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Ab Initio MO Calculations of NMR ^{15}N–^{6}Li Coupling Constants in Lithium Amide Monomers, Oligomers, and Mixed Aggregates with LiCl

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The NMR ^{15}N–^{6}Li coupling constants $^{1}J_{NLi}$ in $LiNH_2$ and $LiN(CH_3)_2$ monomers and their oligomers and mixed aggregates with LiCl were calculated using ab initio self-consistent perturbation theory and the relation between the molecular structure and $^{1}J_{NLi}$ values was examined. The calculated $^{1}J_{NLi}$ values in the monomers are influenced by solvation and agree well with experimetal values when model solvent molecules are coordinated at the lithium atom. The calculated $^{1}J_{NLi}$ values in cyclic oligomers also agree well with experiment and support the structures derived from NMR experiments in solution. For the mixed trimer, $(LiNH_2)_2LiCl$, a ladder form was obtained as the most stable structure when the lithium atoms are solvated by two H_2O or two NH_3 molecules.

Much attention has been paid to the structures of lithium amides in solution[1—4] in relation to their reaction selectivity.[4c—6] Recently, various structures of lithium dialkylamides such as lithium diisopropylamide (LDA) and lithium 2,2,6,6-tetramethylpiperidide (LiMTP) have been determined by ^{15}N and ^{6}Li NMR spectroscopic analyses.[1—4] The one-bond ^{15}N–^{6}Li coupling constant $^{1}J_{NLi}$ of lithium alkylamides in solution depends on the aggregation and solvation states; the $^{1}J_{NLi}$ values are 8.5—10 Hz in monomers and 4.4–6.2 Hz in cyclic oligomers.[1—4]

As models of experimentally-observed lithium dialkylamides, $LiNH_2$ and its oligomers have been investigated by ab initio molecular orbital calculations.[7] These investigations concerned the structural and energetic relationships based on different levels of calculations. Semi-empirical MNDO calculations also have been carried out to elucidate the preferable structures for LDA and LiMTP and their aggregate states in solution.[8] However, there have been no theoretical studies of the $^{1}J_{NLi}$ coupling constants in lithium amides.

For $^{1}J_{CLi}$ in alkyllithiums, a few theoretical studies have been reported.[9,10] Our recent calculations of $^{1}J_{CLi}$ in methyllithium, *t*-butyllithium and methyllithium oligomers using ab initio self-consistent perturbation theory (SCPT) with the MIDI-4* basis set gave $^{1}J_{CLi}$ values which are in excellent agreement with the experimental values.[10a] In this paper, we report the first ab initio calculations of the ^{15}N–^{6}Li coupling constants in $LiNH_2$ and $LiN(CH_3)_2$ monomers, and their oligomers and mixed aggregates with LiCl, **1**—**8**. The effects of geometry, solvation and degree of aggregation on $^{1}J_{NLi}$ are discussed.

Calculation

Ab initio molecular orbital calculations were carried out with the MIDI-4* basis sets.[11] In the MIDI-4* basis set, the d-type polarization functions are included for the C, N, O, and Cl atoms and the p-type polarization functions for the Li atom. Our previous studies have shown that the $^{1}J_{CLi}$ values in alkyllithiums[10] and the $^{1}J_{SiLi}$ values in silyllithiums[12] calculated with the MIDI-4* basis set agreed well with experimental values. In the case of lithium amide monomers, the π-interaction between the Li and N atoms is expected to be important. The 6-31G* basis set,[13] in which p-type functions are involved as valence functions for Li, also was used to evaluate structures and the $^{1}J_{NLi}$ values. The $^{1}J_{NLi}$ values were calculated using the SCPT method,[14] in which the Fermi contact term was taken into account as the perturbation. The following formula[14,15] was used to calculate the $^{1}J_{NLi}$ values:

$$J_{NLi} = \left(\frac{16h\gamma_N\gamma_{Li}\beta^2}{9}\right)\sum_{\lambda\sigma}^{\mathrm{allAO}}\chi_\lambda(R_N)\chi_\sigma^*(R_N)\rho_{\lambda\sigma}^{(1)}$$

where γ is magnetogyric ratio of the nucleus and β is the Bohr magneton. $\chi_\lambda(R_N)$ represents the function value of the atomic orbital λ evaluated at the nitrogen nucleus. $\rho_{\lambda\sigma}^{(1)}$ are the first-order spin-density matrix elements perturbed by the Fermi contact interaction on the lithium atom and were calculated by the procedure given by Ditchfield and Snyder.[14b] The SCPT theory was incorporated into our ABINIT program and calculations were carried out on the HP-735 workstations.

