binding to these amine oxidases invariably produces inhibition.[23,25] It is therefore possible that inactivation is associated with irreversible binding.

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Oligomeric Iminolithium and Amidolithium Compounds: Comments on Previously Reported Theoretical Calculations and Experimentally Determined Structures

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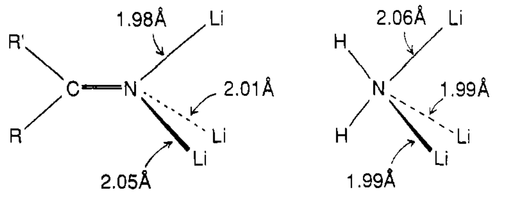
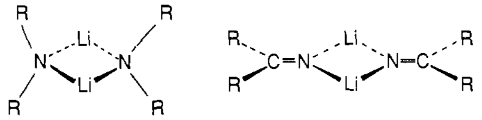
In a recent article,[1] Raghavachari, Sapse, and Jain (henceforth RSJ) described ab initio calculations for prediction of the structures and energies of the hexamers of LiF, LiOH, and $LiNH_2$, and concluded that in all three cases, a D_{3d} clustered structure based on a distorted Li_6 octahedron is significantly more stable than a D_{6h} planar hexagonal ring structure. Contrary to statements by RSJ, our own experimental results,[2] by X-ray crystallography, for the structures of some hexameric iminolithium compounds $[LiN{=}CRR']_6$ (R = Ph, R' = *t*-Bu; R = Ph, R' = NMe_2) do *not* provide direct support for their predictions. The RSJ discussion overlooks features of imides $[LiN{=}CRR']_n$ and amides $[LiNRR']_n$ that are quite different and can be demonstrated from experimentally observed structures of both classes of compounds.

First, the interpretation of our structural results on the iminolithium compounds $[LiN{=}CRR']_6$ by RSJ is incorrect and is at variance with our own already published interpretations. The RSJ calculations for $[LiNH_2]_6$ indicate two "short" Li-N bonds at 1.99 Å and one "long" bond at 2.06 Å for each triply bridging nitrogen atom.[1] The iminolithiums display average lengths of 1.98, 2.01, and 2.05 Å for the Li-N bonds.[2] The "slight asymmetry seen between the two short bonds" is attributed by RSJ to crystal packing effects. This difference is, however, genuine: the short-medium-long pattern of three Li-N bonds is observed for *every* bridging nitrogen in *both* of the molecular structures reported by us[2] (one of them with two crystallographically independent molecules in different environments) and in a previously determined iminolithium hexamer;[3] i.e. this pattern is observed, *without exception*, for no fewer than 24 NLi_3 units. The pattern is too regular to be caused by low-symmetry crystal packing, which in any case is different for each of the structures.



(a) (b)

Figure 1. Orientations of (a) the imido groups N=CRR' and (b) the amide groups NH_2 with respect to the bridged triangles of metal atoms in (a) experimentally observed $[LiN{=}CRR']_6$ and (b) calculated $[LiNH_2]_6$.



(a) (b)

Figure 2. Different positions of substituents R in cyclic lithium amides $[LiNR_2]_n$ (a) and lithium imides $[LiN{=}CR_2]_n$ (b) as typified by dimers, $n = 2$.

What the short-medium-long pattern does clearly reflect, *in every case*, is the orientation of the imino unit N=CRR' with respect to the Li_3 triangle it bridges (Figure 1a).[4] Invariably, the short Li-N contact lies in, or nearest to, the N=CRR' skeletal plane (the plane in which an anion $[N{=}CRR']^-$, with an sp^2-hybridized nitrogen atom, would have lone-pair electron density), while the medium and long Li-N bonding contacts involve pairs of metal atoms that straddle this plane. Their lengths thus reflect differences in electron density between the metal and nitrogen atoms. The Li^+ metal ions are closest to N in those directions where the lone-pair electron density is greatest. Although the bonding in these systems is highly polar, indeed largely ionic, one can effectively rationalize the *differences* in their metal-nitrogen distances in terms of two- and three-center bonding interactions—a short, two-center LiN bond to the metal atom in the N=CRR' skeletal plane, and an unsymmetrical three-center Li_2N bond to the pair of metal atoms straddling that plane. The short-medium-long pattern of Li-N distances experimentally observed for the iminolithium hexamers is thus intimately bound up with the ligand skeletal plane orientation and is an intrinsic geometrical feature of the molecule and not a consequence of its crystalline environment. Although we have only recently discussed this in detail,[4] the main points of our argument were made quite clear in the preliminary report[2] misinterpreted by RSJ.[1] In the RSJ calculations for $[LiNH_2]_6$, the amido groups NH_2 (which are not isolobal with imino groups N=CRR') have an orientation that is consistent with two strong short bonding NLi contacts to two of the three neighboring atoms, the third lying in a direction apparently more suited to a longer three-center NHLi interaction than to involvement of nitrogen lone-pair electron density (Figure 1b). The equivalence of the two shorter Li-N distances is a reflection of the orientation of the NH_2 plane relative to the Li_3 triangle. This is one fundamental difference between RSJ's $[LiNH_2]_6$ geometry and the experimentally observed geometry for the $[LiN{=}CRR']_6$ structures.

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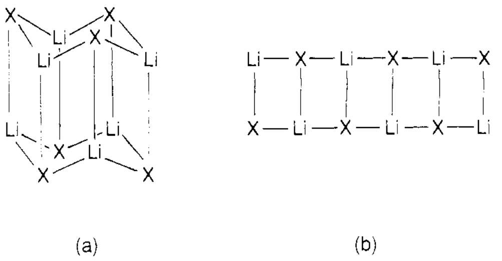

Figure 3. Ring-stacked (a) and laddered (b) structures possible for species $(\text{LiX})_6$.

A second fundamental difference, overlooked by RSJ, is in the way the orientation of the substituents R influences the structures of amides $[\text{LiNR}_2]_n$ and imides $[\text{LiN}{=}\text{CR}_2]_n$ 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 $(\text{LiN})_n$ plane in amides $[\text{LiNR}_2]_n$, but lie in the ring plane in imides $[\text{LiN}{=}\text{CR}_2]_n$ (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 $(\text{LiN})_n$ 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 $(\text{LiN})_3$ rings to be preferred to a $(\text{LiN})_6$ planar cyclic structure for $[\text{LiNH}_2]_6$, 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 $(\text{LiH})_n$ 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 $[\text{LiNH}_2]_4$,[6,9] and a cluster (stacked rings) for $[\text{LiNH}_2]_6$.[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 $[\text{LiNH}_2]_6$ itself, for practically realizable systems $[\text{LiNRR}']_n$ with R, R′ $\neq$ 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 $(\text{LiN})_n$ rings and ladders; there are *no* known examples of amidolithium clusters (stacked rings) $[\text{LiNRR}']_n$ for *any* value of n.

Registry No. LiOH, 1310-65-2; LiNH_2, 7782-89-0; LiF, 7789-24-4.

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Structures of 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 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* ($\text{LiN}{=}\text{CR}_2$) hexamer.[2,3] This comparison was performed since no amidolithium (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 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 LiNH_2 and $\text{LiN}{=}\text{CH}_2$ confirm these ideas. The Li–N bond lengths in the monomer, dimer, and trimer of 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 $\text{LiN}{=}\text{CH}_2$ 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 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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