Effect of Polydentate Donor Molecules on Lithium Hexamethyldisilazide Aggregation: An X-ray Crystallographic and a Combination Semiempirical PM3/Single Point *ab Initio* Theoretical Study

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Abstract: Addition of 1 equiv of polydentate amine or ether donor solvent to hydrocarbon solutions of lithium hexamethydisilazide (LHMDS) yields a variety of complexes with different aggregation states. X-ray crystallographic analyses have been carried out on six new compounds revealing three- and four-coordinate monomers, η^1-coordinated mono- and disolvated dimers, and polymers of dimers. PM3 calculations were able to locate minima for a variety of possible structures for the ligands *N,N,N′,N′*-tetramethylethylenediamine and 1,2-dimethoxyethane. However, the heats of formation from these calculations are found to be unreliable in predicting the relative stabilities of the isomers. Single point *ab initio* calculations at the 6-31G* level on the PM3 optimized structures give energies which correspond well to the known aggregation states of LHMDS species. Deaggregation from dimers to monomers appears to be driven by a combination of steric, electronic, and chelate effects.

Introduction

The role that solvation and aggregation play in the course of lithium-mediated reactions is yet to be fully determined.[1] Numerous studies have revealed a complex relationship between aggregation state and solvation.[2] The view that strong solvation leads to lower aggregation and higher reactivity is too simplistic.[3] An excellent example of this is the use of hexamethylphosphoramide (HMPA) as additive. Although HMPA is well-known to be an excellent solvent molecule for lithium species, its effect on aggregation is not straightforward. Recent spectroscopic studies show addition of HMPA to lithium salts can actually increase the aggregation state,[4] produce solvent separated species (LiS$_n^+$·X$^-$),[5] or make no change to the aggregation state.[6] The effect of the solvent appears to be highly dependent on the nature of the substrate being solvated. Polydentate donor solvents such as *N,N,N′,N′*-tetramethyl-

ethylenediamine (TMEDA) and 1,2-dimethoxyethane (DME) are widely used in both synthesis and to facilitate crystallization of organometallic compounds. However, studies by Collum question the function of molecules such as TMEDA when in the presence of polar media.[3,7] Collum has also carried out extensive investigations into the aggregation of lithium hexamethyldisilazide (LHMDS) with various polydentate amine and ether ligands by [6]Li, ^{15}N, and ^{13}C NMR spectroscopic studies.[8] LHMDS is widely used since it combines the properties of a strong base with weak nucleophilicity. It is also highly soluble in both hydrocarbon and polar media allowing low temperature reactions to proceed homogeneously.

We describe the solid state structures of hexamethyldisilazide (HMDS) aggregates containing either oxygen or nitrogen polydentate molecules. These X-ray studies reveal the presence of chelated monomers, η^1-coordinated mono- and disolvated dimers, and polymers of dimers. We report a comparative study of the utility of PM3 and MNDO semiempirical methods for the prediction of the stability of a variety of solvated species. In addition, we detail the findings of single point *ab intio* calculations (HF/6-31G*) on the PM3 optimized geometries.

Crystal Structure Data

Each of the complexes described was prepared in a similar manner. LHMDS was made by mixing equimolar amounts of HMDS and Bu^{n}Li (in hexanes) in pentane or hexane solution

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Table 1. Aggregates obtained by Mixing 1 Equiv of Donor Solvent with LHMDS (or NaHMDS for **13**)[a]

complex	solvent	aggregation state	no. of ligands per metal
4	p-C$_6$H$_4$F$_2$	polymer of dimers	0.5
5a	C$_6$H$_5$F	monosolvated dimer	0.5
5b	o-C$_6$H$_4$F$_2$	monosolvated dimer	0.5
6	TMEDA	chelated monomer	1
7	PMDETA	chelated monomer	1
8	DMBA	disolvated dimer	1
9	DAP	disolvated dimer	1
10	N-TPD	disolvated dimer	1
11	DME	disolvated dimer	1
12a	1,4-dioxane	disolvated dimer	1
12b	1,4-dioxane	polymer of dimers	0.5
13	TMPDA	polymer of dimers	0.5

[a] Acronyms not in text c: DMBA, dimethylbenzylamine; DAP, 1,3-diaminopropane; N-TPD, *N*,*N*,2,2-tetramethylpropanediamine.

at 0 °C. One molar equiv of donor solvent was added to the mixture, and the products were isolated as crystalline materials upon cooling. Table 1 and Figure 1 detail the products and aggregation states from the various reactions. Figure 1 also depicts the known structural types for LHMDS aggregates **1**−**5**. The most common structural theme is that of a disolvated dimer (**2** in Figure 1). Unsolvated LHMDS is known to be a trimer in the solid state.[9]

Two monomers, **6**[10] and **7**,[11] were elucidated containing TMEDA and *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDETA), respectively (Figures 2 and 3). In **6** the lithium atom is three-coordinate and trigonal planar. In contrast, **7** contains a tetrahedral lithium since three chelating nitrogens are available for coordination. The increase in coordination number for lithium leads to a general elongation of the bond lengths in **7** compared to **6** (0.14 Å for the coordinating nitrogens and 0.10 Å for the anionic nitrogen).[12] A monomeric complex of LHMDS with 12-crown-4 has been reported (**3** in Figure 1).[13] In that instance the metal center is pentacoordinate by binding to all four oxygen atoms of the crown in addition to the amide. NMR spectroscopic studies indicate that LHMDS is mainly dimeric in the absence of donor solvent and deaggregates to a chelated monomer in the presence of 1 equiv of TMEDA.[8,14] The formation of monomers for TMEDA and PMDETA might be explained in terms of high steric strain produced by tertiary amine solvation of the LHMDS dimer. This alone could possibly destabilize the dimer relative to the monomer. However, our studies of monodentate donors containing a NMe$_2$ unit prove this to be untrue. Addition of dimethylbenzylamine to a solution of LHMDS produced the η^1-coordinated disolvated dimer **8** (Figure 4).[15] The Li−NMe$_2$ bond lengths are significantly elongated (2.22 Å averaged) compared to similar amine-solvated three-coordinate lithium

amide dimers (≈2.05−2.15 Å).[16] Although this implies a relatively weak complexation of the dimer by the NMe$_2$ units, there is no inherent instability in the solvation of a LHMDS dimer by NMe$_2$ groups. The benzyl groups sit *cis* to one another, as is clearly seen in Figure 4. These results confirm the NMR solution studies of mono-, di-, and trialkylamines with LHMDS which show a preference for η^1-coordinated disolvation of the dimer at a 1:1 ratio of amine to amidolithium.[17]

We recently elucidated the structure of two LHMDS aggregates which incorporate primary amine as ligand.[18] Complexes **9** and **10** contain the amines 1,3-diaminopropane and *N*,*N*,2,2-tetramethylpropanediamine, respectively. They both adopt a η^1-coordinated disolvated dimeric structure, where one nitrogen binds to lithium and the other sits free (**9 and 10** in Figure 1).[19] These complexes are rare examples of primary amines solvating a secondary amidolithium center.[20] Almost identical bond lengths are observed for both the dative and the ionic Li−N bonds in **9** and **10** (2.06 and 2.04 Å, respectively, averaged over the two structures). It is expected that dative bonds will be approximately 0.1−0.2 Å longer than the corresponding ionic bonds.[12] In this instance the minimal steric repulsions due to primary amine solvation compared to the more common substituted amine solvation may play a part in the relative shortening of the dative bonds.

A similar η^1-coordinated disolvated dimeric structure **11** is found when DME is used as donor solvent (Figure 5).[21] As with **9** and **10**, the lithium centers are trigonal planar with the smaller angles at lithium being those within the dimeric ring. The methyl groups of the DME chains sit *trans* to one another, and as with all the solvents they are in the plane of the Li$_2$N$_2$ ring. All the bond lengths and angles within the structure are typical for an ether-solvated LHMDS dimer.[22] As expected, the coordinating Li−O bonds are slightly shorter (0.10 Å) than the Li−N bonds of the dimeric ring. This type of η^1 coordination using a bidentate ligand seen for **9**, **10**, and **11** has not previously been described for LHMDS complexes in the solid state.

