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Why Are Monomeric Lithium Amides Planar?

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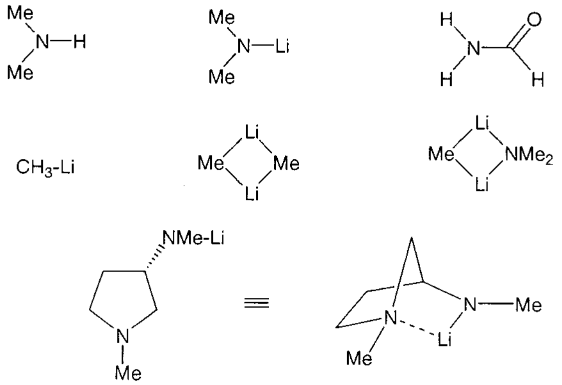
Introduction

Organic chemistry relies, for such fundamental transformations as the creation of a carbon−carbon bond or the abstraction of a moderately acidic proton, on organolithium compounds. Among those, lithium amides probably constitute the most widely used class of bases, and their chiral version has had a major impact on asymmetric synthesis.[1] Understanding the structure, aggregation, and reactivity of these key reagents is therefore the object of sustained efforts, from both experimental[2] and theoretical[2c,3] points of view. One of the striking features of these species is their flat structure, which generally characterizes sp^2 nitrogens and amide-type conjugation, while the well-known pyramidal topology of amines, associated with the sp^3 hybridization of the nitrogen atom, would be expected. This planarity has been first established on theoretical grounds,[4,5] because only in a few cases,[5] such as the $LiN(SiMe_3)_2$/12-crown-4 complex, could monomers be characterized by X-ray crystallography. Simultaneous with our work, millimeter/submillimeter spectroscopy results have given the first experimental evidences in favor of this planarity for the isolated H_2NLi monomer.[6] On the contrary, the large body of spectroscopical data[3c,7] available for aggregates involving lithium amides presents a more or less tetrahedral arrangement of the substituents around the nitrogen. The origin of this discrepancy, possibly important to the understanding of the mechanism of asymmetric induction by chiral lithium amides, has been the object of scarce investigations to our knowledge.[4b,c] We present here our findings on the spatial arrangement of the electronic domains in these molecules, as it emerges from the electron localization function (ELF).[8]

Chart 1. Model Mononomers and Dimers Considered in This Work



Results and Discussion

Chemists' intuitive vision of bonding in molecules implicitly assumes a partition of space into adjacent regions corresponding to chemically meaningful entities such as atomic cores, bonds, and lone pairs. The aim of the topological approach to the chemical bond is the determination of such regions and of their boundaries with the help of rigorous mathematical tools. The theory of dynamical systems is certainly one of the best to reach this goal because it is a generalization and a formalization of the techniques used in geography to determine river basins and watersheds. It usually requires the knowledge of a scalar function of the space coordinates; each of its local maximum is associated with a region of space called a basin. In the case of chemical bonding, the information carried by the local values of the function should be closely related to the pairing of electrons, a cornerstone in all bonding theories. As electrons are half-integer spin particles (fermions), two electrons with

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(1) (a) Duhamel, L.; Plaquevent, J. C. *Tetrahedron Lett.* **1980**, *21*, 2521. (b) Whitesell, J. K.; Felman, S. W. *J. Org. Chem.* **1980**, *45*, 755. Reviews: (c) Cox, P. J.; Simpkins, N. S. *Tetrahedron: Asymmetry* **1991**, *2*, 1−26. (d) O'Brien, P. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1439−1457. (e) O'Brien, P. *J. Chem. Soc., Perkin Trans. 1* **2001**, 95−113.

(2) Inter alia: (a) Rutherford, J. L.; Collum, D. B. *J. Am. Chem. Soc.* **2001**, *123*, 199−202. (b) Hilmersson, G.; Malmros, B. *Chem.—Eur. J.* **2001**, *7*, 337−341. (c) Hilmersson, G. *Chem.—Eur. J.* **2000**, *6*, 3069−3075. (d) Arvidsson, P. I.; Davidsson, Ö *Angew. Chem., Int. Ed.* **2000**, *39*, 1467−1470. (e) van Vliet, G. L. J.; Luitjes, H.; Schakel, M.; Klumpp, G. W. *Angew. Chem., Int. Ed.* **2000**, *39*, 1643−1645. (f) Corruble, A.; Valnot, J.-Y.; Maddaluno, J.; Prigent, Y.; Davoust, D.; Duhamel, P. *J. Am. Chem. Soc.* **1997**, *119*, 10042−10048. (g) Lucht, B. L.; Collum, D. B. *J. Am. Chem. Soc.* **1996**, *118*, 3529−3530. (h) Hilmerson, G.; Ahlberg, P.; Davidsson, Ö. *J. Am. Chem. Soc.* **1996**, *118*, 3539−3540.

