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Ab Initio Analysis of Lithium Dimethylaminoborohydride

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Ab initio calculations were used to determine the equilibrium geometries and energies of lithium dimethylaminoborohydride. Relative energies of the monomeric and dimeric species were calculated in the gas phase and for the dimethyl ether microsolvated molecules. The most stable structure was a dimer in which the lithium and boron atoms were bridged by two hydrogen atoms, similar to the three-center two-electron bonds in diborane. This hydrogen bridging was maintained in the lithium dimethylaminoborohydride bis(dimethyl ether) microsolvate.

Introduction

Lithium dimethylaminoborohydride (LAB) is a versatile reagent with the dual properties of a metal hydride and a nitrogen nucleophile. It has been described as a safer alternative to lithium aluminum hydride (LAH) for the reduction of aldehydes, ketones, esters, amides, and lactams.[1−7] Unlike LAH, LAB does not give off hydrogen upon contact with water and is a much more versatile reagent. Lithium aminoborohydrides have been shown to selectively reduce enones to allylic alcohols.[8] Lithium aminoborohydrides can also be used to reduce tertiary amides to either amines or alcohols by changing the alkyl groups on the amine fragment. LAB also undergoes a unique tandem reduction and nucleophilic aromatic substitution reaction with 2-halobenzonitriles.[9] Unlike amines or simple lithium dialkylamides, unhindered lithium aminoborohydrides are also used to synthesize amines from primary alkyl halides without overalkylation of the amine.[10,11] At elevated temperatures, or with more sterically hindered lithium aminoborohydrides, reduction of the alkyl halide to the corresponding alkane is the principal reaction.

LAB is easily prepared by the addition of methyllithium or butyllithium to a THF solution of the amine−borane complex. Although extensive investigations have been performed on its reactions with carbonyl compounds and alkyl halides, little is known about its structure in solution. A better understanding of the structure and bonding of LAB will be an important first step in understanding the dual nature of LAB as a metal hydride and a nitrogen nucleophile and will aid its further development as a synthetic reagent.

Lithium aminoborohydrides may be described as mixed metal aggregates between a lithium dialkylamide and borane. Lithium dialkylamides are known to form mixed aggregates with other lithium compounds, and these mixed aggregates often have profound effects on the lithium dialkylamide reactivity and reaction stereoselectivity.[12−15] Several lithium dialkylamides and their mixed aggregates have been characterized by ^{6}Li and ^{15}N NMR spectroscopy.[16−18] Other examples of mixed metal aggregates include complexes of dibutylmagnesium or magnesium diisopropylamide with alkali metal compounds,[19−21] while other “superbase” mixtures of alkali metal compounds have been shown not to exist as stoichiometric mixed metal aggregates.[22]

A boron-11 NMR spectroscopic investigation revealed that the boron atom in LAB is bonded to three hydrogen atoms.[23] Because of the large quadrupole moment of ^{11}B, further structural information was not available from that study, and it was not possible to determine the aggregation state of LAB from the NMR spectra. Because of rapid lithium exchange processes, additional hetero-

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nuclear NMR investigations would have to be performed at low temperatures, further compounding the difficulties of observing compounds containing quadrupolar nuclei. Computational methods were chosen for further investigation of this interesting class of reagents.

In recent years electronic structure calculations have become important tools for the study of organolithium compounds. Romesberg and Collum were among the first investigators to make extensive use of semiempirical calculations to determine the solution structures of large lithium dialkylamide molecules, which included the solvating ligands that are important in determining the aggregation state of those compounds.[24] Although semiempirical methods work reasonably well for most lithium dialkylamides, both the MNDO and the PM3 methods were parametrized for lithium with a very limited set of reference compounds, and both fail to accurately reproduce the structures of several types of organolithium compounds. Recent advances in both computer hardware and ab initio quantum chemistry software have largely rendered semiempirical calculations obsolete for moderately sized molecules. Ab initio methods are now routinely used to investigate the structure and bonding in organic lithium compounds.[25−29] In this paper we describe the structure, bonding, and aggregation state of lithium dimethylaminoborohydride. Because the calculations predicted the formation of unusual lithium−hydrogen−boron bridges, the infrared spectrum of LAB was investigated to determine whether these bridges would affect the spectral region corresponding to the B−H stretching vibrations.

