

Lithiation Selectivity in Monoalkylamine/Dialkylamine Mixtures: A Synthetic and *ab Initio* Molecular Orbital Study

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Reaction of $n\text{BuLi}$ with a 1:1 mixture of diisopropylamine or tetramethylpiperidine and a simple alkylamine R^1NH_2 ($\text{R}^1 = n\text{Bu}, s\text{Bu}, t\text{Bu}, n\text{Pe}, 1\text{-Me-}n\text{Bu}, 1,2\text{-Me-}n\text{Pr},$ or $1,3\text{-Me-}n\text{Bu}$), under thermodynamic conditions, results in the exclusive isolation of lithium primary amides: no solid lithium secondary amides are isolated. Preformation of the lithium secondary amides followed by addition of the primary amine leads to complete transamination, to give a lithium primary amide. *Ab initio* molecular orbital calculations at the HF/6-31G* level show that the order of gas-phase Brønsted acidity increases in the sequence $\text{NH}_3 < \text{RNH}_2 < \text{R}_2\text{NH}$ ($\text{R} = \text{Me}, i\text{Pr},$ or $t\text{Bu}$), but the relative stability of the lithium amides, as measured by anion exchange reactions, is in the order $\text{R}_2\text{NLi} < \text{RN(H)Li}$. This reverse is due, in part, to a decrease in steric crowding surrounding the nitrogen and an increase in electrostatic stabilization, resulting in shorter Li–N bond distances. Solvation of the monomeric lithium primary or secondary amides with the corresponding primary or secondary amine, $\text{R}_2\text{NLi}\cdot\text{H}_2\text{NR}$ or $\text{RN(H)Li}\cdot\text{HNR}_2$, leads to anion exchange being essentially thermoneutral. Consideration of increasing aggregation (dimer, trimer, tetrameric ring, cubane, prismatic hexamer, and prismatic octamer) of the lithium primary amide MeN(H)Li results in a relative increase in stability. The possibility of forming aggregates or polymers with each lithium bridging three anionic centers is the main driving force for primary amine lithiation in the systems studied. The bulk of the secondary amides used limits their aggregation to being either rings or primary amine solvated dimers. By considering the effects of solvation, sterics, aggregation, and electronics in combination, a rationalization for selectivity preference can be achieved.

1. Introduction

Deprotonation reactions of acidic organic compounds using alkyllithium reagents are widely used in modern chemistry.¹ It is of fundamental importance when considering these reactions that the location of the proton removed from the organic molecule can be identified.² Complexity arises when examining selective deprotonations of polyfunctional compounds or reactions containing mixtures of protic compounds.³ In these instances, nonselective or polyolithiations may reduce the utility of alkyllithium reagents.⁴ Selective deprotonations can also be either thermodynamically or kineti-

cally controlled.⁵ There is recent precedent that some metalation reactions may be directed by factors other than the simple acidity of the protons present. Examples include the 2,5-double deprotonation of toluene by a bimetallic mixture of magnesium and sodium 2,2,6,6-tetramethylpiperidine and the double deprotonation of 2,2'-bis(2-methoxyethylamino)diphenyl ether or 2,2'-bis(*N,N*-dimethylethylenediamino)diphenyl ether by butyllithium.^{6,7} We are interested in investigating the factors involved in determining the course of lithiation reactions when two apparently similar protic compounds are available for deprotonation. Herein we report an investigation into the reaction of alkyllithium reagents with mixtures of primary alkylamines (RNH_2)

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Table 1. Reactions of 1:1:1 Mixtures of Diisopropylamine, a Primary Amine, and ⁿBuLi

primary amine	isolated product	% yield of solid
^s BuNH ₂	^s BuN(H)Li	73
^t BuNH ₂	^t BuN(H)Li	25
ⁿ BuNH ₂	ⁿ BuN(H)Li	70
ⁿ PeNH ₂	ⁿ PeN(H)Li	55
1-Me- ⁿ BuNH ₂	1-Me- ⁿ Bu(NH)Li	28
1,2-Me- ⁿ PrNH ₂	1,2-Me- ⁿ PrN(H)Li	64
1,3-Me- ⁿ BuNH ₂	1,3-Me- ⁿ BuN(H)Li	62

and secondary dialkylamines (R₂NH). The utility of secondary lithium amides as reagents in synthesis has elevated this class of compounds to one of the most important and widely used at present.^{1c,5} Moreover, the reaction of primary amines with metalating reagents is an area of current interest due to the possibility of forming imido (RN²⁻) and mixed-metal geminal organodimetallic complexes (RNM¹M², M¹ ≠ M²).^{8,9}

2. Results and Discussion

2.1. Synthetic Studies. A series of reactions outlined in Table 1 was performed using diisopropylamine (DPA) as the secondary amine, and *s*-butylamine, *tert*-butylamine, *n*-butylamine, *n*-pentylamine (ⁿPeNH₂), 1-methylbutylamine (1-Me-ⁿBuNH₂), 1,2-dimethylpropylamine (1,2-Me-ⁿPrNH₂), or 1,3-dimethylbutylamine (1,3-Me-ⁿBuNH₂) as the primary amine. One molar equiv of ⁿBuLi was added to a hexane solution of a 1:1 mixture of the primary and secondary amines, followed by stirring for several hours at room temperature. Precipitation of the individual amides was achieved either spontaneously or by cooling (see Experimental Section).