(3) (a) Hayes, J. M.; Greer, J. C.; Mair, F. S. *New. J. Chem.* **2001**, *25*, 262−267. (b) Fressigné, C.; Maddaluno, J.; Marquez, A.; Giessner-Prettre, C. *J. Org. Chem.* **2000**, *65*, 8899−8907. (c) Hæffner, F.; Sun, C.; Williard, P. G. *J. Am. Chem. Soc.* **2000**, *122*, 12542−12546. (d) Henderson, K. W.; Dorigo, A. E.; Liu, Q.-Y.; Williard, P. G. *J. Am. Chem. Soc.* **1997**, *119*, 11855−11863. (e) Sapse, A.-M.; Raghavachari, K.; Schleyer, P. v. R.; Kaufmann, E. *J. Am. Chem. Soc.* **1985**, *107*, 6483−6486.

(4) (a) Viruela-Martin, P.; Viruela-Martin, R.; Tomas, F.; Nudelman, N. S. *J. Am. Chem. Soc.* **1994**, *116*, 10110−10116. (b) McKee, M. L. *J. Am. Chem. Soc.* **1985**, *107*, 7284−7290. (c) Würthwein, E. U.; Sen, K. D.; Pople, J. A.; Schleyer, P. von R. *Inorg. Chem.* **1983**, *22*, 496−503. (d) Dill, J. D.; Schleyer, P. von R.; Binkley, J. S.; Pople, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 6159−6173.

(5) Gregory, K.; Schleyer, P. von R.; Snaith, R. *Adv. Inorg. Chem.* **1991**, *37*, 47−151.

(6) Grotjahn, D. B.; Sheridan, P. M.; Al Jihad, I.; Ziurys, L. M. *J. Am. Chem. Soc.* **2001**, *123*, 5489−5494.

(7) Inter alia: (a) van Vliet, G. L. J.; de Kanter, F. J. J.; Schakel, M.; Klumpp, G. W.; Spek, A. L.; Lutz, M. *Chem.—Eur. J.* **1999**, *5*, 1091−1094. (b) Rutherford, J. L.; Collum, D. B. *J. Am. Chem. Soc.* **1999**, *121*, 10198−10202. (c) Mulvey, R. E. *Chem. Soc. Rev.* **1998**, *27*, 339−346. (d) Clegg, W.; Edwards, A. J. F.; Mair, S.; Nolan, P. M. *Chem. Commun.* **1998**, 23−24. (e) Hilmersson, G.; Arvidsson, P. I.; Davidsson, Ö.; Håkansson, M. *J. Am. Chem. Soc.* **1998**, *120*, 8143−8149. (f) Witte-Habel, H.; Klingebiel, U.; Noltemeyer, M. *Chem. Commun.* **1997**, 771−772.

(8) (a) Silvi, B.; Savin, A. *Nature* **1994**, *371*, 683−686. (b) Savin, A.; Silvi, B.; Colonna, F. *Can. J. Chem.* **1996**, *74*, 1088−1096. For a review, see: (c) Savin, A.; Nesper, R.; Wengert, S.; Fässler, T. F. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1808−1832.