Results and Discussion

Lithium Amide Monomers. The structures and $^{1}J_{NLi}$ values for $LiNH_2$ (**1**), $LiN(CH_3)_2$ (**2**) monomers, and their solvated systems calculated with the MIDI-4* basis set are shown in Table 1 (Chart 1). All $^{1}J_{NLi}$ values calculated in the present study are negative, while the sign of $^{1}J_{NLi}$ was not determined experimentally. The magnitudes of the calculated $^{1}J_{NLi}$ values in unsolvated **1** and **2** are slightly larger

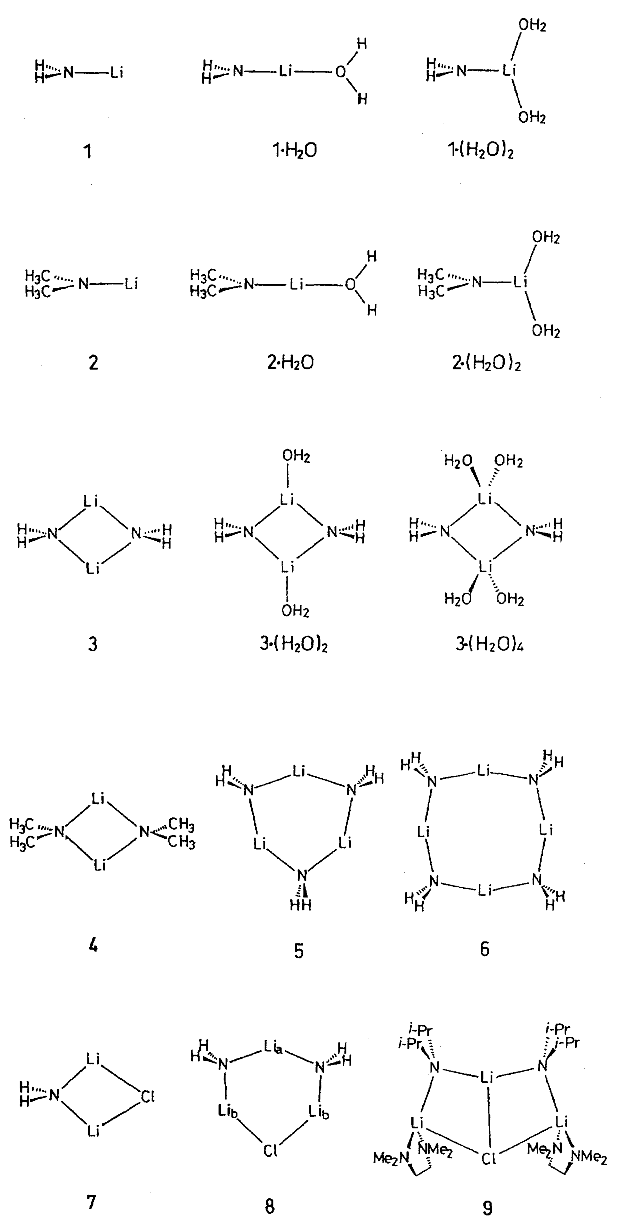


Chart 1.

than the values reported for lithium dialkylamide monomers in solution, 8.5—10 Hz.[1—5]

The coordination of H_2O molecules at lithium reduces the magnitude of $^1J_{NLi}$ in **1** and **2** distinctly; the coordination of two H_2O molecules reduces the magnitude to 70% of the unsolvated species. It should be emphasized that the calculated $^1J_{NLi}$ values in **1**$(H_2O)_2$ and **2**$(H_2O)_2$ agree well with the experimental value of 8.5 Hz for LiTMP,[3b] in which tricoordination of the lithium atom was confirmed by NMR studies.