In all instances the primary amidolithium was exclusively isolated from solution, with no evidence for lithiation of the dialkylamines. Moreover, isolation of the primary amide was independent of the order of addition of the reactants; that is, if the secondary amide was preformed before the addition of primary amine, then anion exchange occurred. Reactions using 2,2,6,6-tetramethylpiperidine (TMP) as an alternative secondary amine to DPA also gave the primary amide as the major product, although small amounts (3–10%) of the lithium secondary amide were present in some cases. However, if the solutions were heated to reflux (≈70 °C) for 1 h prior to crystallization, the primary amide derivatives were exclusively precipitated. Therefore under equilibrating thermodynamic conditions, primary amine deprotonation is highly preferred for the systems studied. It should be noted that, in general, the secondary amides would be expected to be more soluble than the primary amides due to enhanced lipophilicity.

2.2. NMR Spectroscopic Studies. The reaction involving DPA, ^tBuNH₂, and ⁿBuLi was studied by ¹H NMR spectroscopy to investigate if any equilibria were discernible in solution at room temperature. A 1:1

mixture of preformed, crystalline ^tBuN(H)Li and DPA in C₆D₆ (0.1 M) resulted in only lithium primary amide and DPA being detected. The reaction of preformed, crystalline lithium diisopropylamide (LDA) with ^tBuNH₂ in C₆D₆ (0.1 M) resulted in complete anion exchange, again giving exclusively ^tBuN(H)Li and DPA. This confirms that primary amide formation is thermodynamically favored.

2.3. Ab Initio Molecular Orbital Calculations. An ab initio theoretical investigation at the HF/6-31G* level was initiated to rationalize the selectivity of the lithiation reactions.^{10,11} This level of theory was chosen as it has proved reliable both in geometry optimizations and absolute energy predictions for organolithium species and is at our current computational limit for the largest molecules under investigation.¹² Moreover, in this study it is the trends in relative energies that are of most interest, not necessarily a search for quantitative measurements. A selection of the smaller molecules were calculated at B3LYP/6-311+G** to compare the relative energies obtained at HF/6-31G*.¹³ The use of calculations to ascertain stabilities in these systems is justified, since all reactions were performed in hydrocarbon solutions, reducing major solvation effects such as hydrogen bonding from the solvent media.¹⁴ All energy values quoted in the text, equations, and schemes are normalized to a per-lithium basis to simplify analyses. Also, energy differences are presented in kcal/mol.

Deprotonation Energies. Using the simple methylamines as model compounds, the calculated Brønsted acidity follows the sequence Me₂NH > MeNH₂ > NH₃; that is, the secondary amine has a lower deprotonation energy than the primary amine (Table 2).¹⁵ This is consistent with the experimentally measured gas-phase deprotonation enthalpies and was confirmed by calculations at the B3LYP/6-311+G** level.¹⁶ At first this appears contrary to the expected deprotonation sequence considering the inductive effect of the methyl

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Table 2. Calculated (HF/6-31G*) Deprotonation Energies of the Alkyl Amines

R ¹	H	Me	Me	ⁱ Pr	ⁱ Pr	^t Bu	^t Bu
R ²	H	H	Me	H	ⁱ Pr	H	^t Bu
energy (kcal/mol)	+444.4	+435.3	+425.5	+430.4	+418.3	+428.1	+417.1

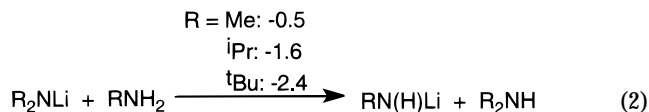
groups. However, for the free anions the charge capacity of the ligand becomes important and a methyl group has a larger charge capacity than a hydrogen atom (2.8 vs 1.0).¹⁷ This leads to the more substituted anions being relatively more stabilized, and hence their amines are more acidic.¹⁸ It is worth noting that solvation, steric, and electronic effects combine to give a rather unclear picture for the order of acidity or basicity of these simple amines when measured in water.¹⁹ Replacing the methyl groups by either an isopropyl or *tert*-butyl function similarly results in a lower deprotonation energy for the secondary amines (eq 1 and Table 2).



Table 2 also illustrates that increasing the branching of the alkyl function decreases the deprotonation energy (^tBu < ⁱPr < Me), which is consistent with the increasing charge capacity of the anions.¹⁷ As expected, this follows the same order as the corresponding C–H acidities for simple alkanes.²⁰ However, the greater electronegativity of nitrogen compared to carbon leads to smaller calculated deprotonation energies for the amines.

Using the common and simplistic assumption that the most acidic proton will be removed upon lithiation, it would be expected that the dialkylamines are more susceptible than monoalkylamines to proton abstraction, if the latter is the crucial step in the lithiation process. This inference is clearly contrary to our experimental findings.