An interesting situation arises when 1,4-dioxane is used as donor solvent. The crystal structure of **12** was determined to

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(10) Data for **6**: C$_{12}$H$_{34}$Li$_1$N$_3$Si$_2$, monoclinic, P2$_1$/n, a = 9.2680(10) Å, b = 12.9690(4) Å, c = 16.1720(10) Å, β = 99.82°, V=1915.3 Å^3, Z = 4, d$_{calc}$ = 0.983 Mg/m^3, T = −40 °C, 2θ$_{max}$ = 45°, 3223 reflections collected, 3019 independent reflections, 3019 reflections used in the refinement, R(1) = 0.0332, wR(2) = 0.0906.

(11) Data for **7**: C$_{15}$H$_{41}$Li$_1$N$_4$Si$_2$, monoclinic, P2$_1$/n, a = 9.5243(10) Å, b = 14.5656(4) Å, c = 16.5197(10) Å, β = 99.09°, V = 2262.9 Å^3, Z = 4, d$_{calc}$ = 1.00 Mg/m^3, T = −40 °C, 2θ$_{max}$ = 47°, 3867 reflections collected, 3808 independent reflections, 3808 reflections used in the refinement, R(1) = 0.0589, wR(2) = 0.1640.

(12) For reviews on the structural chemistry of lithium, see: (a) Weiss E. *Angew. Chem.* **1993**, *105*, 1565; *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1501. (b) Gregory, K. P.; Schleyer, P. v. R; Snaith, R. *Adv. Inorg. Chem.* **1991**, *37*, 47. (c) Mulvey, R. E. *Chem. Soc. Rev.* **1991**, *20*, 167.

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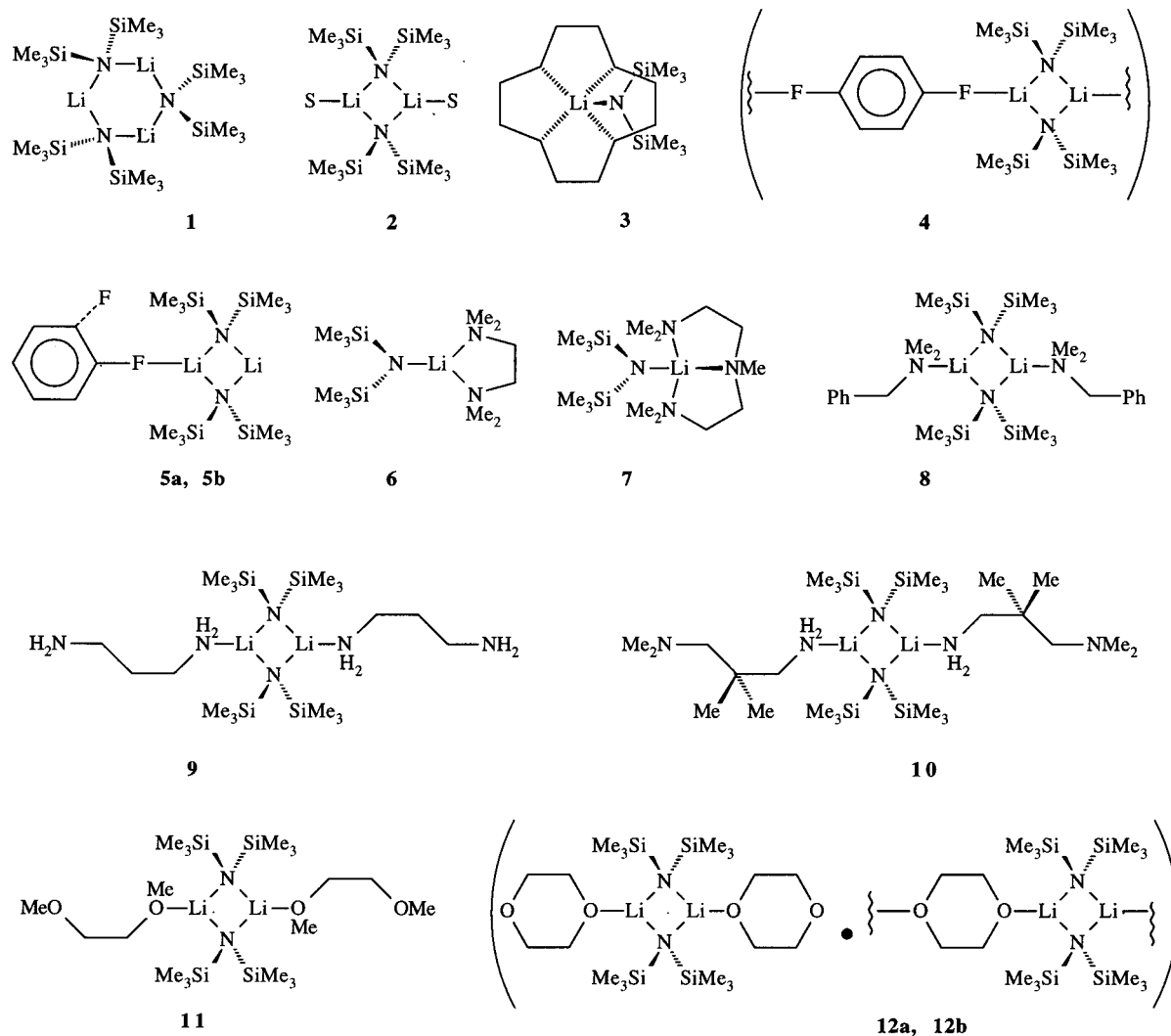(14) Collum, D. B. *Acc. Chem. Res.* **1993**, *26*, 227.

(15) Data fo **8**: C$_{30}$H$_{62}$Li$_2$N$_4$Si$_4$, monoclinic, C2/c, a = 39.732(11) Å, b = 10.839(3) Å, c = 18.357(5) Å, β = 103.17°, V = 7697 Å^3, Z = 4, p$_{calc}$ = 1.044 Mg/m^3, T = −60 °C, 2θ$_{max}$ = 47°, 5792 reflections collected, 5699 independent reflections, 5696 reflections used in the refinement, R(1) = 0.0396, wR(2) = 0.1040.

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(19) A η^1 solvated TMEDA complex has recently been elucidated: Ball, S. C.; Cragg-Hine, I.; Davidson, M. G.; Davies, R. P.; Lopez-Solera, M. I.; Raithby, P. R.; Reed, D.; Snaith, R.; Vogl, E. *J. Chem. Soc., Chem. Commun.* **1995**, 2147. η^2 chelating PMDETA complexes have also been reported: (a) Jutzi, P.; Schluter, E.; Kruger, C.; Pohl, S. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 994. (b) Andrews, P. C.; Clegg, W.; Mulvey, R. E. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1440.

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(21) Data for **11**: C$_{20}$H$_{561}$Li$_2$N$_2$Si$_4$O$_4$, monoclinic, P2$_1$/n, a = 8.7188(10) Å, b = 33.0415(10) Å, c = 11.7451(10) Å, β = 101.70°, V = 3313.3(5) Å^3, Z = 4, d$_{calc}$ = 1.032 Mg/m^3, T = −40 °C, 2θ$_{max}$ = 45°, 5162 reflections collected, 4846 independent reflections, 4842 reflections used in the refinement, R(1) = 0.0412, wR(2) = 0.1131.