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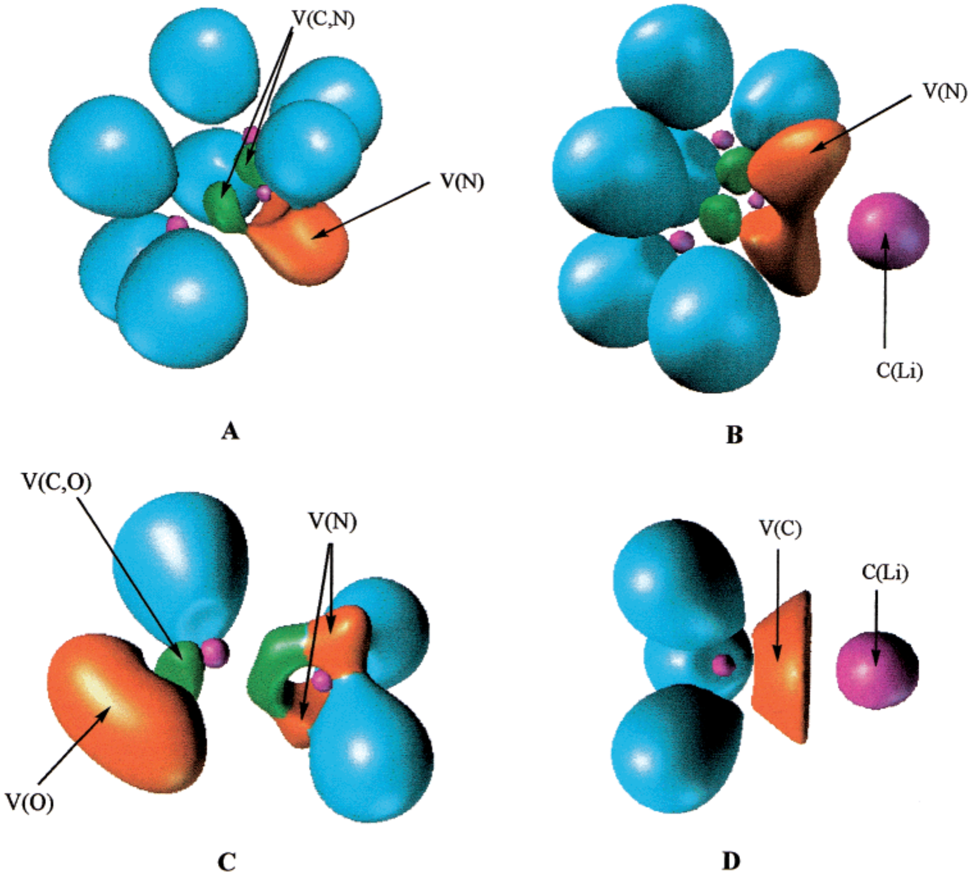

Figure 1. Localization domains (η = 0.8) for Me_2NH (A), Me_2NLi (B), $HCONH_2$ (C), and MeLi (D). Color code is as follows: magenta = core, orange-brown = valence monosynaptic, green = valence disynaptic, blue = hydrogen.

identical spins tend to avoid one another more strongly than two antiparallel spin electrons. This effective Pauli repulsion adds to the simple electron–electron electrostatic interaction. The pairing amount of electrons of the same spin that a reference electron is able to form within an elementary volume around its position and containing a given arbitrary small charge is a good measurement of the local fermionic behavior. Becke and Edgecombe's ELF[9] is derived from this measure of pairing and is confined within the [0,1] interval. It tends to 1 where parallel spins are highly improbable (for example, inside a lone pair or a bond region), whereas it is close to 0 near the boundaries of the electronic domains where parallel spin electrons are compelled to come close one another. The ELF topological analysis[8] provides a partition of the molecular space in basins, which is consistent with the assumptions of Lewis theory. There are accordingly core and valence basins labeled C(A) and V(A,B,...), respectively, with A and B being the atoms concerned. The number of core(s) with which it shares a boundary characterizes each valence basin. This notion of synaptic number[10] introduces a homogeneous nomenclature for the valence basin (monosynaptic, lone pair; disynaptic, two center bond; trisynaptic, three center bond...) that accounts for multicenter bonds in a natural fashion. The ELF basins provide a complementary view to the standard valence one. Instead of counting the atoms coordinated to a given nucleus, one is immersed in the basin of interest and counts the bordering cores. Quantitative information can be further extracted by integrating the electron density over these localization basins. Therefore, we thought that such a population analysis, which implicitly takes into account the superposition of the resonance forms, can provide information on the origin of the planarity of lithium amides and their aggregates.

Calculations on dimethylamine, the monomers and dimers of methyllithium and of lithium dimethylamide, the methyllithium–lithium dimethylamide mixed aggregate, and the 3-*N*-methylamino-*N*-methylpyrrolidine lithium amide (3-MAMP) at their equilibrium geometries[11] (Chart 1) have been carried out using Gaussian98[12] with the 6-31+G** basis set[13] and the Becke3P86 hybrid density functional.[14] Formamide has also been

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[9] Becke, A. D.; Edgecombe, K. E. *J. Chem. Phys.* **1990**, *92*, 5397–5403.