Lithiation Reactions. A different picture becomes apparent when the relative stabilities of the monomeric lithium amides are compared. The anion exchange reactions generalized in eq 2 indicate a slight preference



for lithiation of the primary amines. (Structural details are omitted for brevity. Tables of bond lengths and angles are available in the Supporting Information.)

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Hence, the stability of the lithium amides is in the opposite direction of the acidity of the amines. Calculations for the methyl derivatives using the B3LYP/6-311+G** method correlate well, showing the anion exchange reaction in eq 2 to be exothermic by -0.4 kcal/mol.

Lithium and the other alkali metals are known to localize charge in anions. This negates the negative hyperconjugative stabilization which is critical in determining the order of stability of the free anions.^{18,21} The preference for primary amine lithiation increases with increasing anion size (Me < ⁱPr < ^tBu). In part this is a consequence of steric effects. The C–N–C angles of the lithium secondary amides are less than in the corresponding parent amines (a reduction of between 2.6° and 3.6°). In addition, the free amines have pyramidal geometries at nitrogen, whereas in the amides the geometry at each nitrogen is almost planar. The planarity of the amides is a consequence of the repulsion between the three electropositive atoms surrounding the nitrogen center and has previously been described by Schleyer and others.²² Replacing an alkyl substituent by a hydrogen allows a greater angle between the remaining alkyl and the lithium compared to the secondary amides (an increase of between 1.5° and 14.1°).

An analysis of the distribution of electron density (Mulliken charges quoted) on the molecules reveals little variation in the charge on lithium (between +0.50 and +0.57), but the negative charge on the amido nitrogen decreases substantially on replacing a hydrogen with an alkyl unit (charges on N: -0.95 , -0.77 for MeN(H)Li and Me₂NLi; -0.95 , -0.82 for ⁱPrN(H)Li and ⁱPr₂NLi; and -0.95 , -0.83 for ^tBuN(H)Li and ^tBu₂NLi). Hence, the primary amides provide a greater Coulombic stabilization between the metal and the anion. An increase in charge on the amido nitrogens, combined with a decrease in steric crowding, allows shorter Li–N contacts in the less substituted amides (a decrease of between 0.011 and 0.026 Å). Therefore, in the simple monomers, these effects lead to a stability preference for the primary amides.

Solvation. The next factor to take into account is the role of polar solvent molecules.²³ Lithiation of one amine, as in eq 1, leaves a second amine which is free to act as a donor ligand, and therefore the relative strengths of solvation have to be considered. Regarding only monomeric fragments, the energies of solvation were calculated according to eq 3, and the geometry

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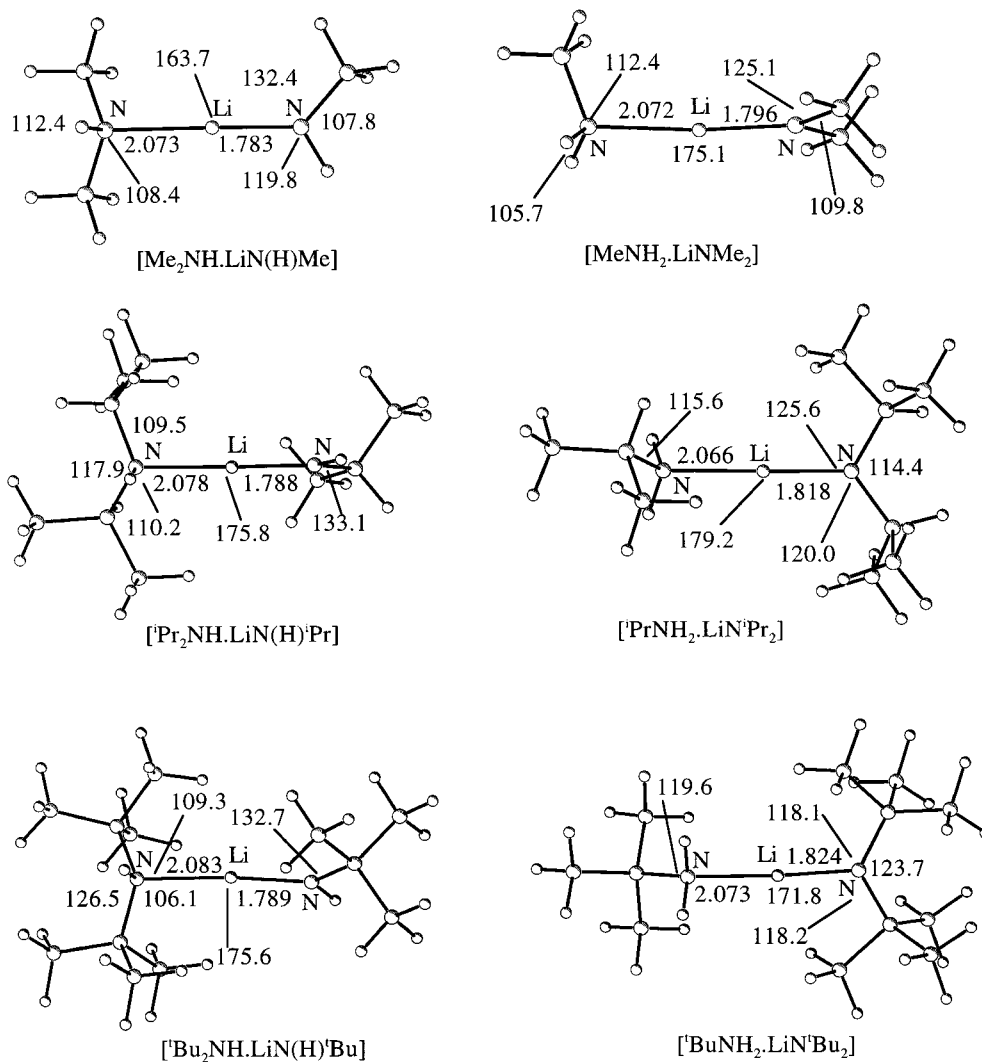
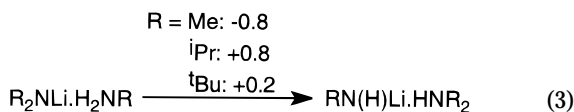