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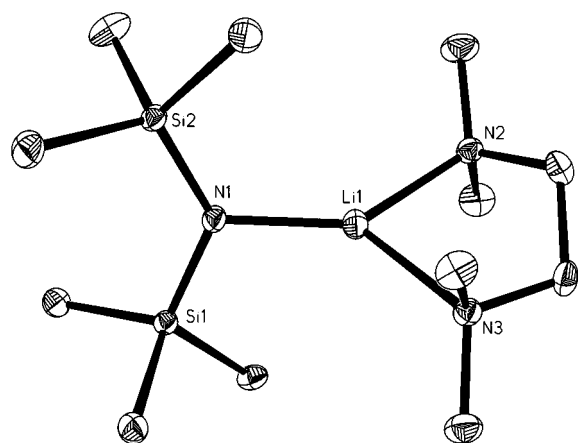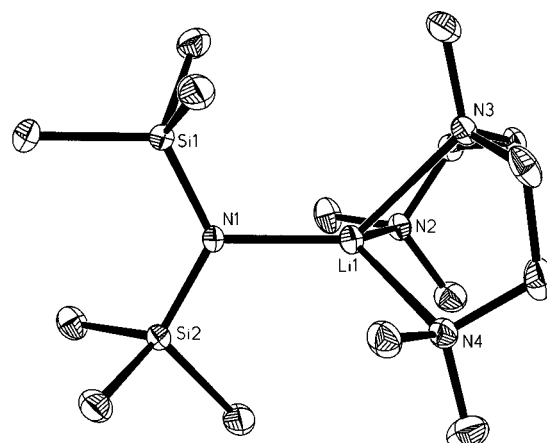**Figure 1.** Structural types elucidated for LHMDS aggregates.

Figure 2. Molecular structure of **6** with hydrogen atoms omitted for clarity. Important bond lengths (Å) and angles (deg): Li(1)−N(1) 1.893(3), Li(1)−N(2) 2.067(3), Li(1)−N(3) 2.095(3), N(1)−Li(1)−N(2) 139.7(2), N(1)−Li(1)−N(3) 132.7(2), N(2)−Li(1)−N(3) 87.19(11).

consist of two independent molecules, a η^1-coordinated disol-vated dimer (**12a**) and a polymer of dimers (**12b**) (Figure 6).[23] The relationship between the molecules is shown by the packing

(23) Data for **12**: $C_{36}H_{96}Li_4N_4Si_8O_6$, triclinic, *P*-1, $a = 9.110(3)$ Å, $b = 18.178(5)$ Å, $c = 18.268(4)$ Å, $\alpha = 90.66$, $\beta = 99.09°$, $\gamma = 101.44$, $V = 2962.1$ (14) Å^3, $Z = 2$, $d_{calc} = 1.047$ Mg/m³, $T = -40$ °C, $2\theta_{max} = 45°$, 9910 reflections collected, 8742 independent reflections, 8741 reflections used in the refinement, $R(1) = 0.0533$, $wR(2) = 0.1414$.

Figure 3. Molecular structure of **7** with hydrogen atoms omitted for clarity. Important bond lengths (Å) and angles (deg): Li(1)−N(1) 1.988(6), Li(1)−N(2) 2.164(6), Li(1)−N(3) 2.265(6), Li(1)−N(4) 2.229(6), N(1)−Li(1)−N(2) 115.6(3), N(1)−Li(1)−N(3) 132.2(3), N(1)−Li(1)−N(4) 119.6(3), N(2)−Li(1)−N(3) 84.8(2), N(2)−Li(1)−N(4) 115.5(3), N(3)−Li(1)−N(4) 82.0(2).

diagram in Figure 7. Both structures have chair conformations of dioxane. The dioxane chairs are *transoid* in the polymer but *cisoid* in the dimers relative to the Li₂N₂ ring. Other 1,4-dioxane solvates of alkali metals have been determined. These include a KHMDS monomer containing two chelating diox-anes,[24] a polymer of dimers for both cesium and rubidium which
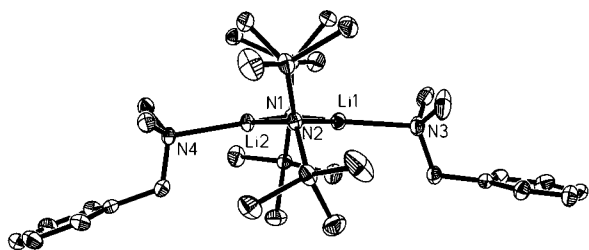
Figure 4. Molecular structure of **8** seen through the Li$_2$N$_2$ ring plane showing the *cis* arrangement of the solvates. Hydrogen atoms are omitted for clarity. Important bond lengths (Å) and angles (deg): Li(1)−N(1) 2.037(4), Li(1)−N(2) 2.095(4), Li(1)−N(3) 2.240(4), Li(2)−N(1) 2.090(4), Li(2)−N(2) 2.039(4), Li(2)−N(4) 2.209(4), N(1)−Li(1)−N(2) 104.1(2), N(1)−Li(1)−N(3) 122.9(2), N(2)−Li(1)−N(3) 84.8(2), N(1)−Li(2)−N(2) 104.3(2), N(1)−Li(2)−N(4) 124.9(2), N(2)−Li(2)−N(4) 124.9(2), Li(1)−N(1)−Li(2) 75.6(2), Li(1)−N(2)−Li(2) 75.5(2).
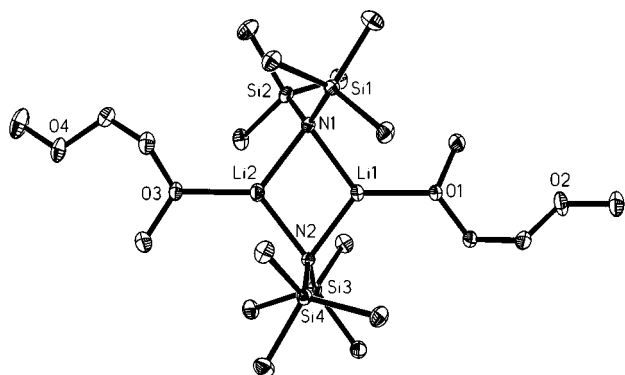

Figure 5. Molecular structure of **11** with hydrogen atoms omitted for clarity. Important bond lengths (Å) and angles (deg): Li(1)−N(1) 2.033(4), Li(1)−N(2) 2.012(4), Li(1)−O(1) 1.938(4), Li(2)−N(1) 2.047(4), Li(2)−N(2) 2.037(4), Li(2)−O(3) 1.962(4), Li(1)−N(1)−Li(2) 73.3(2), Li(1)−N(2)−Li(2) 74.0(2), N(1)−Li(1)−O(1) 126.2(2), N(2)−Li(1)−O(1) 126.7(2), N(1)−Li(1)−N(2) 107.1(2), N(1)−Li(2)−N(2) 105.6(2), N(1)−Li(2)−O(3) 126.2(3), N(2)−Li(2)−O(3) 128.1(2).

contain three bridging dioxanes, a NaHMDS polymer of monomers bonding to four dioxanes,[25] and a polymer of monomers for CsHMDS with three bridging dioxanes and a polymer of RbHMDS with two dioxanes.[26] Hence, the structure of **12** is unique in this series. The dimer **12a** is the only example of an alkali metal HMDS complex with the dioxane molecules having a nonligating oxygen. Also, both **12a** and **12b** are the only such complexes to contain less than two dioxane molecules per alkali metal atom. The conformational constraints of the dioxane molecule decrease the likelihood of a chelated monomer for lithium. However, the larger potassium can accommodate two such chelates as is seen from the structure of [KHMDS·(dioxane)$_2$].[24] A polymer of dimers similar to **12b** using *p*-fluorobenzene as donor was recently described by our group (**4** in Figure 1).[27] An interesting structural variation was discovered when fluorobenzene or *o*-fluorobenzene is used as solvent—the monosolvated dimers **5a** and **5b** (Figure 1).