Experimental Section

Infrared spectra were obtained with a Nicolet model 320 FT infrared spectrometer equipped with a 3 mm calcium fluoride liquid cell with a 0.025 mm path length. The butyllithium, anhydrous THF, and dimethylamine−borane complex were obtained form Aldrich and used as received. A solution of lithium dimethylaminoborohydride was prepared from the dimethylamine−borane complex (10 mmol, 0.59 g and butyllithium (10 mmol, 1.6M in hexanes, 6.25 mL) in 6.0 mL of anhydrous THF. The mixture was stirred for 1 h in an ice bath and the solution transferred to the infrared cell.

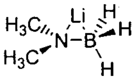
Computational Methods. All ab initio calculations were performed using the Gaussian 98[30] program on a Digital Alpha or Gateway Pentium workstation, or on the NCSA HP Exemplar supercomputer at the University of Illinois. Calculations were performed at the Hartree−Fock level using the 6-31+G* basis set. Density functional geometry optimizations were also performed with the same basis set using the Becke three-parameter hybrid method (B3LYP).[31] To ensure that these levels of theory are sufficient to generate acceptable relative energies of the various species, additional HF/6-31++G**, B3LYP/6-31++G**, and MP2/6-31+G* calculations were performed on some of the smaller molecules. Because the bulk solvation methods currently available in Gaussian do not work well for lithium compounds in ethereal solvents, the solvated structures were modeled by the use of coordinating dimethyl ether ligands. This microsolvation approach has been successfully used for the study of numerous other solvated lithium compounds.[12,24,25,28,32,33] The B3LYP/6-31+G* optimized geometries and energies are given in the Supporting Information.

Table 1. Relative Energies (kcal/mol) of Lithium Dimethylaminoborohydride Monomers

solvation state	method	**1**	**2**
unsolvated	HF/6-31+G*	0	65.5
	B3LYP/6-31+G*	0	63.0
monosolvate	HF/6-31+G*	0	70.5
	B3LYP/6-31+G*	0	67.6
disolvate	HF/6-31+G*	0	73.3
	B3LYP/6-31+G*	0	69.0
trisolvate	HF/6-31+G*	0	70.8
	B3LYP/6-31+G*	N/A	N/A

Results and Discussion

Geometry optimizations were performed on two isomeric LAB monomers (**1** and **2**) and three isomeric dimers (**3**−**5**). Table 1 shows the relative energies of the two monomers. The first structure is consistent with the ^{11}B NMR data described by Singaram and co-workers in THF solution,[23] in which the one-bond B−H spin coupling showed the boron bonded to three hydrogen atoms. The second isomer (**2**) was about 65−70 kcal/mol higher in energy than isomer **1** in both the unsolvated and dimethyl ether solvated states and would be expected to make a negligible contribution to the species in solution. Isomer **2** is also inconsistent with the observed NMR data. At the HF/6-31+G* level of theory, the trisolvate (**1d**) optimized to a stable structure, but further optimization at the B3LYP/6-31+G* level failed to generate a stationary point.



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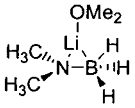

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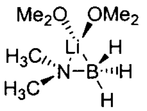

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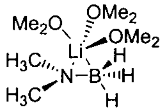

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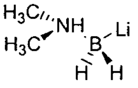

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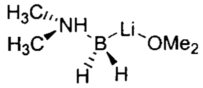

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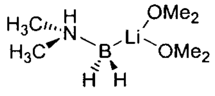

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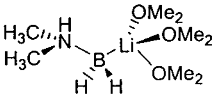

2d

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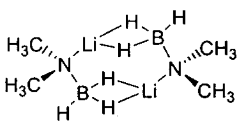
Table 2. Solvation Energies (kcal/mol) of Lithium Dimethylaminoborohydride Monomers

monomer	method	first solvation	second solvation	third solvation
1	HF/6-31+G*	−19.8	−10.0	−0.608
	B3LYP/6-31+G*	−19.2	−9.73	N/A
2	HF/6-31+G*	−14.7	−7.30	−3.10
	B3LYP/6-31+G*	−14.6	−8.26	−3.76

The solvation energies of the monomers by dimethyl ether are given in Table 2. With both monomers, the first two solvation energies were highly exothermic. Although the third solvation energy of **1** was slightly exothermic at the HF/6-31+G* level, addition of a third solvating ligand is expected to be endothermic with the more hindered THF solvent. The greater stability of unsolvated and monosolvated **1** relative to **2** was expected because of the greater coordination number of lithium. It was surprising that the relative stability of **2** did not increase substantially in the disolvated and trisolvated forms because of the greater steric demands of structures **1c** and **1d** relative to **2c** and **2d**, respectively.