Figure 1. Geometry-optimized structures of the solvated monomeric amides, giving key bond lengths (Å) and angles (deg).

optimized structures can be seen along with some key bond lengths and angles in Figure 1.



Each anion exchange reaction is almost thermoneutral. Calculations at the B3LYP/6-311+G** level for the methyl derivatives are consistent with this analysis, giving a -0.3 kcal/mol enthalpy for the anion exchange reaction in eq 3. These calculations take account of solvation of the lithium species which occurs after proton transfer, which is an important factor to consider in determining the position of anion exchange equilibria.²⁴ The values obtained are consistent with the experimental findings, that in general (i.e., except for the smallest amines) primary amines solvate lithium more strongly than secondary amines.²⁵ In these instances, the preference for primary amine lithiation of the unsolvated species (eq 2) is significantly reduced or indeed reversed when solvation of the monomers is

considered. Clearly, additional factors favoring primary amine lithiation must therefore be present.

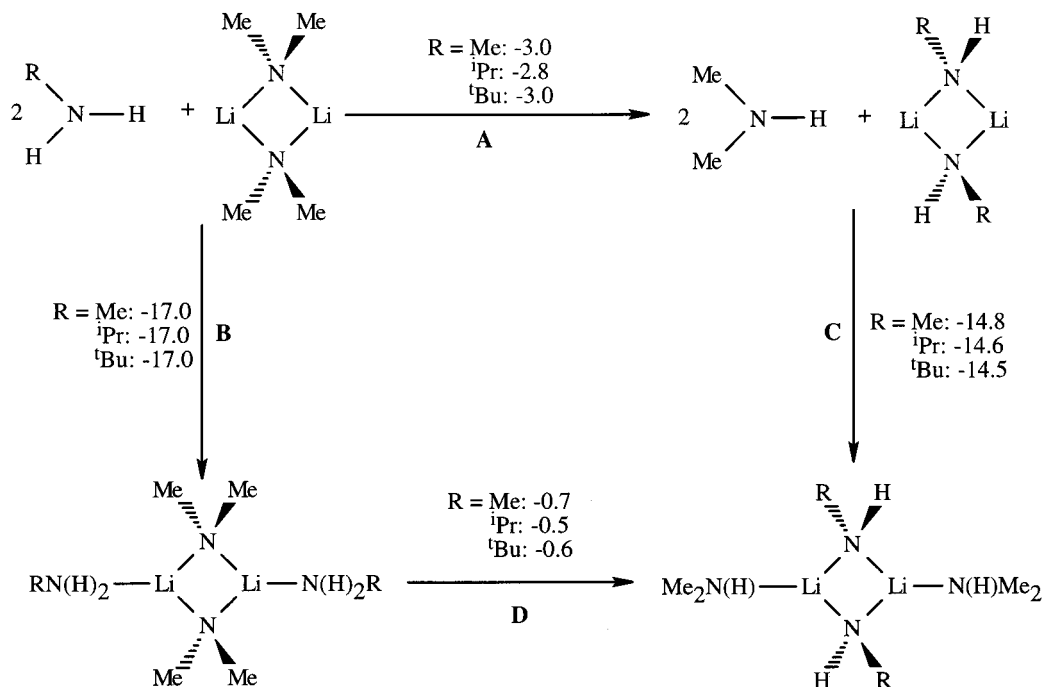
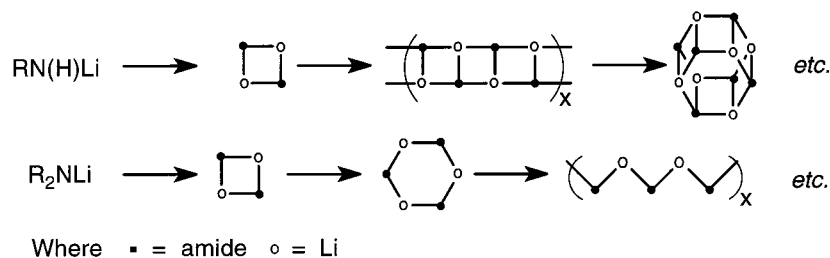
As with the unsolvated amides, there is a reduction in the Li-N(amido) distances in the less substituted amides (by 0.013, 0.030, and 0.035 Å for R = Me, ⁱPr, and ^tBu, respectively). Similarly, the dative bonds from the primary amines to lithium are shorter than for the corresponding secondary amines (by 0.001, 0.012, and 0.010 Å for R = Me, ⁱPr, and ^tBu, respectively). Also, the negative charges on the datively bound nitrogens are greater for the primary amines (an increase of -0.15 , -0.13 , and -0.11 for R = Me, ⁱPr, and ^tBu, respectively). In comparison with the unsolvated monomers, the negative charges on the amido nitrogens are very similar (differences between 0.03 and 0.05), while the positive charges on lithium are decreased (between 0.10 and 0.22) as a consequence of solvation.

