can easily perceive—what she *is* I fear it is impossible to say," a quote of Edgar Allan Poe's,[31] well illustrates the situation. Graph theory offers an alternative way to characterize a structure—a structure is replaced by collection of its *mathematical properties* (graph invariants). Thus the impossible task of correlating structure with property becomes a somewhat less hopeless task when mathematical properties are correlated with physical properties of compounds. Conjugated circuits proved singularly

useful when aromaticity, conjugation, and related molecular properties of homocycles are involved, and the present paper has demonstrated the generality of the method to encompass heterocyclic systems.

(31) Poe, E. A. "The Complete Edgar Allan Poe Tales"; Avenel Books: New York, 1981.

MNDO and ab Initio Study of the Mechanism of Organolithium Amination by Lithium Alkoxyamides

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Abstract: The MNDO method has been used to propose a plausible mechanism for the amination of organolithiums by lithium alkoxyamides. According to this mechanism, an initial lithium complex, formed between a lithium alkoxyamide and an organolithium and having two lithiums bridging the nitrogen and carbon, passes through a transition state which is best described as a trigonal bipyramid with two axial lithium cations and equatorial alkoxyl, methyl, and alkyl nitrene substituents. The product is a more stable complex containing two lithiums bridging carbon and oxygen positions. The specific reactions studied by MNDO were the reaction of methyllithium with lithium methylmethoxyamide and with *N*-lithium hydroxyamide. The former reaction has a calculated barrier of 42.0 kcal/mol and the latter a calculated barrier of 68.9 kcal/mol. Ab initio calculations at the 3-21G and 3-21+G levels were carried out for the reaction between lithium hydroxyamide with methyllithium. At the 3-21G level the barrier is approximately 56 kcal/mol, and this value is reduced to 34.2 kcal/mol at the 3-21+G level. Comparisons have been made between MNDO and ab initio calculations at the 3-21G level for complexation energies. Both methods predict that stabilization of complexes of mixed monomers (such as $LiNH_2:LiCH_3$) is approximately the average of the simple dimers $^1/_2[(LiNH_2)_2 + (LiCH_3)_2]$. Finally the MNDO model has been applied to rationalize recent experimental observations which indicate that intermolecular addition occurs preferentially to intramolecular addition in the rearrangement of *N*,2-dilithio-*N*-methylbenzyloxyamide.
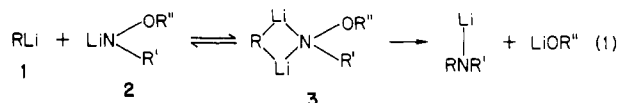
Lithium chemistry has experienced a very rapid growth over the last 5 years. The progress has been led rather than followed by theoretical calculations[1-12] which have been generated largely in Schleyer's group. It is gratifying that many predictions[1,3] have already been confirmed by experimental observations. Unfortunately the known chemistry of lithium is limited in comparison with other second-row elements due to the instability of lithium

compounds. However, this instability is somewhat offset by the stabilization gained by dimer and tetramer formation.[8] Although covalent bonding plays an identifiable role, electrostatic attractions seem to predominate. In calculations[2] in which all lithiums are replaced by a point charge, relative energies are still reproduced.

Results and Discussion

Efforts to date have been largely directed toward determining the most stable structure of a lithium compound given a particular formula.[1-12] The purpose of the present work is to investigate a displacement reaction which has recently[13] been observed for lithium amide complexes.

This reaction, which is shown in eq 1a, occurs rapidly at −15 °C despite the fact that a nucleophilic carbon appears to be reacting with a nucleophilic nitrogen. In order to rationalize the

(1) Schleyer, P. v. R. *Pure Appl. Chem.* **1984**, *56*, 151.
(2) Schleyer, P. v. R.; Kos, A. J.; Kaufmann, E. *J. Am. Chem. Soc.* **1983**, *105*, 7617.
(3) Schleyer, P. v. R. *Pure Appl. Chem.* **1983**, *55*, 355.
(4) Schleyer, P. v. R. In "New Horizons of Quantum Chemistry"; Lowdin, P.-O, Pullman, B., Eds.; Reidel: Dordrecht, 1983; pp 95–109.
(5) Chadrasekhar, J.; Pople, J. A.; Seeger, R.; Seeger, V.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1982**, *104*, 3651. See also ref 3 in this paper.
(6) Hodoscek, M.; Solmajor, T. *J. Am. Chem. Soc.* **1984**, *106*, 1854.
(7) Kaufmann, E.; Clark, T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1984**, *106*, 1856.
(8) Sapse, A.; Kaufmann, E.; Schleyer, P. v. R.; Gleiter, R. *Inorg. Chem.* **1984**, *23*, 1569.
(9) Del Bene, J. E.; Frisch, M. J.; Raghavachari, K.; Pople, J. A.; Schleyer, P. v. R. *J. Phys. Chem.* **1983**, *87*, 73.
(10) Clark, T.; Schleyer, P. v. R.; Houk, K. N.; Rondan, N. G. *J. Chem. Soc., Chem. Commun.* **1981**, 579.
(11) Bachrach, S. M.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 2283.
(12) Waterman, K. C.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 3138.

$$RLi + LiN\overset{OR''}{\underset{R'}{}} \rightleftharpoons R\overset{Li}{\underset{Li}{}}N\overset{OR''}{\underset{R'}{}} \longrightarrow \overset{Li}{\underset{RNR'}{}} + LiOR'' \quad (1)$$

   1   2   3

(a) $R = n\text{-}C_4H_9$, $R' = CHCH_3C_6H_5$, $R'' = CH_3$
(b) $R = CH_3$, $R' = CH_3$, $R'' = CH_3$
(c) $R = CH_3$, $R' = H$, $R'' = H$

facility of this reaction, an initial complex, 3, has been proposed.[13]

(13) Beak, P.; A.; Kokko, B. *J. Am. Chem. Soc.* **1984**, *106*, 1511.

