

Theoretical Studies of LiF, LiOH, and LiNH<sub>2</sub> TetramersAnne-Marie Sapse,<sup>†</sup> Krishnan Raghavachari,\* Paul von Ragué Schleyer,<sup>‡</sup> and Elmar Kaufmann<sup>‡</sup>

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**Abstract:** The structures and energies of the tetramers of LiF, LiOH, and LiNH<sub>2</sub> have been investigated by means of ab initio molecular orbital calculations including large basis sets and electron correlation corrections. Tetrahedral structures are favored by the tetramers of LiF and LiOH whereas a square-planar structure is found for (LiNH<sub>2</sub>)<sub>4</sub>. The results are consistent with the known experimental observations. The energies of tetramerization are computed to be  $\approx 185$ –190 kcal/mol for LiF and LiOH and about 165 kcal/mol for LiNH<sub>2</sub>. Electrostatic models including lone pair orientation effects are used in the interpretation of the relative stabilities of the isomers.

The pronounced tendency of lithium and other alkali metal compounds to form dimers, tetramers, and higher oligomers has long been appreciated from colligative measurements, NMR investigations, and mass spectrometric observations.<sup>1</sup> The first X-ray crystal structures of organolithium compounds, ethyllithium (1963)<sup>2</sup> and methyllithium (1964),<sup>3</sup> revealed the now familiar tetrahedral arrangements of lithium atoms, with the alkyl groups attached to each face. This essentially cubic arrangement of alternating lithium and more electronegative atoms is now represented by dozens of experimental examples<sup>4</sup> and is exhibited by methylsodium as well.<sup>5</sup> It is perhaps less well-known that organometallic tetramers may also adopt planar, eight-membered-ring arrangements. Examples include coinage metal<sup>6</sup> and some mixed metal derivatives involving lithium.<sup>7,8</sup> More particularly, Lappert et al. have found a planar Li–N framework for the tetramer of Li[NCMe<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CMe<sub>2</sub>].<sup>9</sup> In contrast, another lithium–nitrogen derivative, the tetramer of LiN=C(C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>, favors a cubic arrangement in the crystal.<sup>10</sup>

Tetramers of small lithium compounds have been investigated computationally many times before,<sup>11</sup> but definitive results have not been obtained. While most authors have assumed the tetrahedral arrangement for methyllithium tetramer, (CH<sub>3</sub>Li)<sub>4</sub>, found experimentally,<sup>3</sup> a PRDDO study<sup>12</sup> and EHT calculations<sup>8</sup> indicated the eight-membered-ring tetramer to be more stable. However, the available ab initio results<sup>8,13</sup> favor the tetrahedral form. Kato's group investigated (LiH)<sub>4</sub> and found the eight-membered ring to be slightly more stable than the tetrahedral arrangement,<sup>14</sup> but the opposite conclusion was reached earlier by Rupp and Ahlrichs,<sup>15</sup> although the energy difference was not large. They also found (LiF)<sub>4</sub> to prefer a *T<sub>d</sub>* over a *D<sub>4h</sub>* arrangement, but the opposite ordering was indicated for (NaH)<sub>4</sub>, at least at the SCF level. As far as we are aware, there have been no prior theoretical studies of (LiOH)<sub>4</sub> or (LiNH<sub>2</sub>)<sub>4</sub>. The present study thus extends our earlier examinations of the lower aggregates of small lithium compounds<sup>16–18</sup> to these tetramers as well as to (LiF)<sub>4</sub>. Our goal was to establish the relative energies of tetrahedral and planar arrangements. A companion study of (CH<sub>3</sub>Li)<sub>4</sub> is being reported separately.<sup>19</sup>

## Theoretical Methods

The geometries of all the structures involved were determined by complete optimization within the given symmetry constraints using the split-valence 3-21G basis set.<sup>20</sup> This basis set has proved to be reliable in the determination of the structures of a large number of Li compounds.<sup>4</sup> In addition to the tetrahedral and square-planar forms, several lower-symmetry structures were also examined initially, but these were found to be higher in energy. The applicability of the computed geometries was further exam-

ined by optimizing the geometries of (LiF)<sub>4</sub> with the 6-31G basis.<sup>21</sup> Effects of larger basis sets were explored by performing single point computations with the 6-31G+sp+d basis set which augments the 6-31G basis with a set of diffuse sp functions<sup>22</sup> and a set of six d-type functions<sup>23</sup> on F, O, or N. Such addition of diffuse