The most stable LAB dimer was an unusual hydrogen bridged structure (**3**). Similar hydrogen bridging has been observed in crystal structures of lithium aminoborohydrides,[34] but lithium−hydrogen coordination is rare in solution. Even more surprisingly, this hydrogen bridging persisted in the bis(dimethyl etherate) structure (**3b**) despite the strong lithium−oxygen coordination. Several attempts were made to locate minima corresponding to unbridged Li−N−Li−N four-membered rings. The geometry optimizations resulted in unsymmetrical unsolvated (**4a**) and disolvated (**4b**) dimers in which some of the hydrogen bridging was retained. These isomers were about 6−7 kcal/mol less stable than the symmetrically bridged dimers. A third dimer was also found (**5**) that was slightly less stable than **3**. Comparison of the relative energies of **3** and **5** using the 6-31+G* and 6-31++G** basis sets showed that addition of polarization and diffuse functions to the hydrogen atoms had a minimal effect on the relative energies. Further optimization of the B3LYP/6-31+G* structure at the MP2/6-31+G* level also had a minimal effect on the relative energies. A high energy local minimum was also found **6** for a lithium analogue of diborane (**7**), in which the lithium atoms were “solvated” by two dimethylamine ligands. This structure is inconsistent with the ^{11}B NMR studies of Singaram and co-workers[23] and was too high in energy to make a significant contribution to the solution chemistry of LAB. The relative energies of the LAB dimers are listed in Table 3, and the calculated aggregation energy changes of LAB are summarized in Scheme 1.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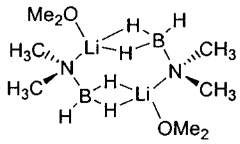
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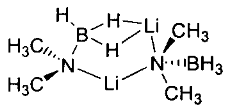
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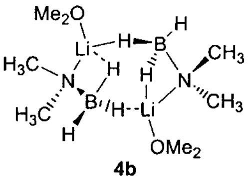
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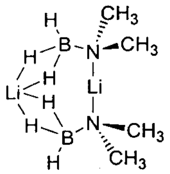
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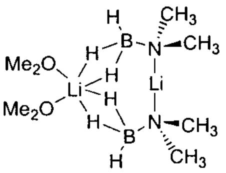
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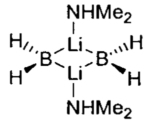
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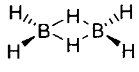
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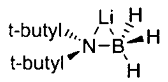
Table 3. Relative Energies (kcal/mol) of Lithium Dimethylaminoborohydride Dimers

solvation state	method	3	4	5	6
unsolvated	HF/6-31+G*	0	7.34	2.14	123.0
	B3LYP/6-31+G*	0	6.17	1.98	140.7
	MP2/6-31+G*	0	N/A	1.94	N/A
	HF/6-31++G**	0	N/A	2.14	N/A
	B3LYP/6-31++G**	0	N/A	1.96	N/A
disolvated	HF/6-31+G*	0	7.21	2.05	N/A
	B3LYP/6-31+G*	0	6.74	0.83	N/A

The dimerization of unsolvated LAB was exothermic by over 35 kcal/mol, as shown in Table 4. Addition of polarization and diffuse functions to the hydrogen atoms changed the calculated dimerization energy by less than one kcal/mole. The dimerization energies for borane and lithium hydride were calculated to be slightly more exothermic than that of LAB. The calculated dimerization energies for the LAB bis(dimethyl ether) microsolvate indicate that the dimer is still the most favorable species in solution, although the dimerization energy is much less exothermic.