Table I. 3-21G (MNDO) Energies of Complexation (kcal/mol)[a,b]

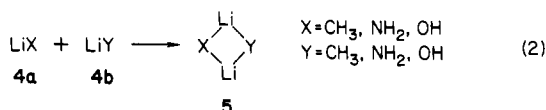|	LiCH$_3$	LiNH$_2$	LiOH
LiCH$_3$	46.2[c] (72.2)	65.4 (66.9)	66.9 (63.6)
LiNH$_2$	64.8 (67.4)	83.4[c] (62.7)	84.4 (59.3)
LiOH	64.4 (63.5)	83.0 (58.7)	82.5[c] (54.7)

[a] The entries on the diagonal refer to 3-21G (MNDO) dimerization energies of the simple monomers. The entries in the upper triangle refer to calculated 3-21G (MNDO) complexation energies, while the entries in the lower triangle refer to the average of the appropriate calculated dimerization energies of the simple monomers. [b] Energies of complexation refer to the negative of the reaction enthalpy of the reaction monomer$_1$ + monomer$_2$ → complex. [c] Reference 7.

In this investigation MNDO (eq 1b,c) and ab initio methods (eq 1c) have been used to evaluate the stability of this initial complex and to explore the energetics of its rearrangement to products.
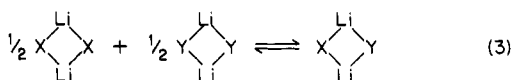
The MNDO[14a] parameters for lithium[14b] have been extensively tested,[1-5] and generally the method gives results consistent with sophisticated ab initio calculations.

As a preliminary step in studying the reaction, MNDO and ab initio methods were used to study the complexation energies of the simple monomers **4a** and **4b**. Complexation energy is defined as minus the enthalpy change in eq 2.

The 3-21G and 3-21+G basis sets, which have been shown[1-12] to be adequate for lithium-containing compounds, were used for all ab initio calculations. The 3-21+G basis is formed by adding to the 3-21G basis a set of diffuse s and p functions on second-row atoms. The diffuse functions are necessary to describe anions

$$\text{LiX} + \text{LiY} \longrightarrow \underset{\underset{5}{\text{Li}}}{X\diamondsuit Y} \qquad \begin{array}{l} X = CH_3, NH_2, OH \\ Y = CH_3, NH_2, OH \end{array} \qquad (2)$$

$$\underset{4a}{} \qquad \underset{4b}{}$$

and greatly reduce basis set superposition errors in ionic compounds such as ethyllithium.[11] All geometries were optimized within the appropriate point group by using the GAUSSIAN 82 program package.[15] The results shown in Table I indicate that MNDO substantially overestimates the stability of the dimers formed between two organolithiums. It has been noted previously[3] that MNDO predicts carbon–lithium bonds to be too stable by approximately 30 kcal/mol. Another interesting conclusion from the MNDO and ab initio results is that the complexation of mixed monomers to a close approximation is the average of the simple dimers, which implies that eq 3 should be nearly thermoneutral.
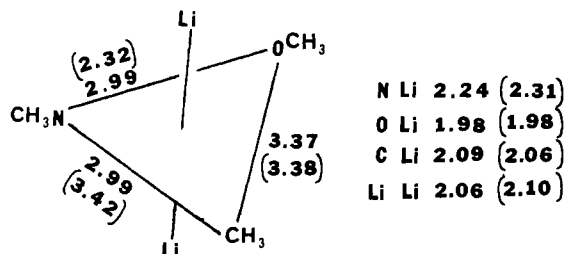
$$\frac{1}{2}\underset{Li}{\overset{Li}{X\diamondsuit X}} + \frac{1}{2}\underset{Li}{\overset{Li}{Y\diamondsuit Y}} \rightleftharpoons \underset{Li}{\overset{Li}{X\diamondsuit Y}} \qquad (3)$$

The complexation energies in Table I are larger than typical solvation energies, and such species would be expected[1,3] to remain complexed in solution phase. The complexation energy in solution, however, may be less, which would allow the equilibrium indicated in eq 3 to take place. Also, if the system contained initially only dimers, entropy would favor complexes of mixed monomers. Furthermore, it is assumed that rearrangement occurs by complete dissociation and recombination. The reaction could proceed by a displacement mechanism for which the barrier might be lower.

Since MNDO seems to predict complexation stabilities adequately, it was used to model the reaction of eq 1b where R = R′ = R″ = CH$_3$ and eq 1c where R = CH$_3$, R′ = R″ = H. Calculations based on eq 1c were performed to compare with ab

(14) (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899. (b) Lithium parameterization: Thiel, W.; Clark, T., unpublished results.