The coordination of two H_2O molecules to the lithium atom changes the N–Li distance of **2** from 1.793 to 1.860 Å. It should be noted, however, that the N–Li bond elongation itself is not a key factor for decreasing the magnitude of the $^1J_{NLi}$ value from −11.4 to −8.0. Then the dependence of $^1J_{NLi}$ on the N–Li bond length was examined for the unsolvated species in which the geometry of the $N(CH_3)_2$ group was fixed. It was calculated that the $^1J_{NLi}$ value in **2** is −11.4 Hz for r(N–Li)=1.793 Å and −10.6 Hz for r(N–Li)= 1.860 Å. Although the elongation of the N–Li bond decreases the magnitude of $^1J_{NLi}$, the change is small. Therefore, it is suggested that the solvation affects the electronic factors of the N–Li bond, which reduces the magnitude of $^1J_{NLi}$ significantly.[16a]

The dependence of $^1J_{NLi}$ of **2** on the hybridization of the N atom also was examined by bending the N–Li bond from the CNC plane. The $^1J_{NLi}$ values were −11.2, −10.1, and −8.2 Hz for the bending angle of 10°, 30°, and 50°, respectively. This decreasing of $^1J_{NLi}$ can be explained simply by the change of the hybridization of the atomic orbital of the N atom directed along the N–Li bond from sp^2 to sp^3.[16b]

Lithium Amide Oligomers. The cyclic structures have been proposed for lithium amide oligomers in solution.[1—4] Lithium dialkylamides exist as cyclic dimers in donor solvents and the disolvated dimer is more preferable than the tetrasolvated dimer.[3] Calculations have been done for **3**—**6**, which are models for the oligomers observed in solution. The structures and $^1J_{NLi}$ values for cyclic dimers **3** and **4** calculated with the MIDI-4* basis set are shown in Table 1. Armstrong et al. reported the X-ray structure of the cyclic dimer of dialkyllithium, in which one ether-type oxygen atom is coordinated at each lithium atom, as is seen in **3**$(H_2O)_2$; the N–Li bond lengths are 1.980 and 1.992 Å and the LiNLi angles are 75.7 and 76.3°.[7e] Their 6-31G calculations[7e] of **3**$(H_2O)_2$ gave 1.971 Å for the N–Li bond and 73.0° for the LiNLi angle. The MIDI-4* N–Li bond length and the LiNLi angle in **3**$(H_2O)_2$ listed in Table 1 also are in good agreement with the reported values. In the cyclic dimers, **3** and **4**, the calculated $^1J_{NLi}$ values agree well with experimental values for LDA and LiTMP dimers, 4.4—5.0 Hz.[3] Although the solvation at lithium atoms in **3** reduces the $^1J_{NLi}$ value to a certain degree, it is difficult to determine the solvated structure in solution from the calculated $^1J_{NLi}$ values.

The crystal structure of the LiMTP tetramer has been reported: the N–Li distance is 2.00 Å and the LiNLi angle is 101.5°.[17] The calculated MIDI-4* N–Li distance is smaller by 0.05 Å and the LiNLi angle is smaller by 6° than experimental values. Trimers and tetramers exist in non-donor solvents and have the $^1J_{NLi}$ value of 6.2 Hz,[4a,4b] which is larger than the $^1J_{NLi}$ values in cyclic dimers. The calculated $^1J_{NLi}$ values for **5** and **6** are slightly smaller than the experimental ones. The calculated $^1J_{NLi}$ values for three cyclic structures: **3**, **5**, and **6** have similar $^1J_{NLi}$ values, despite the large difference in their LiNLi angles.

Mixed Aggregates with LiCl. Collum et al.[3c,4c] assigned the structures like **7** and **8** as the mixed aggregates of LiTMP and those of LDA with lithium chloride in solution. The calculated $^1J_{NLi}$ values of **7** and **8** in Table 1 agree well with the experimental values for the mixed aggregates of LDA and of LiTMP, 4.8—5.9 Hz,[3c,4c] and support the experimental assignments. The calculated $^1J_{NLi}$ values in **7** and **8** resemble those for oligomers **3**, **5**, and **6**. Thus, the magnitude of $^1J_{NLi}$ is determined by the aggregation state, the number of Li atoms bonded to N, even in the mixed aggregates.