To model the effects of steric hindrance on the aggregation state, calculations were performed on lithium di-*tert*-butylaminoborohydride. The monomer (**8**) was structurally similar to the monomeric lithium dimethylaminoborohydride. In the unsolvated form, dimer **9** was favored over **10** by about 7 kcal/mol because of steric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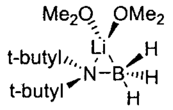
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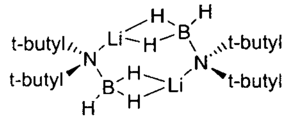
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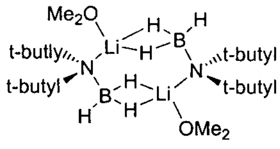
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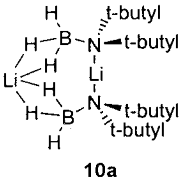
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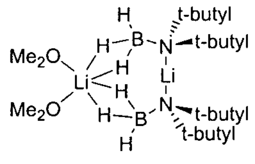
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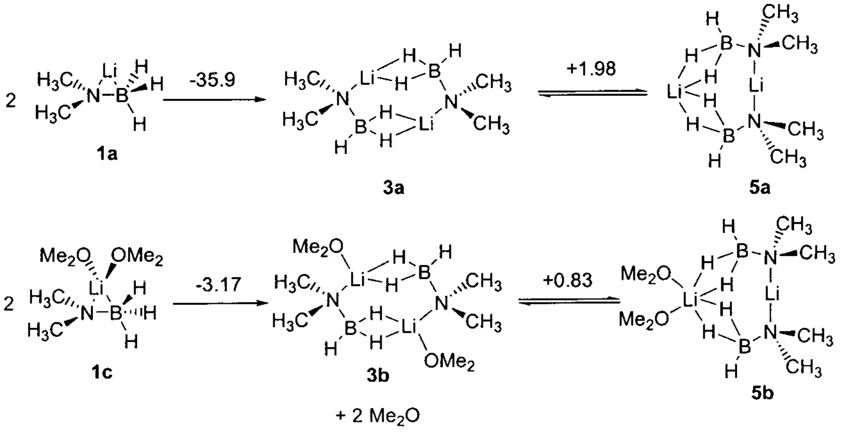
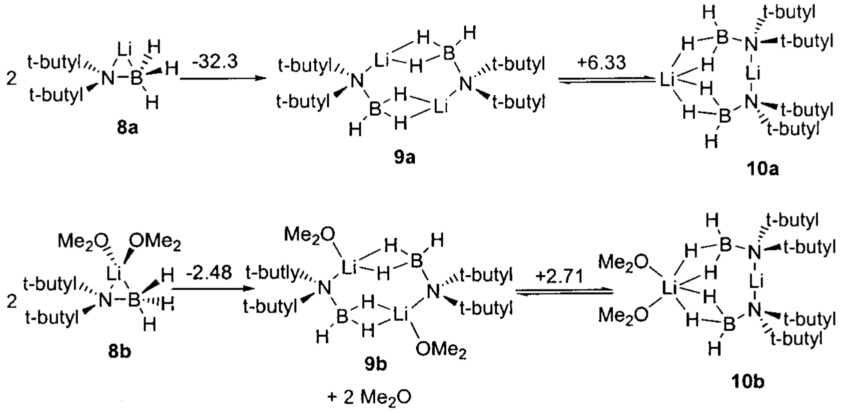
Scheme 1. Energy Changes for Aggregation of Lithium Dimethylaminoborohydride[a]



[a] Energies are in kcal/mol, calculated at the B3LYP/6-31+G* level.

Scheme 2. Energy Changes for Aggregation of Lithium Di-*tert*-butylaminoborohydride[a]



[a] Energies are in kcal/mol, calculated at the B3LYP/6-31+G* level.

Table 4. Dimerization Energies (kcal/mol) of Lithium Dimethylaminoborohydride

dimerization reaction	HF/ 6-31+G*	B3LYP/ 6-31+G*	MP2/ 6-31+G*
2 (**1a**) → (**3a**)	−35.6	−35.9	−40.1
2 (**1c**) → (**3b**) + 2 ether	−3.10	−3.17	N/A
$BH_3 \rightarrow B_2H_6$	−20.1	−38.4	−40.2
$LiH \rightarrow Li_2H_2$	−46.3	−46.9	−47.2

Table 5. Relative Energies (kcal/mol) of Lithium Di-*tert*-butylaminoborohydride dimers

solvation state	method	9	10
unsolvated	HF/6-31+G*	0	7.27
	B3LYP/6-31+G*	0	6.33
disolvated	HF/6-31+G*	0	2.76
	B3LYP/6-31+G*	0	2.71

Table 6. Dimerization Energies (kcal/mol) of Lithium Di-*tert*-butyl Aminoborohydride

solvation state	method	
unsolvated	HF/6-31+G*	−31.19
	B3LYP/6-31+G*	−32.31
disolvated	HF/6-31+G*	−13.59
	B3LYP/6-31+G*	−2.48

hindrance between the *tert*-butyl groups in **10**, as shown in Table 5. In the presence of solvating ligands, the energy difference was reduced to about 3 kcal/mol, apparently as a result of steric hindrance between the solvent and the *tert*-butyl groups in **9b**. The trends in dimerization energies were similar to those found with lithium dimethylaminoborohydride, as shown in Table 6. The calculated aggregation energy changes of lithium di-*tert*-butylaminoborohydride are summarized in Scheme 2.