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**Table I.** Optimized Geometries (Å and deg) and Total Energies (hartrees) of the Tetramers

structure	parameter	tetrahedral ( $T_d$ or $D_{2d}$ )		square planar ( $D_{4h}$ )	
		3-21G	6-31G	3-21G	6-31G
(LiF) <sub>4</sub>	Li-F	1.793	1.823	1.635	1.685
	Li-Li	2.417	2.484	2.956	3.065
	F-F	2.644	2.667	3.077	3.157
	Li-F-Li			129.4	130.9
	F-Li-F			140.6	139.1
	energy	-425.85501	-428.03957	-425.81060	-428.02182
(LiOH) <sub>4</sub>	Li-O	1.854		1.732	
	Li-Li	2.372		2.884	
	O-O	2.832		3.397	
	O-H	0.962		0.964	
	Li-O-Li			112.7	
	O-Li-O			157.3	
	Energy	-330.21474		-330.16070	
(LiNH <sub>2</sub> ) <sub>4</sub>	Li-N	1.962/2.027		1.906	
	Li-Li	2.239/2.426		3.003	
	N-N	3.378/3.063		3.783	
	Li-N-Li			104.0	
	N-Li-N			166.0	
	N-H	1.019		1.019	
	H-N-H	104.4		105.9	
	Energy	-251.09934		-251.11773	

**Table II.** Total Energies (hartrees) and Relative Energies (kcal/mol) Computed with Different Basis Sets Using 3-21G Geometries

structure	symmetry	HF/3-21G	HF/6-31G	MP2/6-31G	MP3/6-31G	HF/6-31G+sp+d
(LiF) <sub>4</sub>	$T_d$	-425.85501	-428.03789	-428.57402	-428.54895	-428.07345
	$D_{4h}$	-425.81060	-428.01716	-428.55224	-428.52638	-428.05975
	$\Delta E^a$	27.9	13.0	13.7	14.2	8.6
(LiOH) <sub>4</sub>	$T_d$	-330.21474	-331.91240	-332.45363	-332.43799	-331.95046
	$D_{4h}$	-330.16070	-331.87305	-332.41372	-332.39716	-331.92466
	$\Delta E^a$	33.9	24.7	25.0	25.6	16.2
(LiNH <sub>2</sub> ) <sub>4</sub>	$D_{2d}$	-251.09934	-252.39517	-252.88984	-252.90201	-252.44684
	$D_{4h}$	-251.11773	-252.41078	-252.90463	-252.91566	-252.46101
	$\Delta E^a$	-11.5	-9.8	-9.3	-8.6	-8.9

<sup>a</sup>Negative sign indicates that the  $D_{4h}$  form is more stable.

**Table III.** Binding Energies of the Tetramers (kcal/mol) at Different Levels of Theory

structure	symmetry	HF/3-21G	HF/6-31G	MP2/6-31G	MP3/6-31G	HF/6-31G+sp+d
(LiF) <sub>4</sub>	$T_d$	275.0	224.8	221.1	224.7	187.8
	$D_{4h}$	247.1	211.8	207.4	210.5	179.2
(LiOH) <sub>4</sub>	$T_d$	252.1	211.8	206.6	210.8	189.8
	$D_{4h}$	218.2	187.1	181.6	185.2	173.6
(LiNH <sub>2</sub> ) <sub>4</sub>	$D_{2d}$	199.9	172.2	172.3	175.1	158.4
	$D_{4h}$	211.5	182.0	181.6	183.7	167.3

functions is usually important in the computation of the binding energies of systems with unshared lone pairs of electrons. Standard exponents<sup>22,23</sup> were used in all basis sets.