(15) References to basis sets used are collected here. The program package GAUSSIAN 82 was used throughout. Carnegie-Mellon University: Binkley, J. S.; Frisch, M.; Raghavachari, K.; Fluder, E.; Seeger, R.; Pople, J. A.; 3-21G basis: Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939. 3-21+G basis: Clark, T.; Chandrasekhar, J.; Spitznagel, G.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294. 6-31G* basis: Hariharan, P. C.; Pople, J. A. *Theoret. Chim. Acta* **1973**, *28*, 213. Gordon, M. S. *Chem. Phys. Lett.* **1980**, *76*, 163. Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *J. Chem. Phys.* **1977**, *77*, 3654.

Table II. Comparison of Dimerization and Complexation Energies (kcal/mol) in the Reaction $\frac{1}{2}(\text{LiR′NOR″})_2 + \frac{1}{2}(\text{CH}_3\text{Li})_2 \rightarrow$ CH$_3$Li:LiR′NOR″

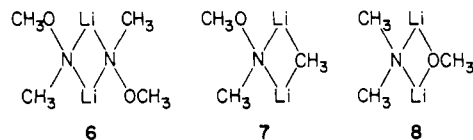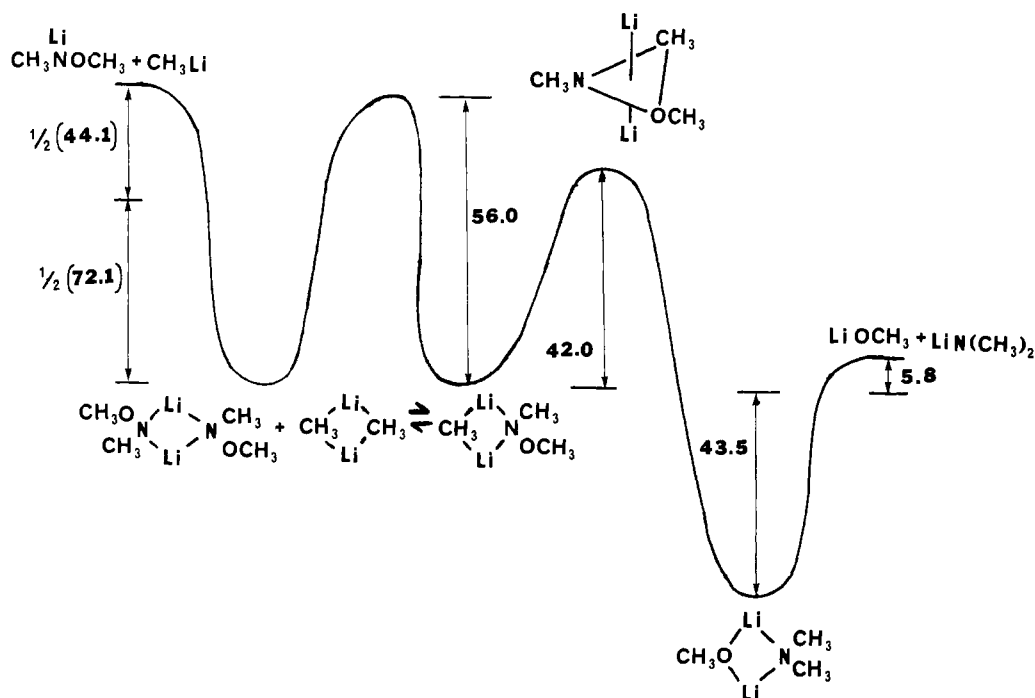|	dimerization energy		complexation energy for CH$_3$Li: LiR′NOR″	heat of reaction for $\frac{1}{2}A_2 + \frac{1}{2}B_2 \rightarrow AB$
	LiR′NOR″	CH$_3$Li		
eq 1b (R′ = R″ = CH$_3$)	44.1	72.2	56.7	1.4
eq 1c (R′ = R″ = H)	48.7	72.2	59.5	0.9

Figure 1. MNDO transition state interconverting **7** and **8** for eq 1b (values for eq 1c are given in parentheses). Mulliken charges by MNDO for eq 1b are as follows: 2Li, 0.66e; NCH$_3$, 0.17e; CH$_3$, –0.35e; OCH$_3$, –0.48e. Charges by MNDO for eq 1c are as follows: 2Li, 0.64e; NH, 0.14e; CH$_3$, –0.37e; OH; –0.41e.

initio results below. The reaction represented in eq 1b is more similar to the actual experimental system (eq 1a) and will be specifically discussed below. The results for eq 1c will follow in parentheses.

The dimerization of LiCH$_3$NOCH$_3$ to form **6** was calculated to be exothermic by 44.1 kcal/mol while the complex **7** was stabilized by 56.7 kcal/mol relative to monomers. Using the

dimerization energy of CH$_3$Li (see Table I), it is seen from Table II that the formation of the complex from dimers is endothermic by 1.4 kcal/mol (see Table II for a comparison involving dimers in eq 1c). If the activation energy for complexation is reduced sufficiently in solution, it is expected that an equilibrium amount of the complex of mixed monomers will be present.