Multicenter electron deficient bonds are well-known in boranes, and a few examples of theoretical interest have been reported for lithium hydrides and related compounds.[35-38] The best known example is diborane in the gas phase. However, in the presence of THF, dimethyl sulfide, ammonia, or other coordinating solvents, borane exists as a solvated monomer. In contrast, the dimerization energies of LAB were calculated to be exothermic in both the unsolvated and solvated cases, as shown in Table 4. The dimerization energy of unsolvated LAB was less exothermic than that of lithium hydride or borane, which would appear to indicate that the Li−H−B bridging interaction is weaker than the Li−H−Li or B−H−B interactions in lithium hydride and diborane, respectively. Closer examination of the LAB unsolvated monomer (**1a**) reveals the coordination of the lithium atom to two of the borane hydrogens. This coordination is also reflected in the B−H bond lengths of 1.249 and 1.210 Å,

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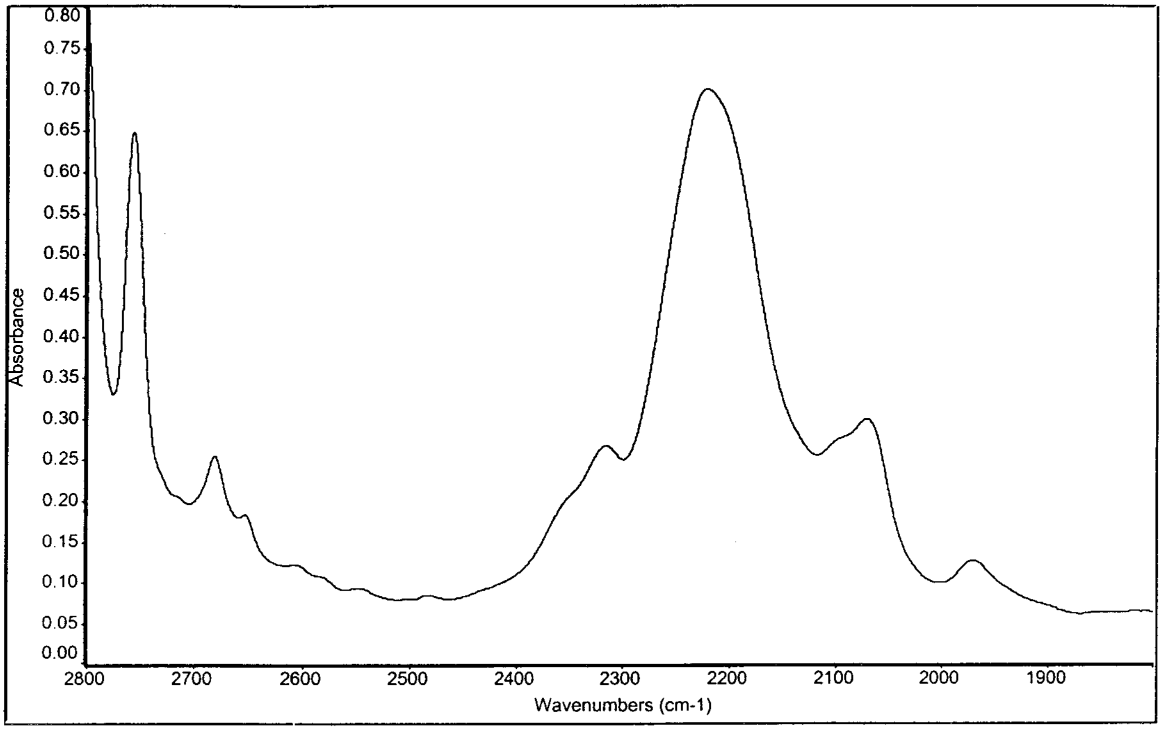

Figure 1. Infrared spectrum of lithium dimethylaminoborohydride in (0.8 M) THF.