We were also able to prepare a sodium HMDS complex containing *N,N,N′,N′*-tetramethylpropanediamine (TMPDA) as ligand. The structure of [NaHMDS·N(Me$_2$)CH$_2$CH$_2$CH$_2$NMe$_2$]$_\infty$ **13** consists of a polymer of dimers (Figure 8).[28] Each dimer is connected through one diamine, giving sodium the coordination number of three. Similar polymers of dimers or tetramers

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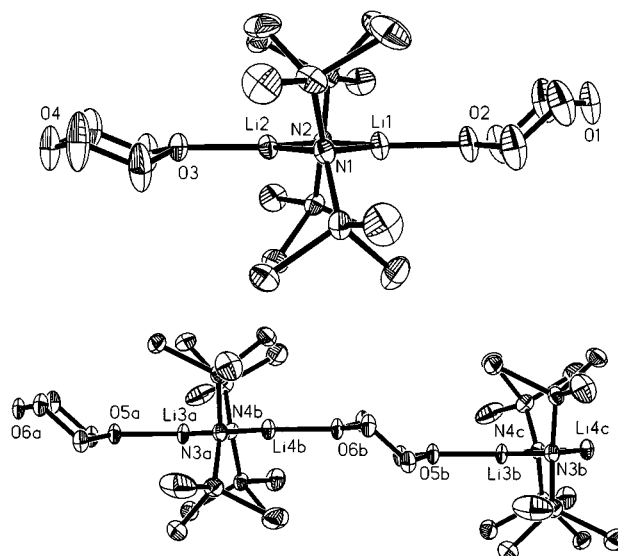

Figure 6. (a, top) Molecular structure of the disolvate **12a** and (b, bottom) molecular structure of the polymer **12b**. Hydrogen atoms are omitted for clarity. Important bond lengths (Å) and angles (deg): (a) Li(1)−N(1) 2.034(7), Li(1)−N(2) 2.045(8), Li(1)−O(2) 1.946(7), Li(2)−N(1) 2.045(8), Li(2)−N(2) 2.023(7), Li(2)−O(3) 1.964(7), N(1)−Li(1)−N(2) 105.8(3), N(1)−Li(2)−N(2) 106.6(3), Li(1)−N(1)−Li(2) 73.8(3), Li(1)−N(2)−Li(2) 73.8(3), O(2)−Li(1)−N(1) 127.0(4), O(2)−Li(1)−N(2) 127.2(4), O(3)−Li(2)−N(1) 127.8(4), O(3)−Li(2)−N(2) 125.7(4) (b) Li(3a)−N(3a) 2.036, Li(3a)−N(4b) 2.045(7), Li(3a)−O(5a) 1.964(7), Li(4b)−N(3a) 2.047(7), Li(4b)−N(4b) 2.018(7), Li(4b)−O(6b) 1.961(7), Li(3a)−N(3a)−Li(4b) 73.1(3), Li(3a)−N(4b)−Li(4b) 73.5(3), N(3a)−Li(3a)−N(4b) 106.3(2), N(3a)−Li(4b)−N(4b) 107.0-(3), N(3a)−Li(3a)−O(5a) 124.5(4), N(4b)−Li(3a)−O(5a) 129.0(4), N(3a)−Li(4b)−O(6b) 130.5(4), N(4b)−Li(4b)−O(6b) 122.4(4).

connected through TMEDA units have been observed for lithiated complexes.[29] However, **13** is the only example of such a polymer of a sodium amide with bridging polyamine. As with the lithium dimers, the more acute angles at the trigonal planar sodium atoms are associated with the dimeric rings. Tricoordinate sodium is rather unusual although not unique; generally, sodium is at least tetracoordinate.[12]

Clearly, the type of organometallic structure crystallized from solutions containing polydentate donor molecules have great variety. This is perhaps not surprising when taken in context of the complex equilibria of aggregates that are known to exist in such solutions.[30] Previously, MNDO calculations have been used to investigate the relative stabilities of some dialkyl-amidolithium species solvated by a number of donor solvents.[7] Similar MNDO studies have proved useful in the rationalization of mechanistic and structural aspects of lithium chemistry.[31] We now outline a computational study of TMEDA and DME solvation of LHMDS using MNDO and the more recently released PM3 parameterization methods.[32] Results from a comparative study using the PM3 optimized geometries for

(28) Data for **13**: C$_{9.5}$H$_{27}$Na$_1$N$_2$Si$_2$, monoclinic, *C2/c*, *a* = 9.7480(10) Å, *b* = 18.774(2) Å, *c* = 17.900(2) Å, β = 95.630(10)°, *V* = 3260.1(6) Å^3, *Z* = 8, *d*$_{calc}$ = 1.013 Mg/m^3, *T* = −80 °C, $2\theta_{max}$ = 50°, 3662 reflections collected, 2879 independent reflections, 2877 reflections used in the refinement, *R*(1) = 0.0761, *wR*(2) = 0.2082.

(29) For example, see: (a) Tecle, B.; Ilsley, W. H.; Oliver, J. P. *Organometallics* **1982**, *1*, 875. (b) Harder, S.; Boersma, J.; Brandsma, L.; Kanters, J. A. *J. Organomet. Chem.* **1988**, *339*, 7. (c) Nichols, M. A.; Williard, P. G. *J. Am. Chem. Soc.* **1993**, *115*, 1568. (d) Barnett, N. D. R.; Mulvey, R. E.; Clegg, W.; O'Neil, P. A. *J. Am. Chem. Soc.* **1993**, *115*, 1573. (e) Andrews, P. C.; Armstrong, D. R.; Baker, D. R.; Mulvey, R. E.; Clegg, W.; Horsburgh, L.; O'Neil, P. A.; Reed, D. *Organometallics* **1995**, *14*, 427. (f) Hoffman, D.; Dorigo, A.; Scheyer, P.v.R.; Reif, H.; Stalke, D.; Sheldrick, G.M.; Weiss, E.; Geissler, M. *Inorg. Chem.* **1995**, *34*, 262.
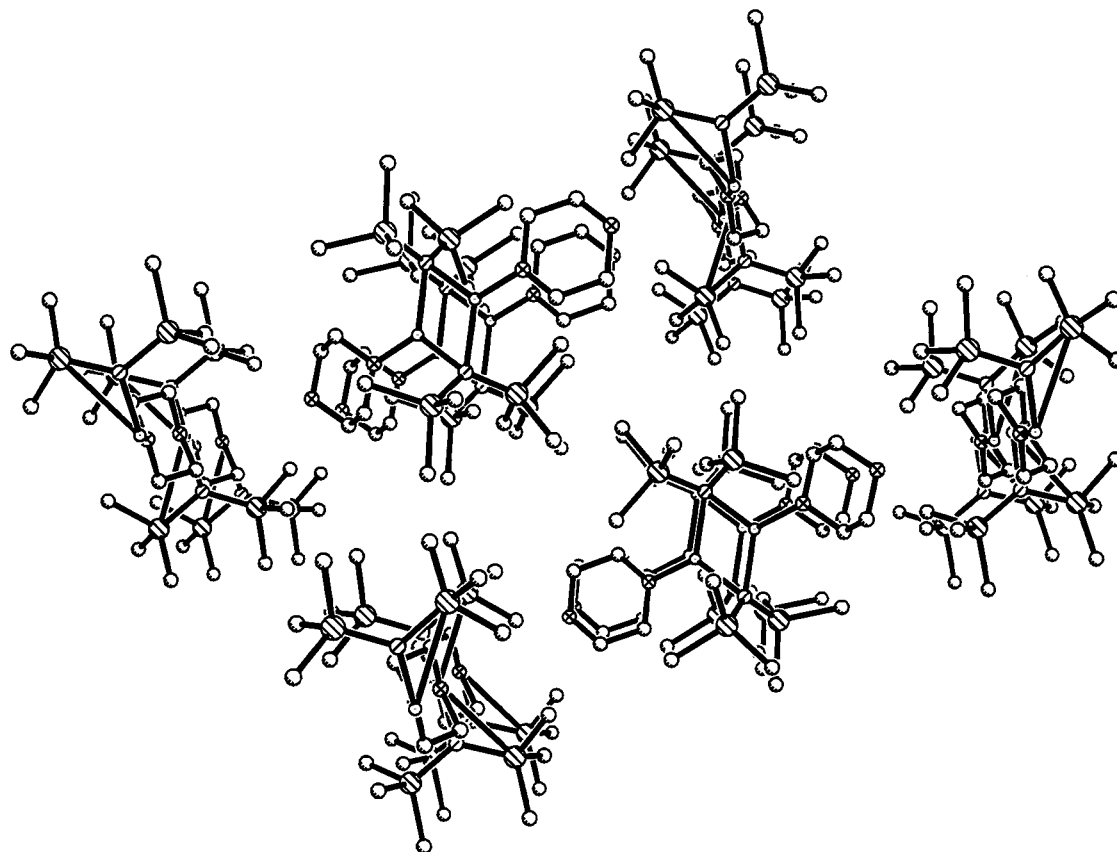
Figure 7. Packing arrangement for complex **12**.