If complex **7** rearranges to complex **8**, followed by decomplexation of **8**, the observed displacement reaction has occurred. MNDO calculations (Tables III and IV) predict that complex **8** is 43.5 kcal/mol (eq 1c; 39.7 kcal/mol) more stable than **7** and represents the MNDO global minimum. Since **7** contains two lithium–carbon bonds which are known to be predicted too stable, the energy separation between complexes must be considered as a lower limit. If a barrier can be found which interconverts the complex **7** and **8**, it will represent the reaction barrier. MNDO calculations indicate that there is no simple reaction coordinate to convert **7** to **8**. If the transannular C–N distance of **7** is reduced, there is no corresponding lengthening of the N–O distance, and likewise if the O–C distance in **7** is increased, there is no decrease of the C–N distance. However, if the C–N distance is decreased *and* the C–O distance is increased, the transition state, shown in Figure 1, resembling a trigonal bipyramid of equatorial N–R, –CH$_3$, and –OCH$_3$ with two axial lithium cations is reached (see Mulliken charges in Figure 1). The transition state was approximated by a two-dimensional search by using the breaking N–O and forming C–N distances and refined by reducing the sum of the squares of all gradients to a small value. The calculated force field yielded one negative frequency (ignoring small imaginary frequencies due to methyl torsions), confirming the transition state. The calculated barrier was 42.0 kcal/mol (eq 1c, 68.9 kcal/mol).

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Table III. Heats of Formation (kcal/mol) for Reactions 1b and 1c Using MNDO and Absolute Energies (−hartrees) for Reaction 1c Using 3-21G and 3-21+G Basis Sets

method and reaction	reactant monomers	reactant complex 7	transition state	product complex 8	product monomers
MNDO eq 1b	−1.4/−11.2[a]	−69.3	−27.4	−112.8	−58.9/−4.6[b]
MNDO eq 1c	−1.4/9.1[c]	−70.0	−1.1	−109.7	−54.6/−0.2[d]
3-21G//3-21G eq 1c	46.752 48[e]	183.948 80	183.859 58	184.082 96	82.453 25[f]
	137.109 21				101.500 01
3-21+G//3-21G eq 1c	46.758 16[e]	183.974 03	183.899 80	184.114 85	82.489 79[f]
	137.141 05				101.517 43
3-21+G//3-21+G eq 1c	46.758 19[e]	183.975 08	183.920 65	184.115 87	82.491 25[f]
	137.142 49				101.517 75

[a] Heat of formation for CH_3Li and $CH_3LiNOCH_3$, respectively. [b] Heat of formation for $LiOCH_3$ and CH_3LiNCH_3, respectively. [c] Heat of formation of CH_3Li and $HLiNOH_3$, respectively. [e] Energy of CH_3Li and $HLiNOH$, respectively. [f] Energy of $LiOH$ and $HLiNCH_3$, respectively.

Table IV. Relative Energies (kcal/mol) for Reactions 1b and 1c Using MNDO and for Reaction 1c Using 3-21G and 3-21+G Basis Sets

| method and reaction	reactant monomers	reactant complex 7	transition state	product complex 8	product monomers
MNDO eq 1b	56.7	0	42.0	−43.5	5.8
MNDO eq 1c	56.4	0	68.9	−39.7	15.2
3-21G//3-21G eq 1c	54.7	0	56.0	−84.2	−2.8
3-i1+G//3-21G eq 1c	46.9	0	46.6	−88.4	−20.8
3-21+G//3-21+G eq 1c	46.7	0	34.2	−88.3	−21.3

Figure 2. MNDO potential energy surface for the interconversion of 7 to 8, indicating the barrier heights and complexation energies (kcal/mol) along with the structure of intermediates and transition states.

A comment is in order for enthalpy of activation for the parallel reaction, equation 1c, which, in contrast to previous comparisons, is considerably different from the case R = R′ = R″ = CH_3 (eq 1b). The lower barrier for eq 1b is due primarily to the difference in electron-donating ability of a methyl group compared to a hydrogen. The former donates electrons to the nitrogen, reducing the positive charge[6] and increasing the electrostatic attraction between the nitrene and the two positively charged lithiums. The distances between nitrogen and oxygen or carbon in the equatorial plane are larger, and therefore those interactions will be less important.

From Figure 1 it can be seen that the distances in the equatorial plane are between 2.99 and 3.37 Å and the Li–Li distance is 2.06 Å. Finally, the product complex 8 is 49.3 kcal/mol (eq 1c; 54.9 kcal/mol) more stable than product monomers, $LiOCH_3$ + $LiN(CH_3)_2$. When the O–N distance in 8 was used as the reaction coordinate, MNDO revealed no reverse barrier in going from the complex to monomers. Figure 2 illustrates the MNDO potential surface for eq 1b. The magnitude of the first barrier, which

represents the interconversion of the initial dimers to the reactant complex, could be reduced by solution effects or a mechanism which does not require complete dissociation, allowing the indicated equilibrium to take place. The second barrier is not believed to be reversible due to the much greater stability of the product complex 8. The rate-determining step would then depend upon which barriers were greater after solvation effects.

An ab initio study would be desirable to test the reliability of MNDO. Accordingly the reaction shown in eq 4 was studied at the 3-21G and 3-21+G levels. The results generally parallel the

$$\text{(4)}$$
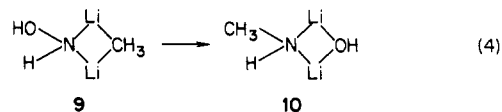
MNDO results (Tables III and IV) and give additional support to the mechanism proposed. In agreement with MNDO, ab initio results using the 3-21G and 3-21+G basis sets predict that lithium forms a more stable complex with nitrogen and oxygen than with
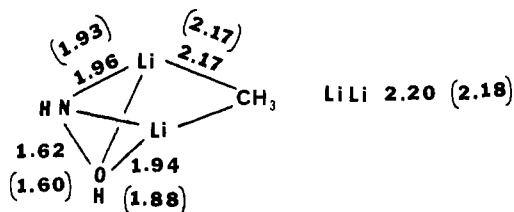
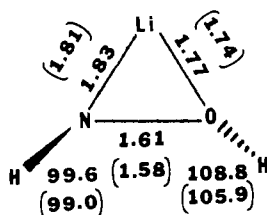**Figure 3.** 3-21+G (3-21G) geometry of 9. Note the short oxygen lithium distances.