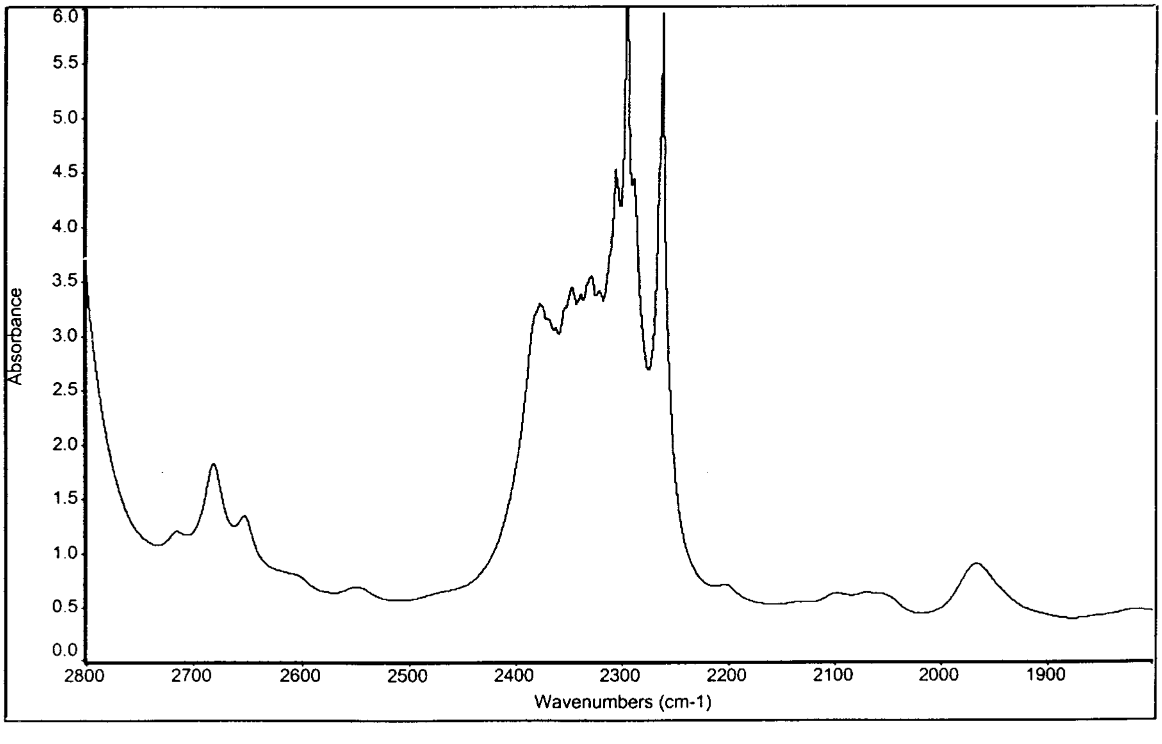

Figure 2. Infrared spectrum of borane–dimethylamine complex (0.8 M) in THF.

respectively, for the lithium-coordinated and -uncoordinated B–H bonds. Therefore, the lower dimerization energy of LAB relative to LiH and borane results not from a lower stability of the Li–H–B multicenter two-electron bond, but from the presence of this type of bonding in the monomer as well as in the dimer.

The infrared spectra of lithium dimethylaminoborohydride and the dimethylamine–borane complex are given in Figures 1 and 2, respectively. The vibrational frequencies for the LAB monomer (**1c**) and the dimers (**3b** and **5b**) were calculated at the B3LYP/6-31+G* level. The most intense infrared absorbances from B–H stretching vibrations were calculated to be in the region between 2230 and 2430 cm^{-1}, which is consistent with the observed spectrum. This region is of a lower frequency than that of the B–H stretches in the borane–dimethylamine complex and is consistent with the weakening of the B–H bonds by coordination of the hydrogen atoms to the lithium, as was predicted by the optimized geometry of the LAB dimer.

Conclusions

Lithium dimethylaminoborohydride exists primarily as a dimeric structure, in which the boron and lithium atoms are bridged by a pair of hydrogens in two-center-three-electron bonds. Similar lithium−hydrogen bridging was found in the unsolvated monomer, resulting in a lower dimerization energy than would otherwise be expected. The hydrogen bridging was maintained in the bis(dimethyl ether) solvated dimer. The most stable calculated structures were consistent with prior ^{11}B NMR investigations, which showed the boron atoms bonded to three hydrogens.

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Supporting Information Available: Tables S1−S23 of optimized geometries of compounds **1**−**10**. This material is available free of charge via the Internet at http://pubs.acs.org.

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