Electron correlation effects were included by means of Møller-Plesset perturbation theory<sup>24</sup> at second (MP2)<sup>25</sup> and third (MP3)<sup>26</sup> orders. The MP2 and MP3 calculations were performed with the 6-31G basis set by using the 3-21G optimized geometries.

### Results and Discussion

Table I displays the geometrical parameters of all the structures optimized in this study. Table II lists the total energies obtained at different levels of theory using the 3-21G optimized geometries as well as the energy difference between the planar and the tetrahedral structures of each tetramer at those levels of theory. Table III lists the energies of tetramerization defined as the difference between the energy of the tetramer and the corresponding energy of the separated monomers.

Examination of Tables I and II reveals that the most stable structures at all levels of theory are the  $T_d$  tetramers of LiF and LiOH and  $D_{4h}$  tetramer for LiNH<sub>2</sub>. The planar Li-N framework computed for (LiNH<sub>2</sub>)<sub>4</sub> is consistent with the experimentally

known<sup>9</sup> structure of the tetramer of Li[NCMe<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>CMe<sub>2</sub>]. The computed geometrical parameters, Li-N = 1.91 Å, Li-N-Li = 104°, and N-Li-N = 166°, are very close to the experimental structural parameters of the larger compound<sup>9</sup> (Li-N = 2.00 Å, Li-N-Li = 101.5°, and N-Li-N = 168.5°).

The energy difference between the  $T_d$  and  $D_{4h}$  forms of the isomers (Table II) appears to be basis set dependent in the case of (LiF)<sub>4</sub> and (LiOH)<sub>4</sub>. For example, at the 3-21G level, the  $T_d$  form of (LiF)<sub>4</sub> is more stable than the  $D_{4h}$  form by 27.9 kcal/mol whereas with the larger 6-31G+sp+d basis the energy difference is only 8.6 kcal/mol. A similar but smaller effect is seen in the case of (LiOH)<sub>4</sub>. Part of the reason appears to be the inadequacy of the small 3-21G basis set where the tighter tetrahedral structure benefits considerably due to the basis set superposition error. Such effects are small for (LiNH<sub>2</sub>)<sub>4</sub>, showing that the 3-21G basis is adequate for N.

Electron correlation effects (evaluated with the 6-31G basis) do not influence the relative stability of the isomers significantly. This is not surprising since correlation effects are expected to be small in systems involving high ionic bonding character. In all cases, correlation effects favor the tetrahedral form by a constant value of about 1 kcal/mol. Assuming additivity of such correlation corrections to the 6-31G+sp+d results gives the final estimated energy differences, the  $T_d$  form is more stable for (LiF)<sub>4</sub> and (LiOH)<sub>4</sub> by  $\approx$ 10 and 17 kcal/mol, respectively, and the  $D_{4h}$  form is more stable for (LiNH<sub>2</sub>)<sub>4</sub> by  $\approx$ 8 kcal/mol.

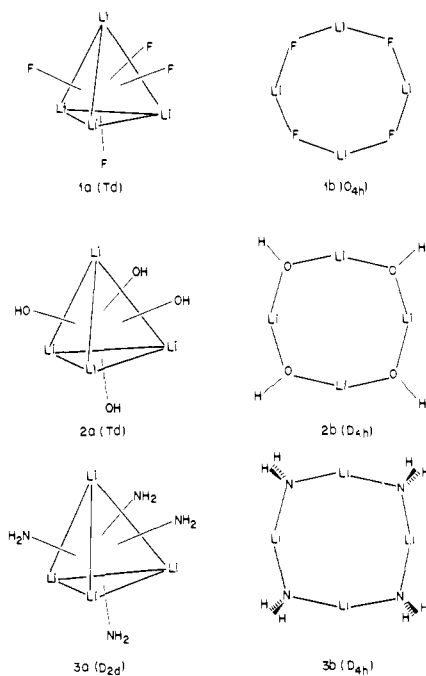
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Chart I



The energies of tetramerization at various levels of theory are listed in Table III. As the basis sets are made larger, the energies of tetramerizations decrease. This is also partly due to the basis set superposition error which yields higher binding energies with smaller basis sets. Previous experience with similar basis sets<sup>16</sup> has shown that the 6-31G+sp+d basis is adequate for such binding energy calculations. The effect of electron correlation on the computed tetramerization energies is small in all cases. The tetramerization energies of LiF and LiOH are about the same ( $\approx 185$ – $190$  kcal/mol) whereas that of LiNH<sub>2</sub> is slightly smaller ( $\approx 165$  kcal/mol). It should be pointed out that zero-point vibrational corrections have not been included in the calculations. Such contributions can be expected to decrease the computed binding energy further.

