13.1	−12.4
$CH_3NLi(CH_2)_3NLiCH_3$	−4.9	−3.6
$CH_3NLi(CH_2)_4NLiCH_3$	−11.1	−9.0
$CH_3NLi(CH_2)_5NLiCH_3$	−5.1	−3.4
LDA dimerization	−1.4	−25.8
LiTMP dimerization	1.0	6.3

the calculated free energy of −1.8 kcal/mol from the microsolvation model. In contrast, the combined use of the microsolvation and IEFPCM models generated a free energy of −8.3 kcal/mol, which implies that LiTMP would exist almost exclusively as dimer. Thus, at least for this system, microsolvation by THF alone generated results superior to the combined microsolvation and continuum models.

To determine how well the IEFPCM model performs alone, i.e., without microsolvation by explicit ethereal ligands, IEFPCM calculations were performed on the dilithiodiamine cyclization shown in Scheme 1, as well as LDA and LiTMP dimerization, and the energies are listed in Table 5. For the free energies of cyclization of the dilithiodiamines, no pattern could be discerned that is consistent with the data in Table 3, although the IEFPCM-solvated cyclizations were much less exergonic than in the gas phase. IEFPCM also predicted the dimerization of LDA and LiTMP to be less exergonic than in the gas phase, but the stabilities of the monomers were significantly overestimated. The calculated LDA dimerization free energy of −1.4 kcal/mol predicts that detectable concentrations of monomer should be present, contrary to published experimental data. The continuum calculations also indicate that LiTMP should exist almost exclusively as monomer, again, contrary to experiment. Of the three solvation models examined (IEFPCM alone, microsolvation alone, and combined microsolvation with IEFPCM), the microsolvation alone generated the lithium dialkylamide dimerization energies in closest agreement with experiment.

The calculated vibrational frequencies of the cyclic form of dilithio-*N*,*N*′-dimethyl-1,3-propanediamine revealed five vibrations that involve significant movement of the lithium and nitrogen atoms, and are of sufficient intensity to be visible in the infrared spectrum. Those vibrations are in the 290−655 cm^{-1} region and are illustrated in Figure 3. No corresponding vibrations occurred in the open form, which, instead, had Li−N bending vibrations below 100 cm^{-1} and an asymmetric Li−N stretching vibration at 727 cm^{-1}. The frequency calculation was repeated on the cyclic dilithio-*N*,*N*′-dimethyl-1,3-propanediamine THF disolvate. The calculated frequencies predicted medium intensity peaks at 631 and 690 cm^{-1} and weaker peaks at 330−360, 425,537, and 590−605 cm^{-1}. The actual spectrum of dilithio-*N*,*N*′-dimethyl-1,3-propanediamine (0.1 M in THF) is shown in Figure 4. The predicted peaks at 631 and 690 cm^{-1} are obscured by the THF peak in that region. The peaks at in the 330−360 cm^{-1} appear as a shoulder on the THF peak centered at about 280 cm^{-1}. Several other small peaks in the 400−600 cm^{-1} region correspond with those in the calculated spectrum but appear at slightly lower wavenumbers.

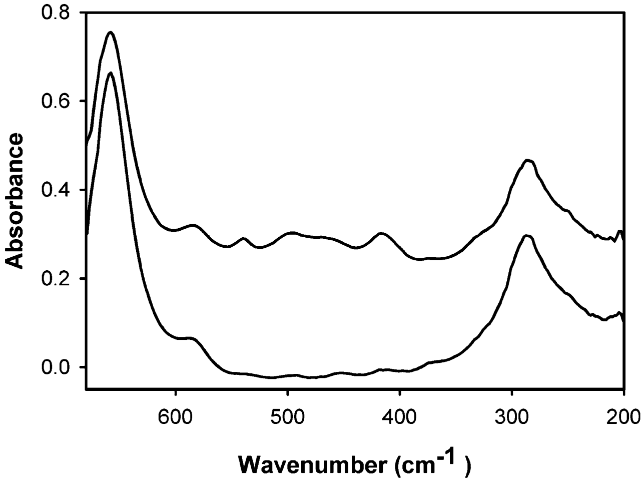

FIGURE 4. Infrared spectrum of dilithio-*N*,*N*′-dimethyl-1,3-propanediamine in THF. Top: dilithio-*N*,*N*′-dimethyl-1,3-propanediamine in solution. Bottom: THF.

Conclusions

Dilithiodiamines exist as bridged intramolecular dimers in THF solution provided that they are soluble. The three solvation models used were the IEFPCM continuum model alone, microsolvation by dimethyl ether or THF, and the combined microsolvation and continuum models. Based on a comparison with the calculated dimerization energies of LDA and LiTMP, the microsolvation model with THF ligands appears to generate free energies in best agreement with the available experimental data. Increasing the temperature makes the dilithiodiamine cyclization slightly less exergonic in the gas phase, but more exergonic in solution. This may be due to the increase in entropy of two THF molecules as they are bonded to lithium in the acyclic form but free in the cyclic form. The infrared spectrum of dilithio-*N*,*N*′-dimethyl-1,3-propanediamine is consistent with the cyclic intramolecular dimer.

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Supporting Information Available: Tables of optimized geomerties and energies of compounds **1**−**4**. This material is available free of charge via the Internet at http://pubs.acs.org.

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