single point *ab initio* calculations at the HF/6-31G* level are also detailed.[33]

Semiempirical PM3 Calculations. TMEDA and DME were chosen for study since they gave very different structures for LHMDS aggregation in the solid state, monomer and dimer, respectively. Schemes 1 and 2 outline the results for the calculated heats of formation for the PM3 geometry optimized

(30) For examples of complex aggregation in solution see: (a) Jackman, L. M.; Scarmoutzos, L. M. *J. Am. Chem. Soc.* **1984**, *106*, 4627. (b) Jackman, L. M.; Scarmoutzos, L. M. *J. Am. Chem. Soc.* **1987**, *109*, 5348. (c) Jackman, L. M.; Smith, B. D. *J. Am. Chem. Soc.* **1988**, *110*, 3829. (d) Jackman, L. M.; Bortiatynski, J. *Adv. Carbanion Chem.* **1992**, *1*, 45. (e) Lucht, B. L.; Collum, D. B. *J. Am. Chem. Soc.* **1994**, *116*, 7949. (f) Bernstein, M. P.; Collum, D. B. *J. Am. Chem. Soc.* **1993**, *115*, 789. (g) Barr, D.; Hutton, K. B.; Morris, J. H.; Mulvey, R. E.; Reed, D.; Snaith, R. *J. Chem. Soc., Chem. Commun.* **1986**, 127. (h) Barr, D.; Snaith, R.; Wright, D. S.; Mulvey, R. E.; Jeffrey, K.; Reed, D. *J. Organomet. Chem.* **1987**, *325*, C1. (i) Barr, D.; Clegg, W.; Hodgson, S. M.; Mulvey, R. E.; Reed, D.; Snaith, R.; Wright, D. S. *J. Chem. Soc., Chem. Commun.* **1988**, 367. (j) Barr, D.; Doyle, M. J.; Mulvey, R. E.; Raithby, P. R.; Reed, D.; Snaith, R.; Wright, D. S. *J. Chem. Soc., Chem. Commun.* **1989**, 318.

(31) (a) Romesberg, F. E.; Collum, D. B. *J. Am. Chem. Soc.* **1994**, *116*, 9187. (b) Romesberg, F. E.; Collum, D. B. *J. Am. Chem. Soc* **1992**, *114*, 2112. (c) Romesberg, F. E.; Collum, D. B. *J. Am. Chem. Soc.* **1995**, *117*, 2166. (d) Bauer, W.; O'Doherty, G. A.; Schleyer, P. v. R.; Paquette, L. A. *J. Am. Chem. Soc.* **1991**, *113*, 7093. (e) Kranz, M.; Dietrich, H.; Mahdi, W.; Mueller, G.; Hampel, F.; Clark, T.; Hacker, R.; Neugebauer, W.; Kos, A. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1993**, *115*. (f) Kaufmann, E.; Raghavachari, K.; Reed, A.; Schleyer, R. v. R. *Organometallics* **1988**, *7*, 1579. (g) Kaufmann, E.; Gose, J.; Schleyer, P. v. R. *Organometallics* **1989**, *8*, 2577. (h) Kaufmann, E.; Tidor, B.; Schleyer, R.v.R. *J. Comput. Chem.* **1986**, *7*, 334. (i) Glaser, R.; Streitweiser, A., *J. Mol. Struct.* (THEOCHEM) **1988**, *163*, 19.

(32) Stewart, J. J. P. *MOPAC*, Version 6.0. For the PM3 parameterization of lithium, see Anders, E.; Koch, R.; Freunscht, P. *J. Comput. Chem.* **1993**, *14*, 1301.

(33) The *Gaussian 92* program was used for all calculations described here: Frisch, M. J.; Trucks, G. W.; Head-Gordon, M.; Gill, P. M. W.; Wong, M. W.; Foresman, J. B.; Johnson, B. G.; Schlegel, H. B.; Robb, M. A.; Replogle, E. S.; Gomperts, R.; Andres, J. L.; Raghavachari, K.; Binkley, J. S.; Gonzalez, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92*, Gaussian, Inc.: Pittsburgh, PA, 1992.
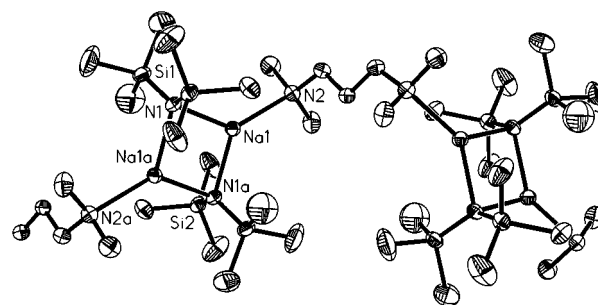

Figure 8. Partial diagram of the molecular structure for polymer **13**. Important bond lengths (Å) and angles (deg): Na(1)−N(1) 2.430(4), Na(1)−N(1a) 2.425(4), Na(1)−N(2) 2.541(4), Na(1)−N(1)−Na(1a) 78.45(11), N(1)−Na(1)−N(1a) 101.55(11), N(1)−Na(1)−N(2) 132.61(13), N(1a)−Na1−N(2) 125.23(13).

structures.[34] The figures shown in the schemes refer to the heats of reaction per 1 equiv of lithium. The unsolvated LHMDS dimer **I** is used as a reference point since this is the dominant species in donor-free media.[35] A comparison of the bond lengths and angles from the PM3 optimized structures and those found from our X-ray data show good agreement. For example, the bond lengths determined for **VII** and **VIII** are within ±0.1 Å of those determined in the X-ray analyses of **6** and **11**.[36]

Similar trends are seen for both ligands. The order of stability for both TMEDA and DME is η^1-coordinated disolvated dimers **II** and **VIII** > η^1-coordinated monosolvated dimers **III** and **IX** > η^2-chelated monosolvated dimers **IV** and **X** > η^2-chelated

(34) Heats of formation in kcal/mol for complexes **I** to **XIV**. **I**: −278.0, **II**: −321.1, **III**: −299.1, **IV**: −290.2, **V**: −289.2, **VI**: −162.7, **VII**: −148.0, **VIII**: −457.6, **IX**: −367.8, **X**: −360.7, **XI**: −356.7, **XII**: −301.6, **XIII**: −210.1, **XIV**: −295.2. Heats of formation for TMEDA and DME are −13.0 and −88.1 kcal/mol, respectively.

(35) Kimura, B. Y.; Brown, T. L. *J. Organomet. Chem.* **1969**, *91*, 7425.

