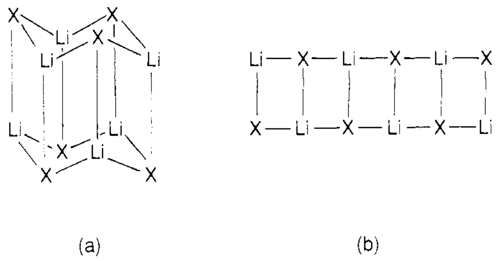

Figure 3. Ring-stacked (a) and laddered (b) structures possible for species $(\mathrm{LiX})_6$.

A second fundamental difference, overlooked by RSJ, is in the way the orientation of the substituents R influences the structures of amides $[\mathrm{LiNR_2}]_n$ and imides $[\mathrm{LiN{=}CR_2}]_n$ for *steric* reasons alone. Simple ring structures for such compounds are found only when further association of the rings is prevented either by coordinative saturation of the metal atoms by additional Lewis bases or by the bulk of the substituents R.[5] These substituents project above and below the $(\mathrm{LiN})_n$ plane in amides $[\mathrm{LiNR_2}]_n$, but lie in the ring plane in imides $[\mathrm{LiN{=}CR_2}]_n$ (Figure 2) and in many organic lithium compounds in general. Thus, the steric requirements of R substituents will inhibit vertical ring stacking (clustering) for amides, but will allow lateral association of rings to give $(\mathrm{LiN})_n$ ladders[6] (or "fences"[7]), provided the substituents are not *too* bulky (Figure 3b). The same steric factors have the reverse effect in the case of imides and many other organic lithium compounds, inhibiting laddering but allowing stacking[2,4,8] (Figure 3a). Since, for finite oligomers, stacking provides a more effective way of raising the coordination numbers of the metal and nitrogen atoms than does laddering (stacking just two rings raises the coordination number of *all* the metal and nitrogen atoms), a stacked structure is expected to be preferred to a laddered structure where, *and only where*, substituent bulk factors permit stacking.

It is not surprising that RSJ find their optimized stacked structure of two $(\mathrm{LiN})_3$ rings to be preferred to a $(\mathrm{LiN})_6$ planar cyclic structure for $[\mathrm{LiNH_2}]_6$, as the planar ring would have very large ring angles; a switch in preference from a ring to a clustered structure had already been predicted for $(\mathrm{LiH})_n$ oligomers when n was increased from 4 or 5 to 6.[7] A similar switch is indicated for the amides, with a ring preferred for $[\mathrm{LiNH_2}]_4$,[6,9] and a cluster (stacked rings) for $[\mathrm{LiNH_2}]_6$.[1] Unfortunately, the RSJ report made detailed comparisons only between the ring and cluster structures, and "preliminary results" on alternative structures, including a ladder, were mentioned only briefly, with an indication that these were intermediate in energy. While we do not dispute the validity of these calculations for $[\mathrm{LiNH_2}]_6$ itself, for practically realizable systems $[\mathrm{LiNRR'}]_n$ with R, R′ ≠ H, steric factors will prevent clustering and will favor structures based on (LiN) rings, with possible lateral association (laddering) of these rings under favorable circumstances to give higher oligomers or polymers.

Reputable theoretical calculations notwithstanding, we stress that amidolithium compounds of *experimentally known* structures contain such $(\mathrm{LiN})_n$ rings and ladders; there are *no* known examples of amidolithium clusters (stacked rings) $[\mathrm{LiNRR'}]_n$ for *any* value of n.

Registry No. LiOH, 1310-65-2; $\mathrm{LiNH_2}$, 7782-89-0; LiF, 7789-24-4.