Aggregation. The propensity for organolithium compounds to aggregate has led to the study of these species being an area of highly active research over recent years.²⁶ Consequences of simple dimeric aggregation in the amide mixtures was assessed according to the anion

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Scheme 1. Anion Exchange and Solvation Energies for the Simple Dimeric Aggregates (normalized to a *per*-lithium basis in kcal/mol)**Scheme 2. Selected Oligomerization Possibilities for Primary and Secondary Lithium Amides**

exchange reactions outlined in Scheme 1. (Structural details are omitted for brevity. Tables of bond lengths and angles are available in the Supporting Information.) Enthalpies are shown for each reaction and are simplified to a monomeric lithium basis.

The reaction shown in equation A shows a clear preference for primary amine lithiation, and moreover the enthalpy is increased compared to the simple monomer anion exchange reactions (eq 2). However, the stronger solvation achieved by the primary amines in comparison to the secondary amines (between 2.2 and 2.5 kcal/mol in equations B and C) leads to little overall energy difference between the solvated dimers (equation D).

The conformation chosen for the diisopropylamide dimers was with the methyl groups of the isopropyl units directed toward the center of the dimeric ring. This is the geometry observed in the structurally characterized compound [ⁱPr₂NLi.THF]₂.²⁷ Rotating the methyl groups away from the dimeric ring resulted in a destabilization of 8.4 kcal/mol for the unsolvated dimer.

A comparison of the structures attainable for both amide mixtures proves enlightening. Over the past two decades a great deal of structural information has been gathered on secondary amidolithium compounds.²⁶ However, it is only recently that the structures of primary amidolithium compounds have been studied in detail.^{8a,c,28} Using this information, it is now possible to

predict the likely aggregates present in our reaction mixtures.

Generally, both primary and secondary amidolithium compounds associate to produce ring systems. The primary amides commonly associate into ring dimers, which can further associate laterally to form ladder structures such as cyclic prismatic oligomers or polymers.²⁹ Secondary amidolithium compounds can only form extended ladder structures if the two groups attached to nitrogen are small or fixed within a ring.³⁰ In general, bulky secondary amidolithium compounds are chain or ring structures (Scheme 2).³¹