Scheme 1. Relative Energies of TMEDA Aggregates of LHMDS[a]
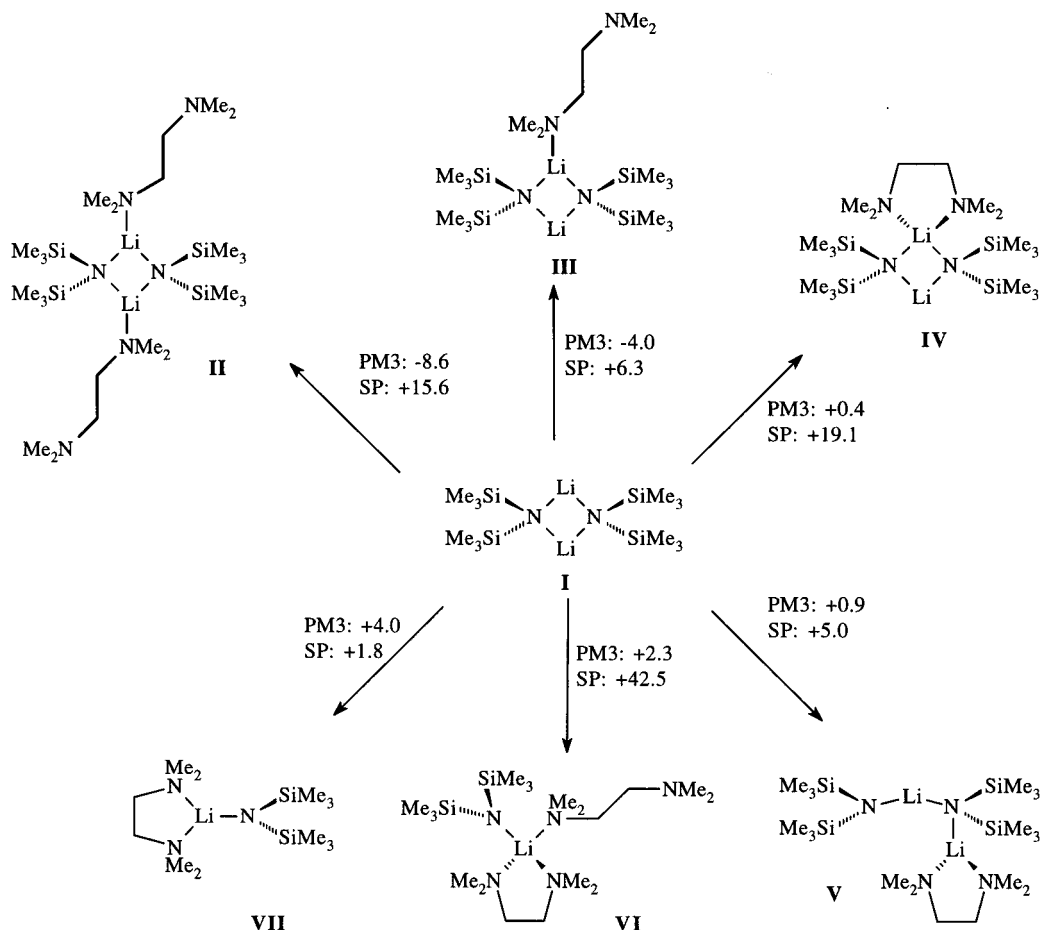
[a] Energies are quoted on a per lithium basis; PM3 and single points (SP) energies are given in kcal/mol.
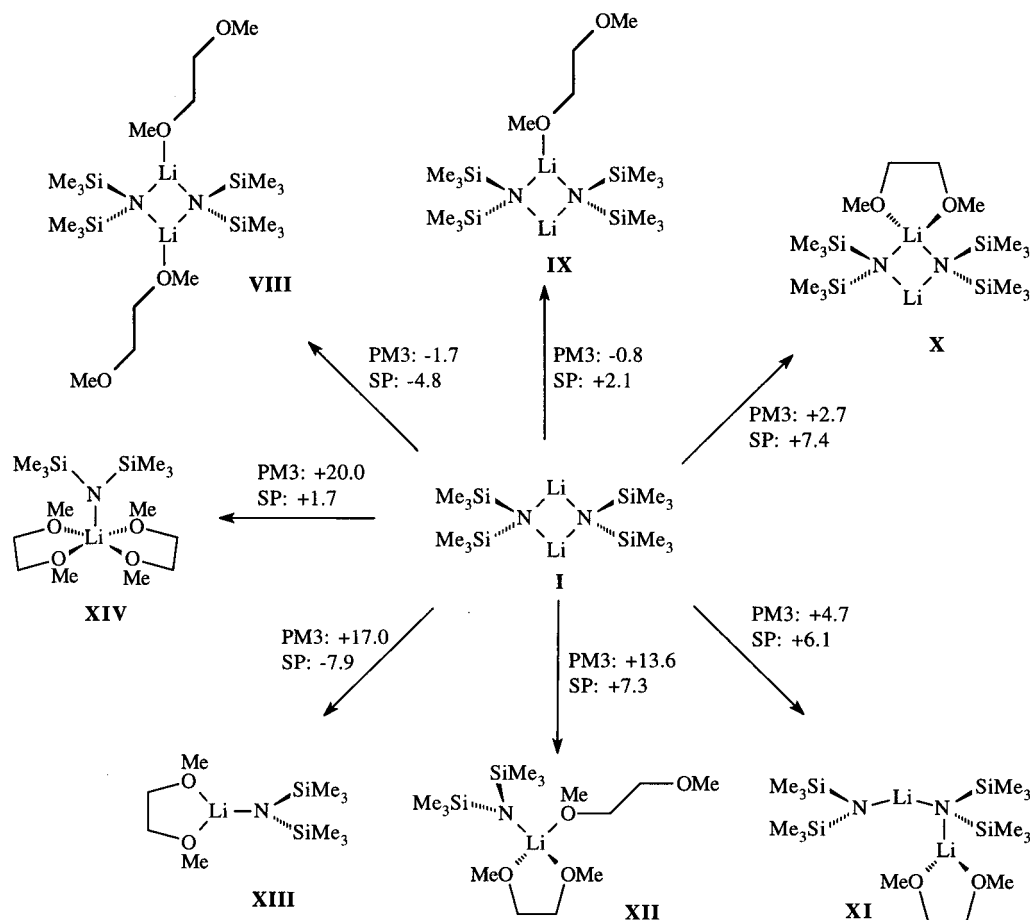
monosolvated open dimers **V** and **XI** > η^1,η^2-coordinated monomers **VI** and **XII** > η^2-chelated monomers **VII** and **XIII** (*i.e.*, decreasing clockwise around Schemes 1 and 2). In addition, the η^2,η^2-chelated monomer **XIV** was located containing DME ligands which was identified as the least stable species. No such monomer was obtained using TMEDA ligands, instead one of the dimethylamine groups is pushed away from lithium reverting to complex **VI**. For both ligands the only stabilized complexes with respect to **I** are the η^1-coordinated mono- and disolvated dimers **II**, **III**, **VIII**, and **IX**. A closer examination of the relative heats of formation of the complexes reveals some worrying inconsistencies with the crystal structure and NMR evidence. The most obvious flaw in the calculations is that the TMEDA η^2-chelated monomer **VII** is disfavored over the other alternatives, with the exception of the η^1,η^2-coordinated monomer **VI**. This is clearly not the case in reality where NMR investigations point to a distinct preference for the η^2-chelated monomer **VII** even in the presence of low concentrations of TMEDA. Similarly, the calculations predict the DME monomers **XII**, **XIII**, and **XIV** to be highly destabilized with respect to the unsolvated dimer **I** (by 13.6, 15.7, and 20.0 kcal/mol, respectively). NMR evidence indicates the presence of monomers at high ligand concentration,[8] and therefore monomer formation would be expected to be exothermic for both TMEDA and DME with respect to **I**.

Semiempirical MNDO Calculations. Changing the semiempirical method from PM3 to MNDO had a drastic effect on the optimized structures obtained. No optimized geometries of the TMEDA- or DME- disolvated dimers or any of the chelates (except the chelated monosolvated monomer **XIII**) were located. Instead both of the donor ligands are pushed out of the complexes reverting to dimer **I** and free donor. The overestimation of steric interactions using MNDO severely limits the utility of this method in these systems.