[10] Krokidis, X.; Noury, S.; Silvi, B. *J. Phys. Chem. A* **1997**, *101*, 7277–7282.

[11] Fressigné, C.; Corruble, A.; Valnot, J.-Y.; Maddaluno, J.; Giessner-Prettre, C. *J. Organomet. Chem.* **1997**, *549*, 81–88.

[12] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A5; Gaussian, Inc.: Pittsburgh, PA, 1998.

[13] (a) Frisch, M. J.; Pople, J. A.; Binkley, J. S. *J. Chem. Phys.* **1984**, *80*, 3265–3269. (b) Pople, J. A.; Head-Gordon, M.; Fox, D. J.; Raghavachari, K.; Curtiss, L. A. *J. Chem. Phys.* **1989**, *90*, 5622–5629.

[14] (a) Perdew, J. P. *Phys. Rev.* **1986**, *B33*, 8822–8824. (b) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648–5652.

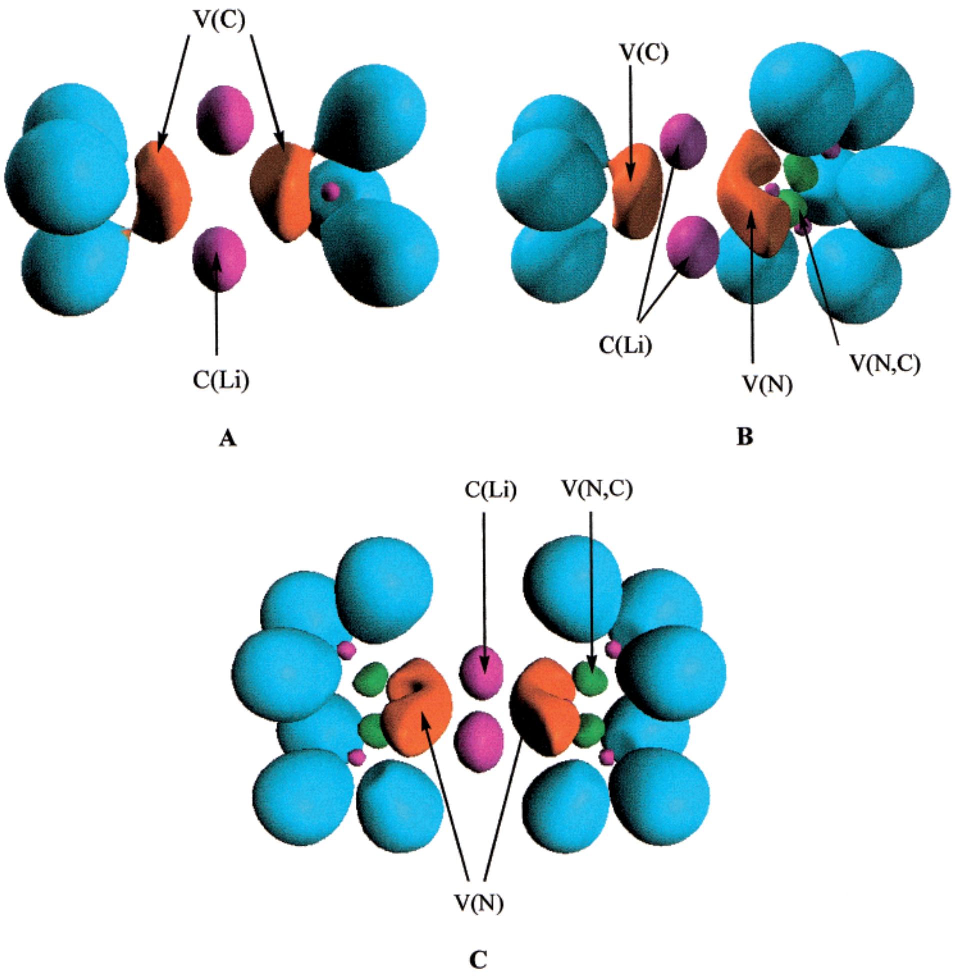

Figure 2. Localization domains ($\eta = 0.8$) for $(MeLi)_2$ (A), $MeLi{-}Me_2NLi$ (B), and Me_2NLi (C).

considered for the sake of comparison with sp^2-hybridized nitrogen situations.