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Structures of $\mathrm{LiNH_2}$ Hexamers: Reply to Comments by Clegg, Snaith, and Wade

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In a recent paper,[1] we reported the results of ab initio calculations on the hexamer of $\mathrm{LiNH_2}$ and concluded that a distorted octahedral (D_{3d}) structure (**1**) was considerbly more stable than a planar hexagonal (D_{6h}) ring structure (**2**) (Figure 1). We had also compared the Li–N bond lengths in our optimized geometry for **1** with the corresponding values found in a substituted *iminolithium* ($\mathrm{LiN{=}CR_2}$) hexamer.[2,3] This comparison was performed since no amidolithium ($\mathrm{LiNR_2}$) hexamers were known experimentally. Nevertheless, the calculated Li–N bond lengths of 1.99, 1.99, and 2.06 Å were found to be in remarkable agreement with the experimental values of 1.98, 2.01, and 2.05 Å. We also suggested that the asymmetry between the two "short" bond lengths in the experiment "is probably due to crystal packing effects". Clegg, Snaith, and Wade[4] (CSW) have now suggested that the comparison of the geometry of an amidolithium cluster with that of an iminolithium cluster is inappropriate since they have different hybridizations at nitrogen. They have also concluded that the asymmetry seen in the experiments[2,3] is genuine and is not due to crystal packing effects.

The detailed discussions by CSW regarding the relative orientations of amidolithium and iminolithium hexamers are based on covalent bonding ideas whereas the *dominant* term that governs the nature of the bonding in these compounds is due to the electrostatic interactions.[5,6] For example, natural population analysis[7] with the 6-31G* basis set[8] indicates that the Li–N bond has 90% ionic character in $\mathrm{LiNH_2}$. While the ionic terms alone are not sufficient to explain *all* aspects of the bonding in these molecules,[5] they are still the principal driving force and other factors such as covalent contributions are of lesser importance. In this context, the charge separations that govern the dominant electrostatic interactions may be expected to be similar in amidolithium and iminolithium compounds. Thus the comparison of the geometries of *similar forms* of amidolithium and iminolithium clusters is entirely appropriate.

Theoretical calculations on smaller oligomers of $\mathrm{LiNH_2}$ and $\mathrm{LiN{=}CH_2}$ confirm these ideas. The Li–N bond lengths in the monomer, dimer, and trimer of $\mathrm{LiNH_2}$ calculated with the 6-31G basis set[9] have values of 1.744, 1.936, and 1.934 Å, respectively. The corresponding bond lengths calculated by CSW and associates[3] in the monomer, dimer, and trimer of $\mathrm{LiN{=}CH_2}$ are *very similar*, having values of 1.720, 1.919, and 1.924 Å, respectively. Thus it is not at all surprising that the Li–N bond lengths in the two hexamers as mentioned earlier are also similar. Though the presence of substituents may affect some of the geometrical parameters involved, the overall agreement is excellent. The slight asymmetry seen in the experimental bond lengths[2,3] does not detract from any of our conclusions.

We performed a complete vibrational analysis[10] on **1** with the STO-3G basis set[11] to see if there is any such asymmetry in the case of the hexamer of $\mathrm{LiNH_2}$. The high-symmetry D_{3d} form of **1** as we had calculated previously was found to be a local minimum and is thus not subject to any such distortion. We intend to

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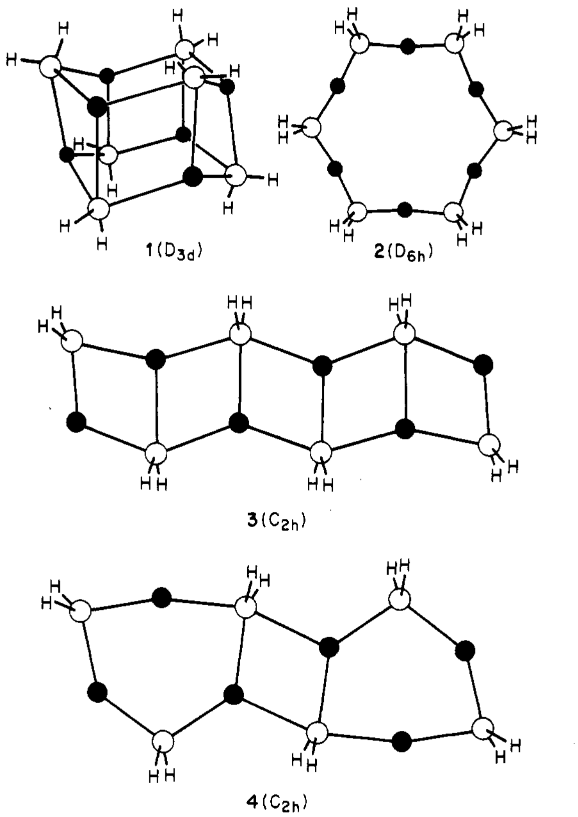