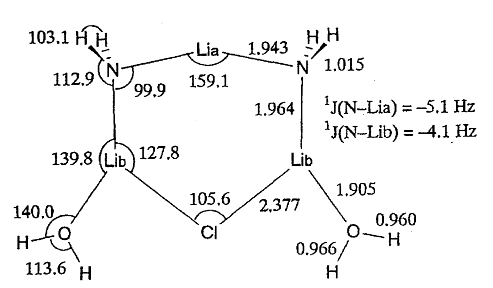
Table 1. Structures (Å and Degree)[a] and $^1J(^{15}N-^6Li)$ Values (Hz) for Lithium Amides and Their Oligomers and Mixed Aggregates with LiCl Calculated with MIDI-4* Basis Set

Species	r(N–Li)	r(N–H)[b]	r(Li–Cl)	∠(HNH)[b]	∠(LiNLi)	∠(LiClLi)	$^1J_{NLi}$
1	1.767	1.011		103.9			−11.2
1H_2O	1.791	1.012		103.8			−9.5
1$(H_2O)_2$	1.828	1.013		103.3			−8.1
2	1.793	1.434		109.9			−11.4
2H_2O	1.818	1.432		110.0			−9.7
2$(H_2O)_2$	1.860	1.430		109.7			−8.0
3	1.951	1.013		102.9	73.7		−4.9
3$(H_2O)_2$	1.986	1.014		102.9	75.1		−4.3
3$(H_2O)_4$	2.030	1.016		101.6	76.9		−3.5
4	1.971	1.446		109.1	72.4		−5.1
5	1.949	1.014		103.0	97.2		−4.9
6	1.949	1.015		102.9	108.5		−4.8
7	1.938	1.013	2.267	103.0	80.7	67.2	−5.2
8	1.953[c] 1.927[d]	1.014	2.245	103.0	100.3	92.9[d]	−4.6[c] −5.3[d]

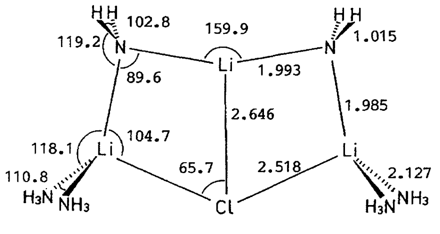
a) Structures were optimized under the symmetry restriction of C_{2v} for **1**, **2**, **7**, and **8**, D_{2h} for **3** and **4**, D_{3h} for **5**, and D_{4h} for **6**. b) r(N–C) and ∠(CNC) for **2** and **4**. c) Values including Li_a. d) Values including Li_b.

Mair et al. observed the X-ray crystal structure of $(LDA)_2LiCl(TMEDA)_2$ as a three-runged ladder **9** which has a near-planar skeleton and possesses the tetrahedral lithium atoms.[18)] Romesberg and Collum recently carried out MNDO calculations for the mixed aggregates of lithium amides and found no energy minima corresponding to the three-runged ladder form.[8b)] We calculated the structure of **8**$(NH_3)_4$ assuming the C_{2v} molecular symmetry and the C_3 local symmetry for the NH_3 groups. The d-type polarization functions on the nitrogen atoms in the NH_3 groups were omitted. As is seen from Fig. 1, the optimized structure is a ladder form; no energy minimum corresponding to the cyclic form was found. The calculated geometrical parameters are in fair agreement with experimental values for **9**; the discrepancies are within 6% for atomic distances and less than 3° for bond angles.

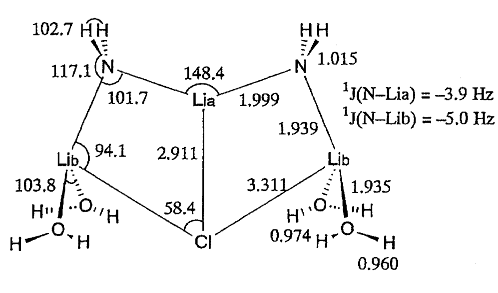
The structures and $^1J_{NLi}$ values for **8**$(H_2O)_2$ and **8**$(H_2O)_4$ were calculated as the models of the mixed trimer in ethereal solution. The C_{2v} symmetry was assumed for each structure and the d-type polarization functions on the oxygen atoms were omitted. The optimized structures are shown in Fig. 2 along with their calculated $^1J_{NLi}$ values. As is seen from Table 1 and Fig. 2, **8** and **8**$(H_2O)_2$ have cyclic forms, while **8**$(H_2O)_4$ has a ladder one. It is suggested that the tetracoordination at lithium (Li_b in Fig. 2) is essential for the stable ladder form. Both structures in Fig. 2 have similar $^1J_{NLi}$ values and the geometry for the mixed aggregate in so-