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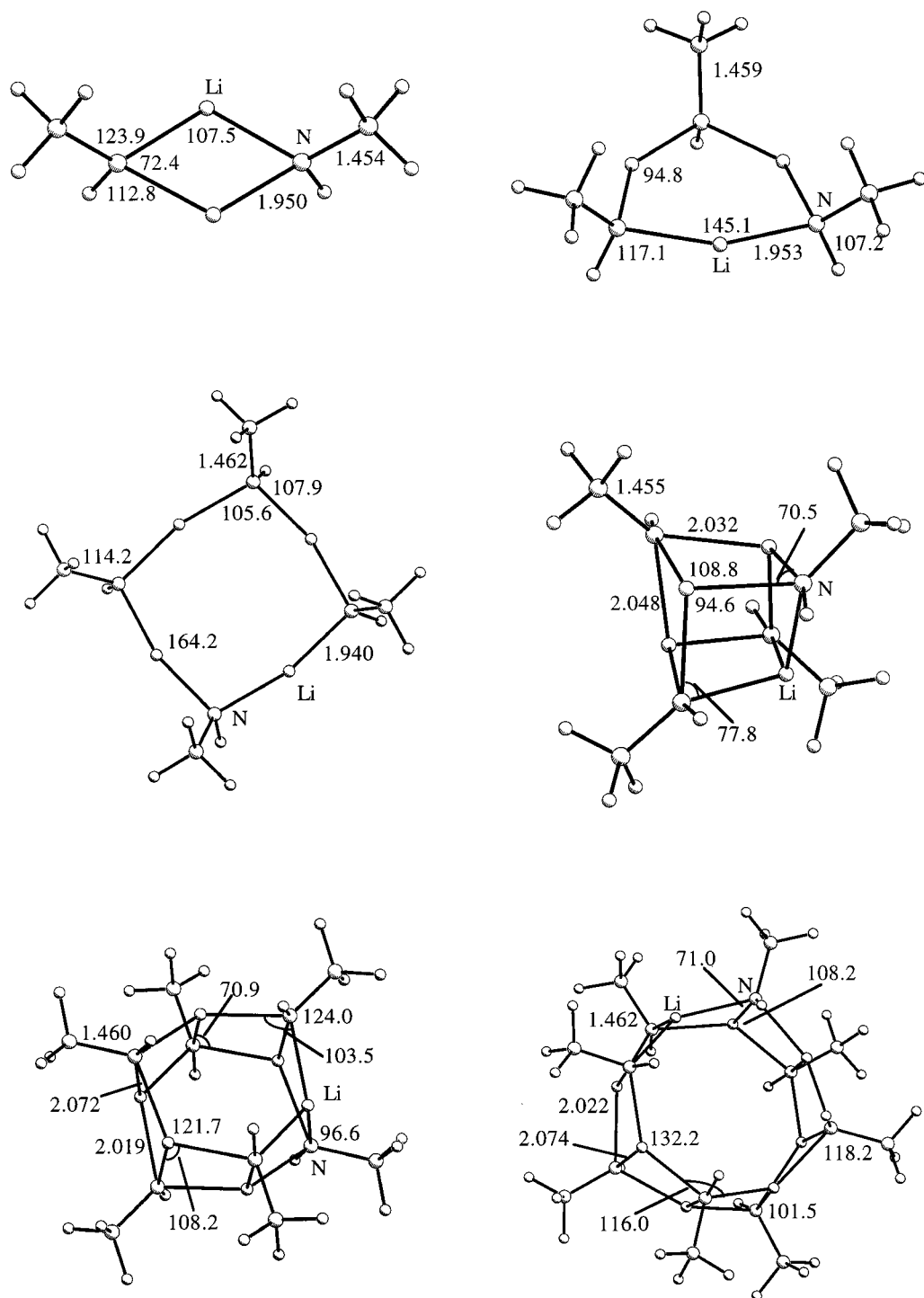


Figure 2. Geometry-optimized structures of the various oligomers of MeN(H)Li, giving key bond lengths (Å) and angles (deg).

In our systems, the likely aggregates will be secondary amide ring dimers solvated by primary amine³² or higher aggregates of primary amides (tetramers, hexamers, octamers, polymers, etc.) with noncoordinated secondary amines.³³

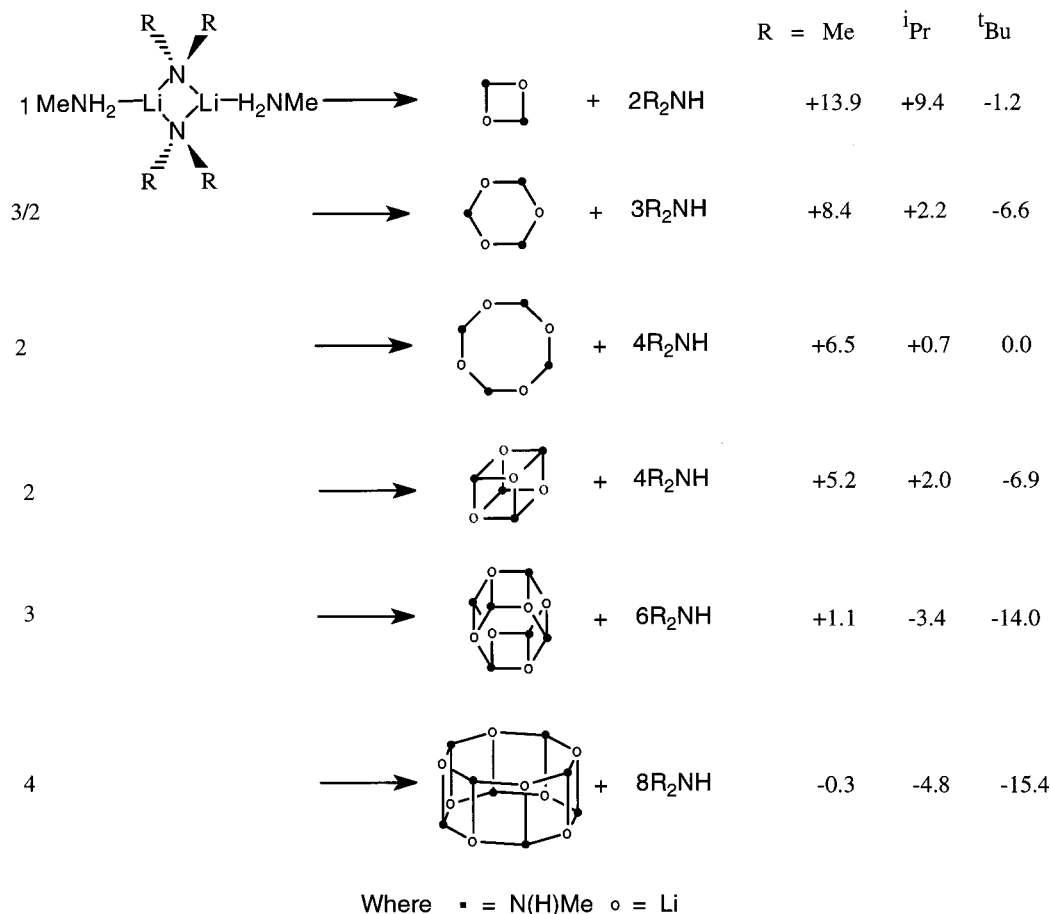
To determine the relative stabilities of these aggregates, calculations were performed on disolvated dimers $[\{R_2NLi \cdot H_2NMe\}_2]$ (where R = Me, ⁱPr, and ^tBu) and various unsolvated primary amide species $[\{MeN(H)Li\}_n]$ (where $n = 2, 3, 4, 6, 8$). (Structural