Figure 4. 3-21+G (3-21G) geometry of LiHNOH monomer.

nitrogen and carbon. An interesting result which was not apparent in the MNDO calculations is the geometry[17] of complex 9 (see Figure 3). The HNOH group has rotated, allowing the oxygen of the hydroxyl group to come within complexing range of the lithiums, resulting in a N–O distance of 1.62 Å and an O–Li distance of 1.94 Å. An increase of the N–O bond and the decrease of the N–C bond will then produce the trigonal bipyramid transition state. It might be reasoned that complex 9, which has an additional mechanism for stabilization, might have a significantly larger stabilization energy compared to monomers. However, the oxygen in the monomer LiHNOH can also complex[18] with lithium as seen in Figure 4. In fact the stabilization of 9 compared to monomers (3-21G, 54.7 kcal/mol; Table IV) is actually less than the complex stabilization of $H_2LiN + CH_3Li \rightarrow H_2NLi:CH_3Li$ (3-21G, 65.4 kcal/mol).

The product complex 10 is stabilized by 81.4 kcal/mol (84.2–2.8 kcal/mol, Table IV) relative to monomers at the 3-21G level. This compares with 84.4 kcal/mol (3-21G, Table I) stabilization for the complex formed between $LiNH_2 + LiOH$. Neither the monomer nor the complex exhibit significant complexation of the methyl group with lithium, presumably because the stabilization due to carbon complexation does not compensate for rehybridization and angle strain necessary in the methyl group.

The 3-21+G basis yields smaller complexation energies for reactant monomers going to the reactant complex 9 (3-21G, 54.7 kcal/mol; 3-21+G, 46.7 kcal/mol) and for the product monomers going to the product complex 10 (3-21G, 81.4 kcal/mol; 3-21+G; 67.6 kcal/mol) but yields a similar difference between the reactant and product complexes (3-21G, 84.2 kcal/mol; 3-21+G, 88.3 kcal/mol). Thus, the 3-21+G basis reduces the barrier between the monomers and complex, which reduces the role that solvation effects would have to play in order to establish a rapid equilibrium
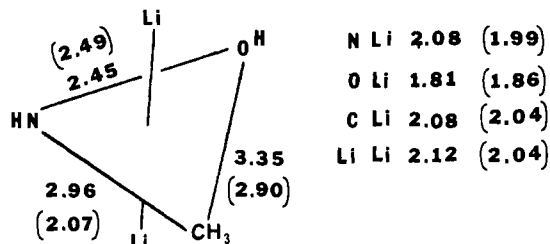

Figure 5. 3-21+G geometry for the transition state interconverting 9 and 10 (approximate 3-21G geometric parameters are indicated in parentheses). Mulliken charges by 3-21+G are as follows: 2Li, 1.18e; NH, 0.08e; CH_3, -0.63e; OH, -0.63e while charge by 3-21G are as follows: 2Li, 0.98e; NH, 0.07e; CH_3, -0.59e; OH, -0.46e.
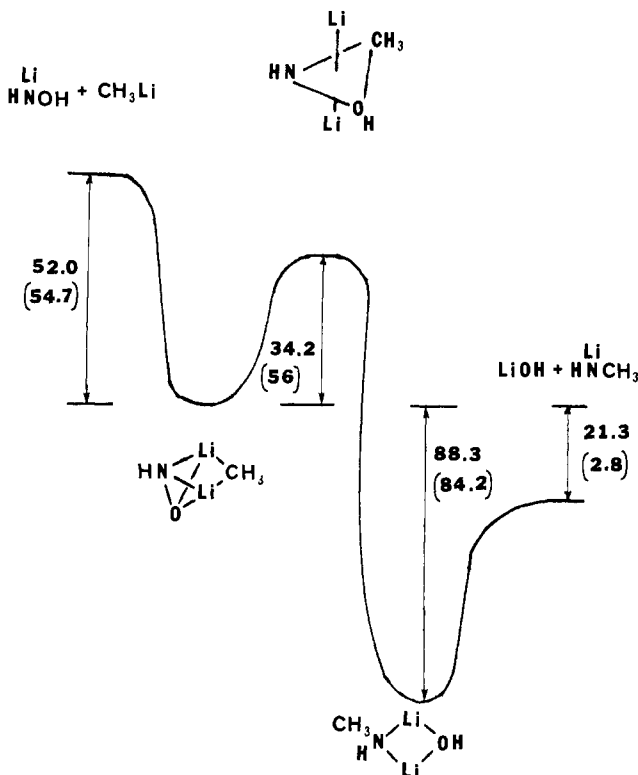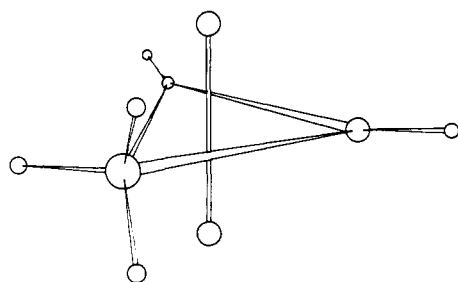

Figure 6. 3-21+G potential energy surface for the interconversion of 9 to 10.

between dimers and the reactant complex.

