LMCT.[4,20] If a comparable separation is applicable to $PtBr_4^{2-}$, then either band VI or band VII (1.13 and 1.35 μm^{-1}, respectively, higher than band V) could be assigned to the σ-LMCT, with the absorptivity quite comparable to that of $AuBr_4^-$. Second, the d $\rightarrow$ p transition to $8E_u$, being a metal-atom-localized transition, is not expected to exhibit a strong shift, as Cl^- is replaced by Br^- so that band VI at 4.75 μm^{-1} could reasonably be assigned to this transition. Finally, the Br^- ion exhibits strong absorption bands in this energy region in acetonitrile that have been assigned to charge transfer to solvent (CTTS), and the lowest energy CTTS transitions are characterized by positive *A* terms in the MCD.[22] It is likely that coordinated Br^- will also exhibit such transitions. Thus, the observed positive *A* term for band VI of $PtBr_4^{2-}$ (the term assignment for band VII is not possible from the present data) is consistent with any of these possibilities. Because they would be internally consistent with the other assignments presented here for $PtCl_4^{2-}$ and previously for AuX_4^-,[15] we assign band VI as the unresolved combination of the σ-LMCT to $5E_u$, the d $\rightarrow$ p transition to $8E_u$, and band VII as Br^- CTTS. The shoulder observed in the MCD at 4.22 μm^{-1}, which has no corresponding band in the absorption spectrum, is then assigned to the d $\rightarrow$ p transition to $7E_u$ and the σ-LMCT transitions to $6E_u$ and $3A_{2u}$. The *A* term for band VI renders the term assignment(s) for these transitions obscure.

Conclusions. The assignment of the intense bands in the PtX_4^{2-} ions to both d $\rightarrow$ p and LMCT transitions is consistent with the present results. Thus, the PtX_4^{2-} spectra can be visualized as resulting from the blue shift of LMCT transitions accompanied by the red shift of d $\rightarrow$ p transitions from AuX_4^-. Both shifts are consonant with the expected changes in orbital stability as the oxidation state is changed from Au(III) to Pt(II).

The negative *A* terms for the π-LMCT transitions to $2E_u$ are clear in the MCD spectra of the PtX_4^{2-} ions, but they are obscured by *B* terms in the MCD spectra of AuX_4^-. This indicates a greater relative magnitude of these *A* terms for Pt(II) than for Au(III). This together with the greater relative intensity for the π-LMCT transitions compared to the σ-LMCT observed for $PtBr_4^{2-}$ compared to $AuBr_4^-$ can be attributed to greater σ–π mixing of the $1e_u$ and $2e_u$ halide orbitals. Stronger mixing might be expected if there is a smaller energy difference between these orbitals in the Pt(II) complex compared to the Au(III) complex. An analogous trend was noted earlier from some comparisons among several octahedral halo complexes[20] and was interpreted as an enhancement of σ donation over π donation as the metal oxidation state was increased.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. H.I. also acknowledges the Middle East Technical University for a leave of absence.

Registry No. $[PtCl_4]^{2-}$, 13965-91-8; $[PtBr_4]^{2-}$, 14493-01-7.

---

(22) El-Kourashy, A.-G.; Grinter, R *J. Chem. Soc., Faraday Trans. 2* **1977**, *73*, 1050.

Contribution from the City University of New York, John Jay College and Graduate School,
New York, New York 10019, Institut für Organische Chemie, Friedrich-Alexander-Universität Erlangen-Nürnberg,
D-8520 Erlangen, Federal Republic of Germany, and Organisch-Chemisches Institut, Universität Heidelberg,
D-6900 Heidelberg, Federal Republic of Germany

Structures and Energies of Lithium Amide Dimers and Trimers: An ab Initio Study

ANNE-MARIE SAPSE,*[1a] ELMAR KAUFMANN,[1b] PAUL VON RAGUÉ SCHLEYER,*[1b] and ROLF GLEITER[1c]

Received December 20, 1982

The structures and energies of $LiNH_2$ dimers and trimers were investigated by ab initio and semiempirical (MNDO) molecular orbital theory. In agreement with X-ray structure results on derivatives, $(LiNH_2)_2$ and $(LiNH_2)_3$ prefer symmetrical D_{2h} and D_{3h} geometries (**4** and **5**, respectively), with all hydrogen atoms perpendicular to the planar heavy-atom rings. The $LiNH_2$ dimerization (−62.5 kcal/mol) and trimerization (about −120 kcal/mol) energies are at least as large as the related values for LiOH and LiF. The $LiCH_3$ dimerization and trimerization energies are much smaller. Since these association energies generally follow electronegativity trends, specific nitrogen lone pair–lithium interactions are indicated in **4** and **5**. When all NH_2 groups are rotated by 90°, these interactions are lost and the resulting isomers, **8** and **9**, are much less stable. Further energetic relationships and the nature of lithium bonding are discussed.