### Interpretation

Why are tetrahedral arrangements favored for most of the tetramers but not for (LiNH<sub>2</sub>)<sub>4</sub>? What factors control the tetramerization energies? Since lithium compounds have a high degree of ionic character, most of the literature interpretations have favored electrostatic explanations. Streitwieser<sup>27</sup> noted that the C...C and Li...Li distances in the methyl lithium tetramer were not the same (as expected in a cubic arrangement) and provided an electrostatic rationalization. If each lithium is replaced by a point positive charge, and the methyl carbon by a point negative charge, the best electrostatic arrangement is found at a distance ratio of 0.783 (rather than 1.0). Since this was rather close to the experimental ratio (0.73), Streitwieser took this to support his ionic model. However, as can be seen from the summary of our results and those from the literature for other lithium compounds (Table IV), Streitwieser's ideal distance ratio,  $\lambda = 0.783$ , does not correspond to the general findings.

Rupp and Ahlrichs<sup>15</sup> rationalized their results in terms of the electronegativities and the ionic radii of the atoms involved. Pointing out that the geometrical parameters of (LiH)<sub>4</sub> and (LiF)<sub>4</sub> were nearly identical, they attributed the higher oligomerization energy of the latter to the more ionic character of the Li–F bond. The lower tetramerization energy of (NaH)<sub>4</sub> over (LiH)<sub>4</sub> was ascribed quite reasonably to the larger ionic radius of sodium, since the electronegativities of the two alkali metals are about the same. Rupp and Ahlrichs also assumed that the more ionic LiX compounds would favor the tetrahedral over the planar arrangement

Table IV. Comparison of Ratios of Distances in Tetrahedral Tetramers

system	$a,^g \text{ \AA}$	$b,^h \text{ \AA}$	$\lambda = b/a$
idealized electrostatic model <sup>a</sup>			0.783 <sup>a</sup>
(LiH) <sub>4</sub> <sup>b</sup>	2.764	2.607	0.943
(LiH) <sub>4</sub> <sup>c</sup>	2.75	2.49	0.905
(LiCH <sub>3</sub> ) <sub>4</sub> <sup>d</sup>	3.658	2.420	0.622 <sup>e</sup>
(LiNH <sub>2</sub> ) <sub>4</sub> <sup>f</sup>	3.378/3.063	2.239/2.426	0.663/0.792
(LiOH) <sub>4</sub> <sup>f</sup>	2.832	2.372	0.838
(LiF) <sub>4</sub> <sup>c</sup>	2.67	2.50	0.936
(LiF) <sub>4</sub> <sup>f</sup>	2.644	2.417	0.914
(NaH) <sub>4</sub> <sup>c</sup>	3.28	3.10	0.945

<sup>a</sup>Reference 27. <sup>b</sup>Reference 14. <sup>c</sup>Reference 15. <sup>d</sup>Reference 19. <sup>e</sup>Experimental value = 0.73, ref 3. <sup>f</sup>This work. <sup>g</sup> $a$  = anion-anion distance. <sup>h</sup> $b$  = cation-cation distance.

electrostatically. However, our Coulomb's law calculations based on unit positive charges do not support this assumption (see below).