Ab Initio **Single Point Calculations.** Although the PM3 calculations were able to locate minima for a variety of complexes, the utility of the heats of formation is limited. For example, as already mentioned, addition of 1 molar equiv of TMEDA to LHMDS solutions results in complete conversion to the chelated monomer with no evidence for the formation of the η^1-coordinated dimer. However, the PM3 calculations predict that dimer **II** is more stable than the monomer **VII** by 12.6 kcal/mol and in addition that monomer **VII** is unstable with respect to the unsolvated dimer **I** by 4.0 kcal/mol. These results illustrate the severe limitation of using semiempirical heats of formation as a predictive tool for these systems. It is possible that a more accurate representation of the relative stabilities of the structures may be obtained using the absolute energies of the optimized geometries using single point *ab initio* calculations at the HF/6-31G* level.[37] This procedure will only be successful if the structures generated by the PM3 method are reasonably close to the geometries that would result from HF/6-31G* optimizations. Using this method relatively large,

(36) Nmuerous previous studies have detailed the accuracy of geometry optimisation for lithium using the PM3 method, see ref 32. For some recent references, see: (a) Koch, R; Anders, E. *J. Org. Chem.* **1994**, *59*, 4529. (b) Hoffmann, D; Dorigo, A.; Schleyer, P. v. R.; Reif, H.; Stalke, D.; Sheldrick, G. M.; Weiss, E.; Geissler, M. *Inorg. Chem.* **1995**, *34*, 262. (c) Pratt, L. M.; Khan, I. M. *J. Comput. Chem.* **1995**, *16*, 1067.

(37) Henderson, K. W.; Dorigo, A. E.; Q. Y., Liu; Williard, P. G.; Bernstein, P. R.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1996**, *114*, 1339.

Scheme 2. Relative Energies of DME Aggregates of LHMDS[a]

VIII

IX

X

PM3: -1.7
SP: -4.8

PM3: -0.8
SP: +2.1

PM3: +2.7
SP: +7.4

PM3: +20.0
SP: +1.7

XIV

I

PM3: +17.0
SP: -7.9

PM3: +13.6
SP: +7.3

PM3: +4.7
SP: +6.1

XIII

XII

XI

[a] Energies are quoted on a per lithium basis; PM3 and single points (SP) energies are given in kcal/mol.

complex molecules may be studied which cannot be realistically modeled by *ab initio* geometry optimizations due to the large number of basis sets and degrees of freedom.

Schemes 1 and 2 show the relative thermicities of the reactions using the single point calculations (labeled SP in the schemes).[38] The order of stability for the TMEDA complexes is **VII** > **V** > **III** > **II** > **IV** > **VI**. Using this method of calculation the most stable TMEDA complex is the η^2-chelated monomer **VII**. This is in agreement with the X-ray and NMR evidence. Interestingly, the next most stable complex is the η^2-chelated monosolvated open dimer **V**, which has been identified as a possible solution species for bulky lithium amides.[39] Next lowest in energy is the η^1-coordinated mono-solvated dimer **III** (1.3 kcal/mol less stable than **V**). The remaining complexes are highly destabilized with respect to the unsolvated dimer. Regarding the specific thermicities of the reactions it was rather disappointing to note that even the formation of the chelated monomer **VII** is endothermic (by +1.8 kcal/mol) with respect to the unsolvated dimer **I**. Since we know this reaction is favorable, it appears that this method of calculation underestimates the influence of solvation. In spite

of this failing, the relative energies correlate very well with the known structural possibilities for bulky lithium amides.

For the DME complexes the order of stability follows the order **XIII** > **VIII** > **XIV** > **IX** > **XI** > **XII** > **X**. As with the TMEDA complexes, the chelated monomer **XIII** is determined to be the most stable complex. However, the next most stable complex is the η^1-coordinated disolvated dimer **VIII** which is the crystalline species and has been identified in solution. The spread of relative energies for the DME complexes is small (−7.9 to +7.4 kcal/mol) compared to those using TMEDA (+1.8 to 42.5 kcal/mol). This is in accordance with Collum's solution state investigations where complex equilibria exist for polyether solvates of LHMDS.[8] Of note is the relatively high stability of the η^2,η^2-coordinated monomer **XIV**. This complex has been proposed as the preferred monomeric state at high ligand concentrations and is calculated to be more stable than the alternative η^2,η^1-coordinated monomer **XII** by +5.6 kcal/mol. The five coordinate lithium center in **XIV** is similar to that seen in the crown complex **3**.[13] Only reactions giving complexes **VIII** and **XIII** are exothermic with respect to unsolvated dimer **I**. Reactions to give **XIV** and **IX** are only slightly endothermic (by +1.7 and +2.1 kcal/mol, respectively) and it may be that again the influence of solvation is underestimated. However, there is a remarkable correspondence with the known solution species for LHMDS solvated by DME complexes. Although monomer **XIII** has not been identified as a solution species, its presence cannot be discounted. Solution complexes identified are **VIII** and **XIV** which are predicted to be the most stable species in our calculations (with the exception of **XIII**). In addition, the spread of energies separating the complexes **VIII**, **XIV**, and **IX** is only 6.9 kcal/

(38) Energies in Hartrees, HF/6-31G*, for complexes **I** to **XIV**: **I**: −1755.162 391, **II**: −2445.850 474, **III**: −2100.511 407, **IV**: −2100.470 491, **V**: −2100.515 365, **VI**: −1568.251 516, **VII**: −1222.947 358, **VIII**: −2369.121 036, **IX**: −2062.127 397, **X**: −2062.110 705, **XI**: −2062.114 699, **XII**: −1491.513 088, **XIII**: −1184.565 555, **XIV**: −1491.522 030 for TMEDA: −345.368 992 6 and DME: −306.971 7489.

(39) An X-ray crystal structure of an open dimer has been elucidated: (a) Williard, P.G.; Liu, Q. Y. *J. Am. Chem. Soc.* **1993**, *115*, 3380. Solution NMR studies reveal the presence of open dimers: (b) Romesberg, F. E.; Collum, D. B. *J. Am. Chem. Soc.* **1991**, *113*, 5751.

mol, indicating the possibility for interconversion of these aggregates under suitable conditions, *e.g.*, concentration, temperature, and entropy effects must be taken into account. An example of this is where high concentrations of DME in LHMDS mixtures forces the formation of the disolvated monomer **XIV**.[8]

Discussion and Conclusions

The formation of chelated monomers for both TMEDA and PMDETA with LHMDS appears to be associated with the destabilization of dimeric LHMDS due to solvation from two or three NMe_2 units. In itself this would not be enough to destroy the dimeric framework as is seen from the crystal structure of the disolvate **8**, which binds to the dimers through a NMe_2 group. Also, the chelate effect must be taken into consideration in the drive toward deaggregation.[40] Each lithium can then bind strongly to two (or three) dative groups in addition to the anion. In a disolvated dimer, lithium would bind weakly to the dimethylamine group (as evidenced by the relatively long $Li-NMe_2$ bonds in **8**). This conjecture is supported by the structures of **9** and **10** (the primary amine solvates). In these cases the minimizing of steric repulsions by replacement of hydrogen atoms for methyl groups in TMEDA and PMDETA gives disolvated LHMDS dimers. Therefore, the lithium atoms can maintain bonding to two anions while still coordinating strongly with the ligands (averaged $Li-NH_2$ distance is 2.06 Å).

The reduction in steric strain of an OMe unit in DME compared to a NMe_2 unit leads to a preference for η^1-coordinated disolvation of the LHMDS dimer. As with the primary amines, lithium can maintain a strong interaction with the donor molecule without causing undue steric repulsions. This is clear from the $Li-O$ bond lengths of **11**, which are average for ether-solvated LHMDS complexes. In this instance the lithium centers can remain in the dimer while still bonding strongly to the ether units and hence the η^1-coordinated disolvated dimer is preferred. A second point to note is that the solvation energy of ethers are significantly less than those of amines.[8] The increase in solvation energy for TMEDA compared to DME combined with the increase in steric bulk of a NMe_2 unit versus an OMe unit leads to preferential monomer formation for the LHMDS·TMEDA system.

Since chelation of 1,4-dioxane to a lithium center is unlikely, it is not surprising that no monomer is produced. In fact, the structure of **12** reveals two of the most likely possibilities, a η^1-disolvated dimer and a polymer of dimers. The reason for the inclusion of two different types of structure within the crystal is uncertain. Each lithium is again three-coordinate, and in each instance the dimeric form of LHMDS is maintained.