1(D_{3d})

2(D_{6h})

3(C_{2h})

4(C_{2h})

Figure 1. Structures considered in this study. Dark circles represent Li and open circles represent N. The Li–N frameworks in the figures have been computer generated and are true to scale based on the optimized 3-21G geometries.

perform similar calculations on the hexamer of LiN=CH$_2$ to investigate this aspect further.

CSW have now suggested that a 3-dimensional cluster structure such as **1** is unlikely to be the ground state of substituted amide hexamers and that they "will favor structures based on (LiN) rings, with possible lateral association of these rings". In our previous work, we had reported only preliminary investigations of such structures. Since then, we have finished more accurate calculations on such structures which show convincingly that **1** is significantly more stable than such structures, at least in the case of (LiNH$_2$)$_6$.

We now report the results on two such structures based on lateral association of planar (LiN)$_n$ rings, viz. (i) a ladder[12] or "fence"[13] structure **3** with C_{2h} symmetry which is a lateral association of cyclic dimers[14] and (ii) a structure **4**, also with C_{2h} symmetry, consisting of two cyclic trimers[14] associated laterally. Since **1** can be considered as a 3-dimensional association of two trimers, the 2-dimensional association as in **4** illustrates an important contrast. The geometries of both **3** and **4** were completely optimized with the valence-double ζ 3-21G basis set.[15] In addition, 6-31G calculations,[9] which have been previously shown to be reliable for the prediction of relative energies of LiNH$_2$ clusters,[1,5] were performed. Though both **3** and **4** are slightly more stable than the D_{6h} form **2**, they are *significantly less stable* than the D_{3d} cluster structure **1**, lying 15 and 18 kcal/mol higher in energy, respectively, at the 6-31G level. On the basis of our previous experience[1,5] with (LiNH$_2$)$_4$ and (LiNH$_2$)$_6$, we estimate that the uncertainity in the calculated relative energies is less than 5 kcal/mol.

CSW have also stated that steric reasons will prevent the formation of structures such as **1** in the case of substituted amides. Though we have not yet performed any calculations on substituted amides, inspection of the geometry of **1** indicates that the orientation of the hydrogens is such that there may not be large steric effects if the hydrogens are replaced by alkyl groups. In any case, 3-dimensional cluster structures are known experimentally[16] even in cases such as [LiSi(CH$_3$)$_3$]$_6$, which have even larger steric effects. Further calculations on the hexamers of substituted amides may be necessary to resolve this matter further.

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Registry No. LiNH$_2$, 7782-89-0.

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Proton NMR Studies of Paramagnetic Polypyridyl μ-Oxo Complexes of Ruthenium(III) and Their Diamagnetic Ruthenium(II) Precursors

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The use of nuclear magnetic resonance spectral techniques as a structural probe for diamagnetic (dπ)^6 polypyridyl complexes has been extensive.[1] As the synthetic chemistry of these complexes has evolved, important structural and dynamic problems have arisen involving oxidation states with unpaired spins. X-ray crystallographic and, in some instances, EPR methods have been utilized successfully for the determination of solid-phase molecular and electronic structures, but questions of stereochemistry, fluxional behavior, or substitution dynamics in solution remain to be addressed through the application of paramagnetic NMR techniques.[2]

High-valent oxo complexes of Ru have proven to be efficient stoichiometric and/or catalytic oxidants in a series of organic and

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