In our earlier work on a series of LiXH<sub>n</sub> dimers (XH<sub>n</sub> = F, OH, NH<sub>2</sub>, CH<sub>3</sub>, BH<sub>2</sub>, BeH, and Li),<sup>17</sup> we showed that there was a clear trend toward increasing dimerization energies with increasing electronegativity of X. Indeed, a simple electrostatic model reproduced the ab initio dimerization energies of most LiXH<sub>n</sub> compounds extremely well. In this model, the ab initio geometries of LiXH<sub>n</sub> and of the corresponding aggregates were employed, Li being replaced by a point positive charge and the X atom by a point negative charge. Only the ab initio results of (LiNH<sub>2</sub>)<sub>2</sub> and (LiOH)<sub>2</sub> deviated from the correlation; this was attributed in the original work to involvement of multicenter lithium bonding, but in a later paper charge orientation effects (e.g., the negative charge in NH<sub>2</sub><sup>-</sup> resides in lone-pair orbitals extending from the nucleus) were invoked as a possible alternative.<sup>18</sup>

Other, more sophisticated analyses of LiXH<sub>n</sub> dimers have been based on other models. Hodošček and Šolmajer,<sup>28</sup> employing Morokuma's energy decomposition scheme, found (especially for the more electronegative groups), that the electrostatic term parallels the overall interaction energies and dominates over polarization, charge-transfer, exchange, and mixing contributions. Gowda and Benson<sup>29</sup> applied modified Rittner and "truncated" Rittner potentials, which model ion-ion, ion-dipole, and dipole-dipole interactions, to the complete set of alkali halide dimers. For (LiF)<sub>2</sub>, the Coulombic term dominated over the polarization, repulsion, and dispersion energy terms. Thus, one is encouraged to examine the application of electrostatic models more widely.

However, such point charge models fail completely to account for the behavior of the tetramers. The tetramerization energies again are calculated by treating Li and the heavy atom of a first row substituent (F, OH, NH<sub>2</sub>, etc.) as point positive and negative charges and employing the 3-21G calculated atom positions in the monomer and in the corresponding tetramer. The tetramerization energies then are the increase in the electrostatic energies on going from four monomers to a tetramer. The calculated tetramerization energies with this model are the following: (LiF)<sub>4</sub> ( $D_{4h} = 233.1$ ;  $T_d = 199.3$  kcal/mol), (LiOH)<sub>4</sub> ( $D_{4h} = 163.7$ ;  $T_d = 158.1$  kcal/mol), and (LiNH<sub>2</sub>)<sub>4</sub> ( $D_{4h} = 143.7$ ;  $D_{2d} = 131.7$  kcal/mol). In all cases, the planar forms ( $D_{4h}$ ) are found to be more stable than the tetrahedral arrangements. This is especially noteworthy in the case of (LiF)<sub>4</sub>, which surely is the system most closely approaching the ionic limit. While the point charge energy for the tetrahedral tetramerization,  $-199.3$  kcal/mol, is not far from the best theoretical value,  $-187.8$  kcal/mol (Table III), the  $D_{4h}$  tetramerization energy is overestimated by 54 kcal/mol by this Coulomb model. The Rupp and Ahlrichs geometries for the (LiF)<sub>4</sub> isomers give somewhat different values ( $D_{4h} = -217.9$ ;  $T_d = -213.2$  kcal/mol), but the planar ring form still is indicated erroneously to be more stable. In addition, the calculated tetramerization energies for both geometrical forms fall off markedly

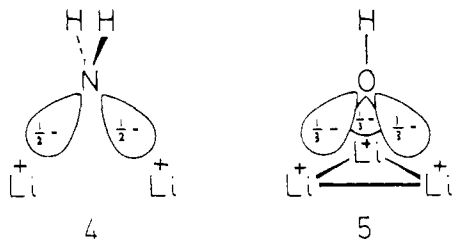
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along the series  $(\text{LiF})_4 > (\text{LiOH})_4 > (\text{LiNH}_2)_4$ , contrary to the results of the full ab initio calculations. The tetramerization energy of LiF is overestimated, but that of  $\text{LiNH}_2$  is underestimated on the electrostatic basis.

Our companion study of  $(\text{LiNH}_2)_2$  and  $(\text{LiNH}_2)_3$  emphasized the importance of lone-pair orientation effects.<sup>18</sup> In both cases (as in the  $D_{4h}$   $(\text{LiNH}_2)_4$  tetramer), the perpendicular orientation of the  $\text{NH}_2$  groups is preferred greatly over conformations in which all atoms lie in the same plane. In these perpendicular orientations, the negative charge, considered in a localized model as residing in  $\text{sp}^3$ -hybridized orbitals, is not centered on nitrogen but extends toward the lithium cations as depicted in **4**.