The search for a trigonal bipyramid transition state relating the reactant and product complexes was carried out by constructing a search direction based on the negative eigenvalue obtained from diagonalizing the approximate force constant matrix.[19] However, for the 3-21G basis in the region of the transition state, severe energy convergence problems were encountered and the transition state was not completely optimized. It is likely that the SCF is oscillating between different possible solutions due to the restrictive nature of the 3-21G basis. The unrefined transition state is probably within several kilocalories/mole of the optimal geometry (see Figure 5 for approximate geometrical parameters). When the 3-21+G basis was used, the transition state was located without difficulty. Presumably the diffuse functions allow charge to accumulate on the methyl and hydroxyl groups and avoid large oscillations in the SCF. The single calculated negative mode ($476i$ cm^{-1}) confirms the transition state, and the associated eigenvector corresponds to a motion which would interconvert reactants and products. Without zero-point correction, a barrier of 34.2 kcal/mol is predicted. The reaction profile is shown in Figure 6, and its similarity to the MNDO reaction profile (Figure 2) is immediately apparent. Once the

(16) The charge on nitrogen in eq 1b is -0.01e, and in eq 1c the charge is +0.09.

(17) Three optimizations were carried out for the CH₃Li:HNLiOH complex by using the 3-21G basis. In two optimizations C_s symmetry was maintained with the unique methyl hydrogen pointed toward the nitrogen or oxygen. The third optimization maintained only C_1 symmetry in which the methyl group tilts toward one of the lithiums. At the 3-21G level, the lowest energy was obtained from the conformation in which the unique methyl hydrogen pointed to the oxygen followed by the C_1 conformation and the C_s conformation in which the unique hydrogen pointed to the nitrogen, 0.04 kcal/mol and 0.05 kcal/mol higher, respectively. When the 3-21+G basis and optimizing geometries are used, the C_1 conformation is predicted to be more stable than the C_s conformation with the unique methyl hydrogen pointed toward the oxygen but by less than 0.01 kcal/mol. The structure in Figure 3 is for the more stable C_s structure at both the 3-21G and 3-21+G levels.

(18) The monomer HNLiOH is isoelectronic with CH₂LiOH and Li-(OH)₂⁺ which have been studied computationally.[9,10] The most stable structure of Li(OH)₂⁺ is found[9] to be a lithium-bridged complex with both hydrogens out of the lithium–oxygen plane. A similar structure is found for the monomer HNLiOH which is 6.0 kcal/mol lower in energy than the planar structure at the 3-21G level. The HNOH dihedral angle is 92.1° at the 3-21+G level and 107.8° at the 3-21G level.

(19) Schlegel, H. B. *J. Comput. Chem.* **1982**, *3*, 214.

TRANSITION STATE

Figure 7. Plot of the 3-21+G transition state. The nitrene is furthest away from the viewer, while the methyl group is to the left and the hydroxyl group to the right. Two lithiums cap the trigonal bipyramid.
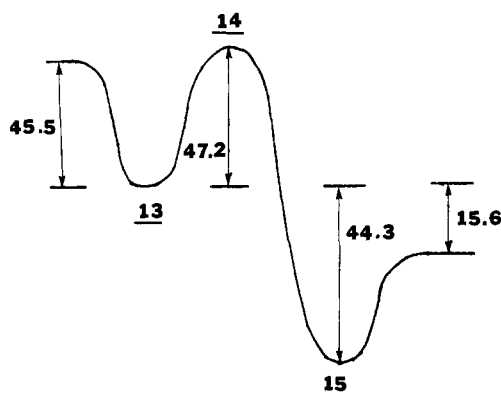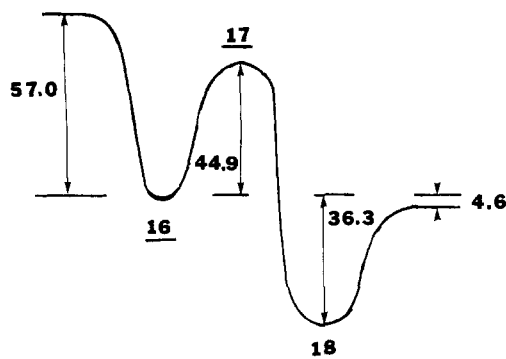

Figure 8. MNDO potential energy surface for the intramolecular conversion of **13** to **15**.

Figure 9. MNDO potential energy surface for the Intermolecular conversion of **16** to **18**.

Table V. Heats of Formation (kcal/mol) by MNDO for the Species Involved in the Intramolecular (**13–15**) and Intermolecular (**16–18**) Displacement Reactions

molecular species	intramolecular displacement	molecular species	intermolecular displacement
reactant monomer[a]	10.4	reactant monomers[b]	14.3/−11.2
13	−33.4	16	57.0
14	13.3	17	−12.1
15	−78.2	18	−93.3
product monomer[c]	−49.2	product monomers[d]	−58.9/−2.7

[a] The reactant monomer was chosen to be CH$_3$LiNOCH$_2$CH=CH-Li in the all-trans conformation in which no complexing interactions were possible. [b] The first heat of formation is for LiCH=CH$_2$ and the second is for CH$_3$NLiOCH$_3$. [c] The product monomer was chosen to be CH$_3$LiNCH=CHCH$_2$OLi in the all-trans conformation in which no complexing interactions were possible. [d] The first heat of formation is for LiOCH$_3$ and the second is for CH$_3$NLiCH=CH$_2$.

reactant complex has passed over the barrier to the product complex, the species is trapped by the greater thermodynamic stability of the product complex. Treating with water would then lead to the observed amine.