The ELF analysis has been performed with the TopMoD program,[15] and the visualization of the isosurfaces has been performed with the SciAn software.[16]

Figure 1 displays the localization domains of Me_2NH (A), Me_2NLi (B), and $HCONH_2$ (C). The lithiated compound is found to be purely ionic because the Li^+ basin is clearly detached from the remaining part of the molecular system, even at very low ELF values such as $\eta(r_c) = 0.03$ where r_c denotes the atoms-in-molecules (AIM[17]) bond critical point. The dimethylamine molecule and the Me_2N^- moiety in the lithium amide have the same number of valence basins; replacing the amine proton by a lithium decreases the synaptic order of the V(N,H) basin that becomes V(N). The plane defined by the nitrogen and the carbon nuclei is therefore a symmetry plane in the Me_2N^- anion. As the lithium cation forms an ionic bond, its equilibrium position minimizes the Pauli repulsion between the C(Li) and the two V(N) basins, and therefore, both the anion and the lithium amide belong to the C_{2v} point group. In Me_2NH, the V(N) and V(N,H) basin populations are 2.14 and 2.06 e^-, respectively. In Me_2NLi, the population of the nitrogen lone pairs is the average of the two latter values, i.e., 2.09 e^-. The ionic character of the $Me_2N{\cdots}Li$ interaction is testified by the importance of the lithium atomic basin's contribution to the V(N) basins (2.05 e^-). These results show that, in both dimethylamine and lithium dimethylamide, the nitrogen atom has a tetrahedral environment (sp^3) of valence basins, while in formamide, five maxima disposed along a trigonal bipyramid are associated with the sp^2 nitrogen valence basins.[18] The analysis of the bonding in formamide, thoroughly investigated by Chesnut within the same topological approach,[18] shows that the amide group is characterized by the splitting of the nitrogen lone pair into two basins with low populations (0.87 e^- each). Therefore, and as previously highlighted,[5] the term "amide" appears rather awkward and confusing when applied to lithium amides because it suggests that they are more closely related to amides than to amines.

The V(N) population in the lithium amide dimer (Figure 2C) is larger than that of the monomer by 0.04 e^- resulting from a weak transfer from the V(C,N) basins whose populations are 1.62 and 1.58 e^- in the monomer and dimer, respectively. In the dimer, the ELF maxima for the V(N) and C(Li) basins are in the same symmetry plane. The two lithium cations are now directed along

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[15] Noury, S.; Krokidis, X.; Fuster, F.; Silvi, B. *ToPMoD package*; Université Pierre et Marie Curie: Paris, France, 1997. Noury, S.; Krokidis, X.; Fuster, F.; Silvi, B. *Comput. Chem.* **1999**, *23*, 597−604.

[16] Pepke, E.; Murray, J.; Lyons, J.; Hwu, T.-Z. *SciAn*: Supercomputer Computations Research Institute, Florida State University: Tallahassee, Florida, 1993.

[17] Bader, R. F. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: Oxford, U.K., 1994.

[18] Chesnut, D. B. *J. Phys. Chem. A* **2000**, *104*, 7635−7638.