Introduction

Association is a principal characteristic of lithium compounds.[2-4] The energies involved are very large, and aggregated species, rather than monomers, are typical. While this paper is concerned with oligomers of $LiNH_2$, the simple alkyllithiums are the best known examples. Thus, methyllithium is a tetramer, $(CH_3Li)_4$, in ether solvents,[2,4] in the crystal,[5] and even in the gas phase.[6] The association energy is not known experimentally, but values (kcal/mol) for the formation of the dimer (42), trimer (82), tetramer (128), and higher oligomers are available from a number of calculations.[7] Gas-phase association energies for $(LiF)_2$ (61.4 ± 8 kcal/mol), for $(LiF)_3$ (116.8 ± 12 kcal/mol), and for $(LiOH)_2$ (62.4 ±

---

(1) (a) City University of New York. (b) Friedrich-Alexander-Universität Erlangen-Nürnberg. (c) Universität Heidelberg.

(2) Wakefield, B. J. "The Chemistry of Organolithium Compounds"; Pergamon Press: Oxford, 1974.

(3) Lappert, M. F.; Power, P. P.; Sanger, A. R.; Srivastava, R. C. "Metal and Metalloid Amides"; Wiley: New York, 1980.

(4) Wardell, J. L. In "Comprehensive Organometallic Chemistry"; Wilkinson, G., Stone, G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, 1982; Vol. 1, p 43 ff.

(5) Weiss, E.; Hencken, G. *J. Organomet. Chem.* **1970**, *21*, 265. Köster, H.; Thoennes, D.; Weiss, E. *Ibid.* **1978**, *160*, 1.

(6) Chinn, J. W., Jr.; Lagow, R. J. *Organometallics* **1984**, *3*, 75. Landro, F. J.; Gurak, J. A.; Chinn, J. W., Jr.; Lagow, R. J. *J. Organomet. Chem.*, in press.

(7) The values given are the best theoretical estimates: Raghavachari, K.; Kaufmann, E.; Clark, T.; Schleyer, P. v. R., to be submitted for publication. For other studies, see: Cowley, A. H.; White, W. D. *J. Am. Chem. Soc.* **1969**, *91*, 34. Baird, N. C.; Barr, R. F.; Datta, R. K. *J. Organomet. Chem.* **1973**, *59*, 65. Guest, M. F.; Hillier, I. H.; Saunders, V. R. *Ibid.* **1972**, *44*, 59. McLean, W.; Pedersen, L. G.; Jarnagin, R. C. *J. Chem. Phys.* **1976**, *65*, 2491. Clark, T.; Schleyer, P. v. R.; Pople, J. A. *J. Chem. Soc., Chem. Commun.* **1978**, 137. McLean, W.; Schultz, J. A.; Pedersen, L. G.; Jarnagin, R. C. *J. Organomet. Chem.* **1979**, *175*, 1. Clark, T.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Chem. Soc., Chem. Commun.* **1980**, 672. Graham, G.; Richtsmeier, S.; Dixon, D. A. *J. Am. Chem. Soc.* **1980**, *102*, 5759. Herzig, L.; Howell, J. M.; Sapse, A.-M.; Singman, E.; Snyder, G. *J. Chem. Phys.* **1982**, *77*, 429.

0020-1669/84/1323-1569\$01.50/0

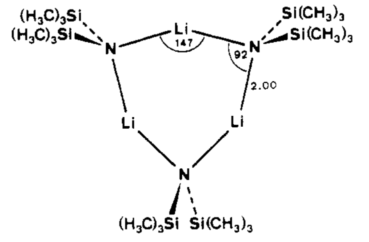
Table I. Calculated Energies of $(LiNH_2)_n$ Species[a] and Relative Energies of Perpendicular vs. Planar Forms[b]