A word is in order concerning the relative stability of the reactant and product complexes. At the 3-21G level, the LiN-H$_2$:LiOH complex has a complexation energy of 84.4 kcal/mol (Table I) compared to 81.4 kcal/mol for the product complex (**10**). In comparison the CH$_3$Li:LiNH$_2$ complexation energy is significantly greater than the complexation energy for the reactant complex **9** (81.4 kcal/mol for CH$_3$Li:LiNH$_2$ compared to 54.7 kcal/mol for reactant complex at the 3-21G level). The monomer LiNH$_2$ does not have a comparable mode of stabilization as is possible for the monomer HNLiOH (Figure 4), and hence formation of the complex LiCH$_3$:LiNH$_2$ is more exothermic than the formation of the reactant complex LiCH$_3$:HNLiOH. Thus, the driving force for the reaction can be thought of as the formation of a more stable complex as well as the formation of stronger bonds in the product monomers than in the reactant monomers (a Li–C and N–O bond is replaced by a Li–O and N–C bond).

The barrier predicted by using the 3-21+G basis (34.2 kcal/mol) is much lower than the barrier predicted by using the 3-21G basis. Part of the difference could be due to that fact that the 3-21G transition state was not completely refined. However, when the 3-21+G basis is used with geometries determined at the 3-21G level, the barrier (46.6 kcal/mol, Table IV) is still significantly lower than the 3-21G barrier (56 kcal/mol). With the exception of the transition state, relative energies at the 3-21+G level are almost identical whether using 3-21+G geometries or 3-21G geometries (last two rows of Table IV).

Considering the sensitivity of the reaction barrier to substituents (MNDO, eq 1b, c) and basis set effects (eq 1c, 3-21+G and 3-21G), it should be pointed out the barrier for the experimentally studied reaction (eq 1a) might be much lower than the barrier predicted here for model compounds. A plot of the trigonal bipyramid transition state is shown in Figure 7.
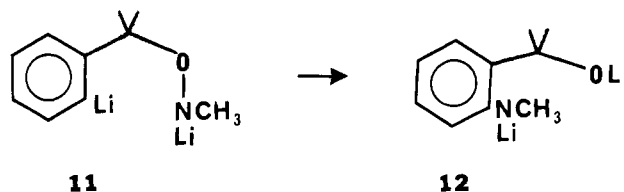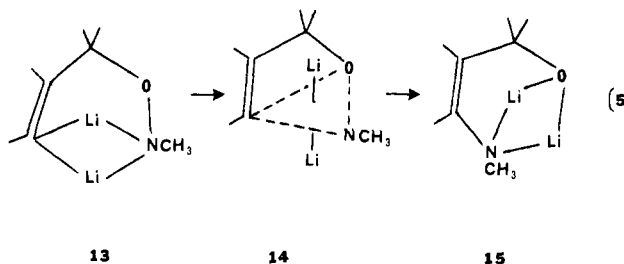
Beak, Basha, and Kokko[13] (BBK) have found in an elegant experiment that **11** undergoes an intermolecular reaction to **12** rather than an intramolecular reaction. When the interpretation


developed here is used, two mechanisms can be written: eq 5 for

the intramolecular addition and eq 6 for the intermolecular addition using **13** and **15** to represent the reactant complex of **11** and the product complex of **12** respectively.

The rearrangement from the reactant complex to the product complex can occur in two steps in eq 6 where each section can go through a separate transition state to the more stable reaction complex independently.

In order to study the difference in the two possible mechanisms, MNDO calculations were performed on a model system in which the phenyl groups of **11** and **12** are replaced by a double bond (see **13–15**). The intermolecular mechanism was modeled by replacing two C–C bonds with C–H bonds and thereby isolating