A rationale for the monofluoro-solvated dimers **5a** and **5b** may lie in the relative strength of solvation by a fluorine group which should be relatively weak with respect to an ether or an amine. Schleyer calculated the stabilities of various complexes between lithium hydride and fluorobenzene.[41] It was found that lithium preferred to coordinate to the aromatic ring in preference to the fluorine. Inspection of the bond distances in **5a** and **5b** reveals that the trimethylsilyl groups tilt toward the unsolvated lithium center.[27] It may be that there is insufficient energy gained from solvation by a second fluoro group to offset the increase in steric interactions associated with disolvation.

PM3 calculations have shown their utility by giving reasonable optimized geometries for the TMEDA and DME-solvated

LHMDS dimers and monomers. MNDO calculations fail to locate minima for most of the complexes of interest and is therefore an inadequate method for these systems. However, the PM3 heats of formation leave a lot to be desired. For example, PM3 predicts that the disolvated dimer **II** is 12.6 kcal/mol more stable than the chelated monomer **VII**. This must be questioned in light of the monomeric structure elucidated for **6**. Similarly the DME η^2,η^2-chelated monomer **XIV** is predicted to be 20.0 kcal/mol less stable that the unsolvated dimer **I**. These predictions do not correlate with the solid or solution state data and illustrate the care with which the heats of formation should be handled.

The single point HF/6-31G* *ab initio* calculations using the PM3 optimized geometries have shown their utility in predicting the relative stabilities of the TMEDA and DME-solvated complexes. It should be noted, however, that the influence of solvation appears to be underestimated for the ligands. Even so, the relative energies indicate the most stable TMEDA complex to be the chelated monomer **VII**, which is consistent with the NMR and X-ray data. A more complex picture is observed for the DME compounds. Again the chelated monomer **XIII** is predicted to be the most stable species. No direct evidence exists for the existence of **XIII** since the crystal structure and NMR evidence point to a disolvated dimer being the most stable species at a 1:1 ligand LHMDS molar ratio. Nevertheless, the existence of **XIII** cannot be discounted entirely. It is pleasing that the next most stable complexes using DME ligands are predicted to be the disolvated dimer **VIII** and the chelated monomer **XIV**, this again is consistent with the NMR and X-ray data.

In conclusion, the driving force in determining the structural motif found for LHMDS complexes appears to be due to a combination of factors including (i) the strength of solvation by the donor, (ii) the steric requirements of the donor, and (iii) the stabilization due to the chelate effect. Using a combination of PM3 geometry optimizations followed by single point *ab initio* calculations at the HF/6-31G* level, a good correlation between experiment and theory has been achieved which shows the potential of this technique as a predictive tool for complex lithium systems.

Experimental Section

All solvents were distilled over sodium/benzophenone until blue and used directly from the still. Amines and ketones were distilled over CaH_2 prior to use. Standard Schlenk techniques were employed for the preparation and manipulation of the highly air and moisture sensitive materials.[42] All reactions were carried out under a prepurified argon blanket. Bu^{n}Li was standardized by titration with 2,5-dimethoxybenzyl alcohol before use.

X-ray Crystallography. Suitable crystals were mounted in an oil drop directly from the crystallization vessels, to the diffractometer, under a stream of cooled nitrogen gas. Data were collected on a Siemens P4 X-ray crystallographic system fitted with a LT-2 low temperature device. The structures were solved by direct methods using SHELXTL or SHELXL-90. All atoms were refined isotropically with the exception of the hydrogens (fitted in idealized positions), which were allowed to ride the atoms to which they were attached. Full matrix least-squares refinement on F^2 was completed using SHELXL-93 or SHELXTL. Complete crystallographic data are available in the Supporting Information.

Computational Studies. PM3 calculations were performed using the Spartan molecular modeling package on a Silicon Graphics Indigo2. Gaussian 94 ready files were prepared on the optimized geometries within the Spartan program, and single point *ab initio* calculations were run at the HF/6-31G* level on an Silicon Graphics Origin 200. Care

(40) (a) Reich, H. J.; Kulicke, K. J. *J. Am. Chem. Soc.* **1995**, *117*, 6621. (b) Klumpp, G. W. *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 1.

(41) van Eikema Hommes, N. J. R.; P. v. R. Schleyer *Angew. Chem.* **1992**, *104*, 768; *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 755.

(42) *The Manipulation of Air Sensitive Compounds*, 2nd ed.; Shriver, D. F., Drezdzon, M. A., Eds.; Wiley: New York, 1986.

needs to be taken when judging the relative energies involved due to conformational changes in the side chains. Optimised structures were obtained after starting from several different starting geometries. The energies quoted for the DME complexes are the lowest values obtained for *trans* methyl groups in the ligand since this is the observed conformation from the X-ray data.

LHMDS. All LHMDS solutions were prepared in a similar manner. Addition of Bu^nLi (2.5 M in hexanes or 2 M in pentane solution) to a 0 °C cooled mixture of HMDS (1.1 equiv) in hexanes (1 mL per mmol) yielded a white suspension after stirring for 15 min. These suspensions were then subjected to the further reactions outlined below.

Preparation of [LHMDS·TMEDA] 6. These crystals were first prepared fortuitously in an attempt to obtain a mixed aggregate between LHMDS and lithium pinacolate. Pinacolone (2 mmol) was added at once to a 0 °C cooled suspension of LHMDS (2 mmol). After stirring for 10 min Bu^nLi (1 mmol) was introduced, and the mixture was allowed to stir for a further 2 min. TMEDA (4 mmol) and THF (1.2 mmol) were added as donor solvent, and the solution was allowed to warm to 25 °C. Crystals suitable for diffraction analysis were grown in a −10 °C freezer over 12 h.

By adding 1 equiv of TMEDA to a LHMDS suspension in hexanes, crystallization of **6** could be repeated.

Preparation of [LHMDS·PMDETA] 7. Addition of PMDETA (5 mmol) to a LHMDS (5 mmol) suspension in hexanes (2 mL) at 0 °C was followed by warming to room temperature. A clear solution was obtained on addition of 1 mL of THF as cosolvent. On cooling the solution to −10 °C for 12 h crystals of **7** were deposited.

Preparation of [LHMDS·N(Me$_2$)CH$_2$Ph]$_2$ 8. A clear solution resulted from the addition of benzyldimethylamine (2.5 mmol) to a LHMDS (2 mmol) suspension in hexanes at 0 °C. After stirring for several minutes, a precipitate formed which was redissolved by adding 2 mL of hexanes and warming to room temperature. Large crystals grew after several weeks on cooling to solution to −10 °C.

Preparation of [LHMDS·DME]$_2$ 11. DME (10 mmol) was added to a LHMDS (10 mmol) solution in 1 mL of hexanes at 0 °C yielding a clear solution. Thin needles were obtained on cooling the mixture to −30 °C for 2 h. All solvents were then removed by syringe, and 1 mL of fresh hexanes was added at 0 °C. The clear solution deposited good quality crystals within 5 h after being cooled to −10 °C.

Preparation of [{(LHMDS·dioxane)$_2$ }·{(LHMDS)$_2$·dioxane}$_\infty$] 12. 2,*N*,*N*-dimethylaminoethyl ether (0.20 mL) was used as cosolvent in the reaction between a LHMDS suspension (1.25 mmol) and 1,4-dioxane (1.25 mmol). The reaction was carried out as before at 0 °C, and a white precipitate resulted. This was dissolved upon warming to 40 °C with the addition of 2 mL of hexanes. After cooling the solution to 0 °C for 12 h crystals were obtained.

Preparation of [NaHMDS·N(Me$_2$)CH$_2$CH$_2$CH$_2$NMe$_2$]$_\infty$ 13. Bu^nNa (1 mmol) was mixed with 2 mL of pentane and cooled to 0 °C. HMDS (1.1 mmol) was added dropwise, and the suspension was stirred for 15 min. TMPDA (1.1 mmol) was added, and the solution turned clear after warming to 25 °C. The solution was cooled to −50 °C for 2 days after which crystals of **13** were precipitated.

Supporting Information Available: Full crystallographic details including atomic coordinates, thermal parameters, bond lengths and angles, and atomic displacement parameters for complexes **6**−**8** and **11**−**13** (43 pages). See any current masthead page for ordering and Internet access instructions.

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