details are omitted for brevity. Tables of bond lengths and angles are available in the Supporting Information.) The all-cis forms of the dimer, trimer, and ring tetramer were found to be very slightly more stable than any combination of cis and trans (by <1 kcal/mol.) The results of the anion exchange reactions are summarized in Scheme 3. Figure 2 shows the optimized structures of the methylamide oligomers and lists some key bond lengths and angles.

All of the calculations indicate a significant increase in stabilization for the primary amide with increasing aggregation.³⁴ In part, this is due to increasing the

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Scheme 3. Enthalpies of Exchange between Methylamide Disolvated Secondary Amide Dimers and Oligomers of Primary Amides (normalized to a *per*-lithium basis in kcal/mol)

coordination number of the metal from two, for the dimer, trimer, and tetrameric ring, to three, for the prismatic aggregates. As calculated previously for the LiNH₂ complexes, the ring tetramer of MeN(H)Li is found to be more stable than the corresponding cubane (by 1.3 kcal/mol per lithium).³⁵ In contrast, Sapse found the hexameric cyclic ladders (*D*_{3h}) of LiF, LiOH, and LiNH₂ to be more stable than the planar ring (*D*_{6h}) structures.³⁴ These results are in accord with a significant alleviation of strain on moving from a cubic tetramer to a prismatic hexamer.³⁶

Charge distributions on the methylamide oligomers show only small variations (Li +0.57 ± 0.02; N 1.08 ± 0.04). The charge distribution on the disolvated dimers similarly shows only small differences (Li +0.50 ± 0.07; N(amido) -0.86 ± 0.01; and N(dative) -0.95 ± 0.01). However overall, the metal centers in the primary amide prismatic oligomers (cubane, hexamer, octamer) are surrounded by more negative charge than the corresponding primary amine disolvated secondary amide dimers; that is, they are electrostatically favored.

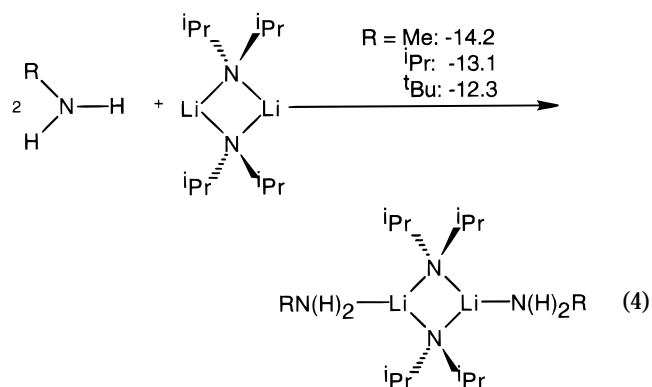
(34) The increase in binding energy per monomer with increasing aggregation has been noted previously for LiF, LiOH, and LiNH₂ oligomers: Raghavachari, K.; Sapse, A. M.; Jain, D. *Inorg. Chem.* **1987**, *26*, 2585.

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(36) The relative stabilities of ladders and stacks of mixed anion aggregates of MeLi/LiOH and MeLi/LiNH₂ have been studied: Sorger, K.; Schleyer, P. v. R.; Fleischer, R.; Stalke, S. *J. Am. Chem. Soc.* **1996**, *118*, 6924.

The geometry around lithium moves toward planarity with increasing aggregation (sum of angles at Li are 298.0° 338.1° and 348.6° for the cubane, hexamer, and octamer, respectively). Similarly, there is an overall increase in the internal ring bond angles at nitrogen (sum of angles at N are 218.0°, 245.3°, and 258.0° for the cubane, hexamer, and octamer, respectively). The movement toward planar lithium leads to a more even, isotropic, distribution of electron density at the metal center.

In addition, the solvation energy decreases with increasing steric bulk of the coordinating primary amine.²⁵ Equation 4 shows the general reaction for the solvation



of a lithium diisopropylamide dimer. (Structural details are omitted for brevity. Tables of bond lengths and

angles are available in the Supporting Information.) As expected, the larger the primary amine, the weaker the solvation. The calculations in Scheme 3 are limited to examining only the methylamine derivatives; however, the solvation energy calculations from eq 4 predict that the primary amidolithium aggregates will be further favored when sterically more demanding primary amines are used. Entropy will also favor formation of the primary amidolithium oligomers due to an overall increase in the number of free molecules in solution.