$$R:H \quad R':CH_3 \qquad\qquad R:H \quad R':CH_3 \qquad (6)$$

16   **17**   **18**
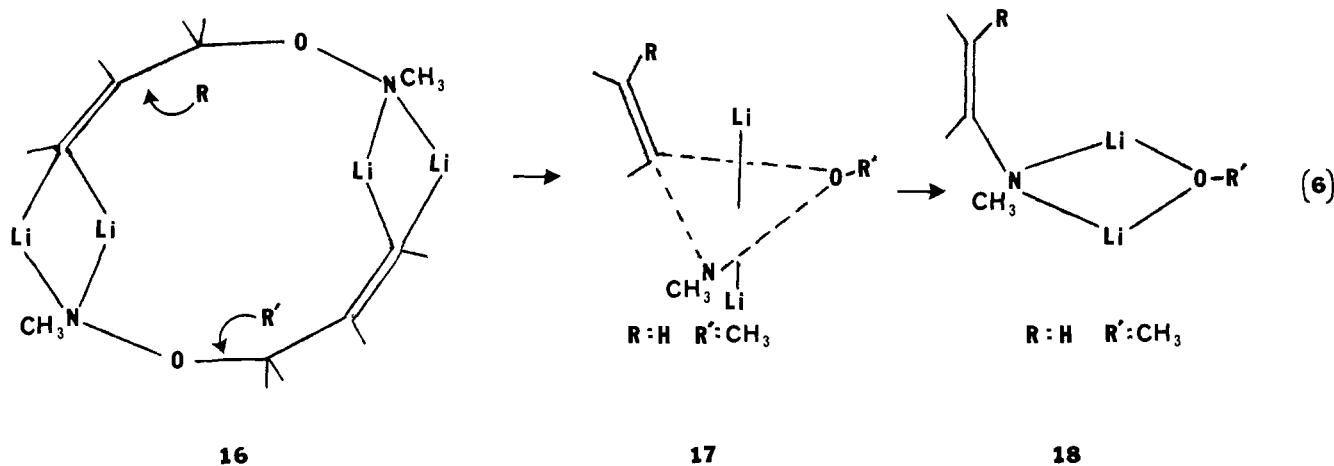
one of the reaction centers of the complex (**16–18**).

Figures 8 and 9 are potential energy diagrams for the intramolecular and intermolecular additions, respectively. The significant difference between the two mechanisms is the stability of the reactant complex. The intramolecular complex **13** is constrained by a bicyclic system which destabilizes the complex by 11.5 kcal/mol (Table V) relative to the intermolecular model, **16–18**. The transition state relating the reactant and product complexes of the intramolecular mechanism is located 47.2 kcal/mol higher than the reactant complex. The barrier for the MNDO model of the intermolecular process was 44.9 kcal/mol (Table V), which is similar to the barrier calculated for eq 1b (43.9 kcal/mol) and the barrier calculated for the intramolecular mechanism (47.2 kcal/mol). It is seen that the energy of the

N Li	2.25/ 2.23
O Li	2.08/ 2.10
C Li	2.02/ 2.02
Li Li	2.02

Figure 10. MNDO geometries for the intramolecular addition potential energy surface: (a) reactant complex, (b) transition state, (c) product complex.

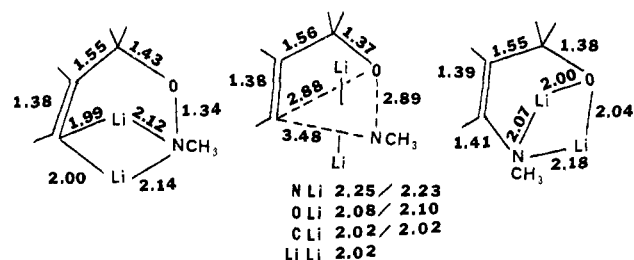| N Li | 2.40/2.31 |
O Li	1.97/1.99
C Li	2.05/2.05
Li Li	2.07

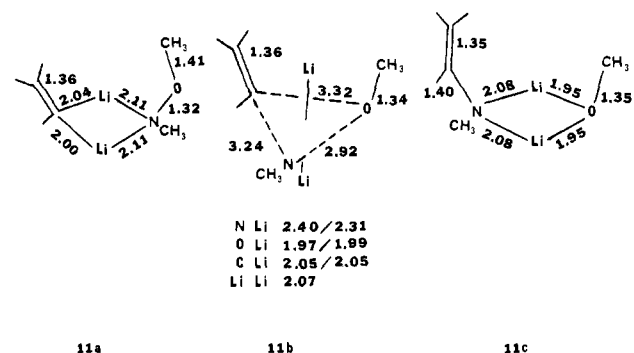**11a**   **11b**   **11c**

Figure 11. MNDO geometries for the intramolecular potential energy surface: (a) reactant complex, (b) transition state, (c) product complex.

transition state (**17**) is lower than the energy of the monomers (Figure 9) in contrast to the energy of the intramolecular transition state (Figure 8 and Table V).

The MNDO results suggest that after solvation effects, a sufficiently large barrier remains in the intramolecular case to make reaction by this route negligible. The reactant complex, transition state, and product complex of the intramolecular model are presented in Figure 10, where those for the intermolecular model are presented in Figure 11.

Conclusion

MNDO and ab initio calculations support the suggestion by BBK that the reaction proceeds through a lithium complex as **7** and provide a very plausible reaction mechanism for the amination of alkoxylamines. The propensity for lithium to form bridges is clearly seen as the transition state contains two lithiums capping $^-OCH_3$, $^-CH_3$, and NCH_3 in a bipyramidal arrangement. The MNDO barrier is 42.0 kcal/mol for eq 1b and 68.9 kcal/mol for eq 1c. The 3-21+G barrier for eq 1c is 34.2 kcal/mol, which is much lower that the barrier predicted by MNDO for the same reactions.

The reaction **11 → 12** which was observed by BBK to go through an intermolecular process is rationalized on the basis of a smaller dimerization energy of the reactant complex for intramolecular reaction. In an equilibrium situation, the concentration of the intramolecular complex will be much less than the concentration of the intermolecular complex which is more stable, and hence reaction by the former pathway is less likely. It is suggested that mechanistic consequences based on this mechanism be explored.

Note Added in Proof. G. Boche and H. Wagner in a recent paper[20] used MNDO to study the reactant complex **3** in the amination reaction eq 1c.

(20) Boche, G.; Wagner, H. *J. Chem. Soc., Chem. Commun.* **1984**, 1591.