This orientation also favors the planar over the tetrahedral tetramer. If electrostatic models are employed where half-negative charges extend as in **4** from the nitrogen nucleus (e.g., by 0.6 Å), the planar model is stabilized much more than the tetrahedral (actually  $D_{2d}$ ) form. In the latter, the two nitrogen lone-pair lobes cannot point at all three  $\text{Li}^+$ s on a tetrahedron face simultaneously.

The opposite is true in the  $(\text{LiOH})_4$  tetramers. Here, the localized model of  $\text{HO}^-$  has the three  $\text{sp}^3$ -hybridized lone pairs oriented roughly tetrahedrally. Such arrangements, which should model the total electron density accurately, allow each lobe to point at a lithium cation on a tetrahedral face, **5**. In contrast, these lobes do not engage the lithium cations optimally in the planar,  $D_{4h}$  tetramer. If  $\text{F}^-$  is considered to undergo a similar charge polarization when interacting with lithium cations, the tetrahedron (with three  $\text{Li-F}$  interactions) would be preferred over the planar arrangement, which has only two such interactions.

The progressive change in the calculated  $\text{Li-X-Li}$  angles in the planar,  $D_{4h}$  isomers also is indicative:  $\angle \text{Li-F-Li} = 129.4^\circ$  in **1b**,  $\angle \text{Li-O-Li} = 112.7^\circ$  in **2b**,  $\angle \text{Li-N-Li} = 104.0^\circ$  in **3b**, and  $\angle \text{Li-C-Li} = 81.0^\circ$  in planar methyl lithium tetramer ( $C_{4h}$ ).<sup>19</sup>

The nature of these "interactions",<sup>4</sup> assumed to be ionic in the above discussion, may also have multicenter covalent character, involving molecular orbitals over several centers which cannot be localized. While the bonding is primarily electrostatic, the electrons in multicenter orbitals are shared to some extent among all the atoms involved. Significant  $\text{LiX}$  overlap would be present in such cases. The net result, however, would be the same:  $T_d$   $(\text{LiF})_4$  and  $T_d$   $(\text{LiOH})_4$  would be favored over the  $D_{4h}$  forms, but  $D_{4h}$   $(\text{LiNH}_2)_4$  should be better than  $D_{2d}$ .

The contribution of multicenter covalent bonding, expected to be higher in  $(\text{LiNH}_2)_4$  and  $(\text{LiOH})_4$  than in  $(\text{LiF})_4$ ,<sup>30</sup> helps explain the discrepancy between the electrostatic model and the ab initio tetramerization energies. The latter for  $T_d$   $(\text{LiOH})_4$  is 32 kcal/mol higher than that calculated electrostatically and a comparable value is found for  $D_{4h}$   $(\text{LiNH}_2)_4$ .

Similar reasoning accounts for the preference of both  $(\text{C}_6\text{H}_5)_2\text{C}=\text{NLi}^{10}$  and  $\text{CH}_3\text{Li}^3$  for tetrahedral tetramers. In the former the electron distribution of nitrogen has essentially cylindrical symmetry (far more so than in a  $\text{R}_2\text{NLi}$  grouping), while in the latter there is only a single lone-pair orbital. Conical, cylindrical, or spherical anions generally interact more favorably with the three lithium cations on a tetrahedral face than with two adjacent lithium cations in an eight-membered ring.