8(H₂O)₂



8(NH₃)₄



8(H₂O)₄

Fig. 1. Structure (Å and degree) for **8**$(NH_3)_4$ calculated with the MIDI-4* basis set. Geometry optimization was carried out under the restriction of C_{2v} molecular symmetry and C_3 local symmetry for the NH_3 groups. The d-type polarizaiton functions on the nitrogen atoms in NH_3 were not included.

Fig. 2. Structures (Å and degree) and $^1J(^{15}N-^6Li)$ values (Hz) for **8**$(H_2O)_2$ and **8**$(H_2O)_4$ calculated with the MIDI-4* basis set. Geometry optimization was carried out under the restriction of C_{2v} symmetry and the d-type polarization functions on the oxygen atoms were not included.

Table 2. Structures (Å and Degree)[a] and $^1J(^{15}\mathrm{N}-^{6}\mathrm{Li})$ Values (Hz) for Lithium Amides and Their Oligomers and Mixed Aggregates with LiCl Calculated with 6-31G* Basis Set

Species	r(N–Li)	r(N–H)[b]	r(Li–Cl)	∠(HNH)[b]	∠(LiNLi)	∠(LiClLi)	$^1J_{\mathrm{NLi}}$
1	1.749	1.005		105.2			−5.5
1H_2O	1.771	1.005		105.1			−4.8
1$(H_2O)_2$	1.811	1.006		104.6			−4.5
2	1.765	1.447		109.3			−9.0
2H_2O	1.789	1.445		109.2			−7.7
2$(H_2O)_2$	1.835	1.446		108.7			−7.1
3	1.943	1.007		104.1	73.3		−4.4
3$(H_2O)_2$	1.978	1.008		104.2	74.1		−3.9
3$(H_2O)_4$	2.026	1.010		102.7	76.1		−3.6
4	1.957	1.457		108.6	71.7		−5.3
5	1.940	1.009		104.0	96.6		−3.3
6	1.939	1.009		103.9	107.8		−2.8
7	1.923	1.007	2.276	104.3	80.7	66.3	−3.8
8	1.946[c]	1.009	2.254	104.0	100.1	92.3[d]	−3.1[c]
	1.911[d]						−3.4[d]

a) Structures were optimized under the symmetry restriction of C_{2v} for **1**, **2**, **7**, and **8**, D_{2h} for **3** and **4**, D_{3h} for **5**, and D_{4h} for **6**, and a fixed structure of the CH_3 groups (C–H=1.093 Å and HCH=109.5°). b) r(N–C) and ∠(CNC) for **2** and **4**. c) Values including $\mathrm{Li_a}$. d) Values including $\mathrm{Li_b}$.

lution, a cyclic form or a ladder one, can not be determined on the basis of the calculated $^1J_{\mathrm{NLi}}$ values.

6-31G* Calculations. The structures and $^1J_{\mathrm{NLi}}$ values for **1**—**8** which were calculated with the 6-31G* basis sets are listed in Table 2. In all species, MIDI-4* and 6-31G* basis sets give similar structures. In oligomers and mixed aggregates, the N–Li distances agree within 0.01 Å and the LiNLi angles within 1°. A distinct difference is found between 6-31G* and MIDI-4* $^1J_{\mathrm{NLi}}$ values for the $LiNH_2$ monomer. The 6-31G* $^1J_{\mathrm{NLi}}$ values for **1** and its solvated species are much smaller than the MIDI-4* values, although no distinct differences are recognized between the 6-31G* and MIDI-4* electron populations in **1**. For dimethyl-substituted lithium amide monomer, **2**, and the cyclic dimer, **4**, the 6-31G* $^1J_{\mathrm{NLi}}$ values agree well with experimental values. The solvent effect on $^1J_{\mathrm{NLi}}$ is similar in MIDI-4* and 6-31G* calculations. The 6-31G* $^1J_{\mathrm{NLi}}$ values of oligomers decrease as the degree of aggregation increases and the LiNLi angle increases, although such a correlation has not been reported experimentally.

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