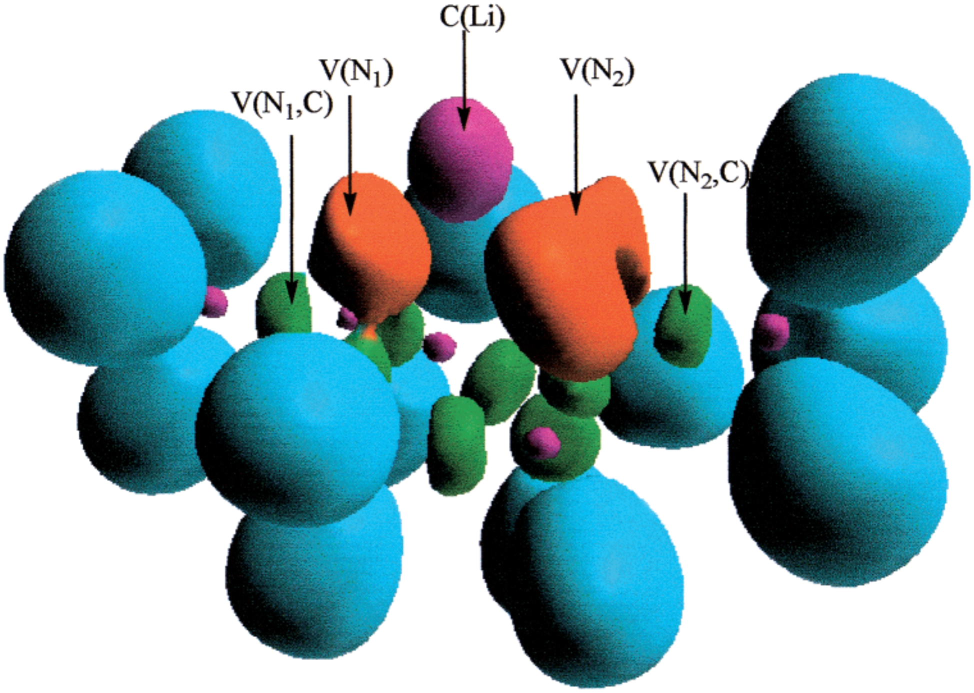

Figure 3. Localization domains ($\eta = 0.8$) for 3-MAMP lithium amide.

the two nitrogen lone pairs, and the angle between the V(N) maxima is open wider with respect to the monomer because of the Pauli repulsion occurring between the lithium cores.

The localization domains of methyllithium are represented in Figure 1D, while its dimer and its complex with lithium dimethyl amide are in Figure 2, panels A and B. According to electronegativity criteria, the LiC bond is expected to be less ionic than the LiN one. Actually, even if the contribution of the Li atomic basin to the V(C) population of MeLi is very small (0.09 out of 2.06 e^-), it is twice as large as the corresponding value in Me_2NLi. The synaptic order (one) of the funnel-shaped V(C) basin is in complete agreement with the dominant ionic character of C−Li.[19] In the methyllithium dimer (Figure 2A), the V(C) populations are increased with respect to their value in the monomer (2.11 versus 2.06 e^-) at the expense of the hydrogens. The mixed aggregate (Figure 2B) exhibits three lone pair basins, one V(C) and two symmetrical V(N) basins. Their populations, 2.11 and 2.15 e^-, are very close to the values calculated for the homodimers. The 3-MAMP lithium amide has finally been considered to determine whether the hybridization pattern could be altered in the case of a chelated chiral compound in which the lithium cation occupies a bridging position between the two nitrogens (Figure 3).[11] The amide nitrogen atom is involved in two CN bonds and therefore has two lone pairs left to interact with the lithium atom. The populations of these two V(N) basins, 2.10 and 2.07 e^-, are close to the values found in the case of Me_2NLi, whereas the lone pair of the tertiary amino group is more populated (2.25 e^-). Thus, the chelation hardly alters the lithium amide planarity and bonding scheme.

In conclusion, the ELF provides an explanation for the planarity of the lithium dimethylamide sp^3 nitrogen; because of the highly ionic character of the N−Li bond,[4c] the nitrogen atom carries two lone pairs located symmetrically with respect to the C−N−C plane on one hand and with respect to the lithium cation on the other. Because it takes into account all of the electrons of the system studied rather than the only frontier orbitals analysis previously applied to this system,[3e,4c,5,20] ELF also gives indications on the origin of the preference for the planar D_{3h} or D_{4h} structure obtained from theory in the cases of the trimer and tetramer of $LiNH_2$.[3d,19] Such arrangements correspond to an optimal location of the lithium atoms with respect to the nitrogen's sp^3 lone pairs. This result suggests that comparable tetrahedral geometrical arrangements are to be found in lithium amide complexes, provided that the steric strains are compatible with such supermolecular structures.

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Supporting Information Available: Optimized Cartesian coordinates and corresponding energies for Me_2NH, Me_2NLi, $HCONH_2$, MeLi, $(Me_2NLi)_2$, $(MeLi)_2$, MeLi−Me_2NLi, and 3-MAMP lithium amide. This material is available free of charge via the Internet at http://acs.pubs.org.

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(19) Kaufmann, E.; Raghavachari, K.; Reed, A. E.; Schleyer, P. von R. *Organometallics* **1988**, *7*, 1597−1607.

(20) Sapse, A.-M.; Kaufmann, E.; Schleyer, P. von R.; Gleiter, R. *Inorg. Chem*. **1984**, *23*, 1569−1574.