The behavior of  $\text{LiH}$  is interesting in this context. Whereas Rupp and Ahlrichs<sup>15</sup> found the electron correlation contributions to be small ( $<1$  kcal/mol) for the association energies of the planar rings,  $(\text{LiH})_2$ ,  $(\text{LiH})_3$ , and  $(\text{LiH})_4$ , a significantly larger effect (ca. 4 kcal/mol) was found for the tetrahedral isomer. This

**Table V.**  $\text{LiXH}_n$  Association Energies per Monomer, kcal/mol

association energy per monomer	$\text{LiNH}_2$	$\text{LiOH}$	$\text{LiF}$
dimerization, exptl		$-32 \pm 8^a$	$-30.6^b$
dimerization, calcd	$-31.3^c - 35.9^a$	$-31.6^d, -34.5^a$	$-32.8^e, -34.3^a$
trimerization, best calculations	$-40^c$		$-38.9^b, -43.2^e$
tetramerization, best calculations	$-41.8^f$	$-47.4^f$	$-47.6^e, -47.0^f$

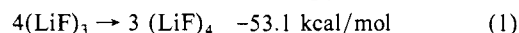
<sup>a</sup>Reference 17; the calculated values are somewhat overestimated. <sup>b</sup>Calculated from data in the NBS tables; Wagman, D. D., et al. *J. Phys. Chem. Ref. Data* **1983**, *11*, Suppl. 2. <sup>c</sup>Reference 18. <sup>d</sup>Reference 16. <sup>e</sup>Reference 15. <sup>f</sup>This work.

suggests the possibility of some multicenter covalent bonding in the latter. The small size of hydrogen is responsible for the similar energies of  $D_{4h}$  and  $T_d$  forms.

### Energetic Consequences for Degrees of Association

Experimentally,  $\text{R}_2\text{NLi}$  derivatives are peculiar in another way: they are the only class of lithium compounds where trimers are known in crystal structures.<sup>4,18</sup> While the degree of aggregation of organolithium and other lithium compounds depends on the substituents, solvation, temp., etc., only dimers, tetramers, and higher oligomers are found. The association energies summarized in Table V, taken from our work and from the literature, provide a basis for understanding this behavior.

Contrast LiF with  $\text{LiNH}_2$ . With use of the data of Rupp and Ahlrichs<sup>15</sup> for uniformity, the disproportionation (reaction 1) favoring the tetramer over the trimer is strongly exothermic. Most



other lithium trimers also appear to be similarly unfavorable. Experimentally, many equilibria between tetramers and dimers are now known in donor solvents. (Solvation favors the dimers at low temperature where the entropy loss due to attachment of additional solvent molecules is less significant).<sup>31</sup>

Although the data are not available at the same high levels, the results of eq 2 indicate that the disproportionation of  $(\text{LiNH}_2)_3$



$$-25.9 \text{ kcal/mol for } 3\text{-}21\text{G} // 3\text{-}21\text{G}$$

$$-24.1 \text{ kcal/mol for } 6\text{-}31\text{G} // 3\text{-}21\text{G}$$

trimer to give the tetramer is much less exothermic than that of eq 1. Such trimers involving nitrogen are more likely to be formed when planar tetramers are the alternatives. We will develop this point further in our next paper in this series.

### Conclusions

The structures and energies of the tetramers of LiF, LiOH, and  $\text{LiNH}_2$  have been calculated by means of ab initio molecular orbital techniques, including large basis sets and electron correlation corrections. Tetrahedral structures are favored by the tetramers of LiF and LiOH whereas a square-planar structure is found for  $(\text{LiNH}_2)_4$ . Electron correlation effects on the isomer energy differences are very small. The structural parameters calculated for  $(\text{LiNH}_2)_4$  are in good agreement with the known experimental structure of the tetramer of a larger derivative. The energies of tetramerization are computed to be  $\approx 185$ – $190$  kcal/mol for LiF and LiOH and about 165 kcal/mol for  $\text{LiNH}_2$ . Electrostatic models including lone-pair orientation effects have been used in the interpretation of the relative stabilities of the isomers.

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**Registry No.**  $(\text{LiF})_4$ , 98331-81-8;  $(\text{LiOH})_4$ , 98331-82-9;  $(\text{LiNH}_2)_4$ , 98331-83-0.

(30) Natural population analysis (Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735) indicates the ionic character to be about 93% in LiOH and LiF and 90% in  $\text{LiNH}_2$  (6-31G\* basis).

(31) Seebach, D.; Hässig, R.; Gabriel, J. *Helv. Chim. Acta* **1983**, *66*, 308 and references cited.