These results are now consistent with the experimental findings; that is, lithium primary amide is preferred. The crystal structure of ^tBuN(H)Li has recently been determined to be a cyclized octameric ladder.²⁸ The low solubility in hydrocarbon solution of many of the primary amides studied is consistent with polymeric ladder structures (Scheme 2).^{26,37} Lithium dibenzylamide is known to form a polymeric ladder structure even in the presence of coordinating benzylamine or tetrahydrofuran.^{28b,c} Our finding of increasing stabilization with higher aggregation dictates that the polymeric ladders should be at least as stable as the calculated octamer.

2.4. Conclusions. As expected, gas-phase acidity measurements are of limited value in predicting lithiation selectivity. A principal driving force for primary amine lithiation in the systems studied is the stability gain on forming aggregates in which lithium can triply bridge three anionic nitrogens, in comparison to disolvated dimers of bulky secondary amides which contain two anionic and one dative linkage to each lithium; that is, the structural arrangement adopted in the products is a critical factor in determining which amine is preferentially lithiated.³⁶ Increasing stabilization of the primary amides with aggregation is, in part, a result of the move toward a more trigonal-planar geometry at lithium (alleviation of ring strain) and hence a more even distribution of electron density around the metal. The effects of solvation, sterics, aggregation, and electronics need to be considered in combination when predicting lithiation selectivity. This study has deliberately been limited to the analysis of relatively simple systems; an understanding of numerous other factors influencing lithiation selectivity, such as solvent media, possible chelation, coaggregation, and kinetics, will require further detailed investigations. The results reported are of practical significance when using protic amines or related compounds in lithium-mediated transformations.^{3a,38}

3. Experimental Section

Syntheses. All solvents were distilled over sodium/benzophenone until blue and stored over 4 Å molecular sieve before use. Amines were distilled over CaH₂ prior to use.

Standard Schlenk techniques³⁹ were employed for the preparation and manipulation of the highly air- and moisture-sensitive materials. All reactions were carried out under a prepurified argon blanket. Glassware was flame dried before use. A Saffron Omega glovebox was used for the manipulation of solids. BuⁿLi was standardized by titration with diphenylacetic acid before use.⁴⁰ ¹H NMR spectra were recorded on a Bruker AMX 400 spectrometer at 298 K.

General Procedure for the Lithiation Reactions. A typical experiment involved mixing the amines (5 mmol of each) in a hexane solution (10 mL), followed by slow addition of ⁿBuLi (5 mmol of a 1.6 M solution in hexane). The solution was then stirred at room temperature for several hours and the reaction mixture placed in a -20 °C freezer to maximize crystallization. All products were characterized by ¹H NMR spectroscopy (pyridine-*d*₅, 400 MHz, 25 °C) and IR spectroscopy and compared directly with spectra of the individual lithium amides. NMR spectra were run in pyridine-*d*₅ to completely dissolve the products. The splitting patterns of the individual signals were commonly difficult to distinguish due to the broad peaks attained. The NH peaks were not located, except for ^tBuN(H)Li, which dissolved in C₆D₆, due to fast exchange with the solvent. ^sBuN(H)Li: δ 1.01, CH₃; 1.25, β-CH₃; 1.50, CH₂; 3.21, α-CH. ⁿBuN(H)Li: δ 0.86, CH₃; 1.23–1.54, CH₂–CH₂; 2.78, α-CH₂. ^pPeN(H)Li: δ 0.87, CH₃; 1.31, CH₂–CH₂; 1.52, β-CH₂; 2.98, α-CH. 1-Me-ⁿBuN(H)Li: δ 0.34, CH₃; 0.54, CH₂; 0.77, CH₂–CH₂; 2.34, α-CH.

1,2-Me-ⁿPrN(H)Li: δ 0.87, CH₃(×2); 1.00, CH₃, 1.41, β-CH; 2.66, α-CH. 1,3-Me-ⁿBuN(H)Li: δ 0.96, CH₃(×2); 1.28, CH₃, 1.37, β-CH; 1.43, β-CH; 1.90, γ-CH, 3.44, α-CH. ^tBuN(H)Li in C₆D₆: δ -1.53, NH; 1.37, CH₃(×3).

Theoretical Calculations. The Gaussian 94 program, revision E.2, was used for the calculations. No constraints were used in any of the optimizations.¹⁰ Mulliken charges are quoted in the text. Care needs to be taken when locating minima for the isopropyl derivatives due to numerous conformational possibilities.⁷ Absolute energy values for the species calculated are available in the Supporting Information. In some instances more than one minimum was obtained, but for brevity only the lowest energy is quoted.

Supporting Information Available: Tables 1 and 2 listing important bond lengths and bond angles for (i) the unsolvated monomeric amines and amides and (ii) the methyl amine disolvated secondary amide dimers, respectively. Table 3 listing the absolute energy values for all the calculated species. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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