		$(LiNH_2)_2$		$(LiNH_2)_3$	
theor level	$LiNH_2$	perpendicular (**4**)	planar (**8**)[b]	perpendicular (**5**)	planar (**9**)[b]
MNDO[c]	7.6	−47.5	−25.5 (22.0)	−91.1	−45.7 (45.4)
3-21G//3-21G	−62.695 19	−125.523 24	−125.461 45 (38.8)	−188.327 99	−188.232 65 (59.8)
6-21G//3-21G	−62.975 60	−126.082 63	−126.020 74 (38.8)		
6-31G//6-31G	−63.030 5	−126.176 6		−189.298 5	
MP2/6-21G//3-21G	−63.096 78	−126.324 04	−126.254 78 (43.5)		
3-21+G/3-21G//3-21G[d]	−62.716 34	−125.539 73	−125.503 32 (22.8)	−188.346 46	−188.278 65 (42.6)
3-21+G//3-21+G	−62.717 18	−125.540 38	−125.504 63 (22.4)		
6-31G*//3-21G	−63.041 42	−126.198 12	−126.152 67 (28.5)		
6-31G*//6-31G*	−63.041 95	−126.199 41	−126.154 15 (28.4)		
6-31+G*/6-31G*//6-31G*[d]	−63.050 28	−126.204 23	−126.169 37 (21.9)		

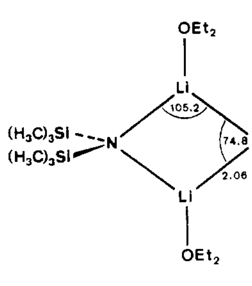
[a] In atomic units (1 au = 627.53 kcal/mol) unless otherwise indicated. [b] Energies (kcal/mol) relative to perpendicular forms in parentheses. [c] $\Delta H_f°$ in kcal/mol. [d] The diffuse orbitals were omitted from lithium in these calculations.

12 kcal/mol) are derivable from the JANAF tables;[8] high-level theoretical studies of these species have been published.[9,10] This paper, part of a systematic investigation of the association of lithium compounds,[11] provides the first data for the dimer and trimer of $LiNH_2$. These are simple models for derivatives for which X-ray structures are available.[12-14]

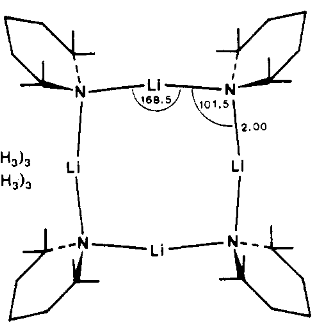
The degree of association of [bis(trimethylsilyl)amino]lithium, $[(CH_3)_3Si]_2NLi$, varies considerably with the conditions. A monomer–dimer equilibrium is present in tetrahydrofuran, but a dimer–tetramer equilibrium is indicated in hydrocarbon solvents.[15] Nevertheless, a crystalline *trimer*, **1**, was obtained from petroleum ether or benzene. The X-ray structure, first determined in 1969, showed a six-membered ring with N's and Li's alternating.[12] A subsequent redetermination by Atwood's group established the planarity of the Li_3N_3 ring conclusively.[13] The same compound gives a crystalline *dimer* diethyl etherate, **2**, whose X-ray structure has just been reported.[14] The same paper also presents details for a *tetramer*, **3**, this time of $Li[NCMe_2(CH_2)_3CMe_2]$.



1[12,13]



2[14]



3[14]

Table II. $LiNH_2$ Dimerization and Trimerization Energies (kcal/mol)

	dimerization energies		trimerization energies	
theor level	perpendicular	planar	perpendicular	planar
MNDO	−62.7	−40.7	−113.9	−68.5
3-21G//3-21G	−83.4	−44.6	−152.1	−92.3
6-21G//3-21G	−82.5	−43.6		
MP2/6-21G//3-21G	−81.9	−38.4		
6-31G//6-31G	−72.5		−129.8	
3-21+G/3-21G//3-21G[a]	−67.2	−44.3	−123.9	−81.3
3-21+G//3-21+G	−66.5	−44.1		
6-31G*//6-31G*	−72.5	−44.1		
6-31+G*/6-31G*// 6-31G*[a]	−65.1	−43.2		
correlation cor (est)[b]	+0.6	+5.2		
ZPE cor (est)	+2.0	+2.0		
final est	−62.5	−36.0	ca. −120	ca. −70

[a] Diffuse functions on nitrogen, but not lithium. [b] On the basis of the 6-21G//3-21G → MP2/6-21G//3-21G difference.

Monomeric $LiNH_2$ was included in a general theoretical study of compounds containing lithium and nitrogen.[16] We now report calculational results on $(LiNH_2)_2$ and $(LiNH_2)_3$. The ab initio geometries are compared with X-ray results. The question of the orientation of the NH_2 groups is addressed, as well as the planarity of the N–Li rings. Systematic improvements in the theoretical description of these species lead to values of the dimerization and trimerization energies which we feel will be reliable.

Methods

Calculations were carried out at the restricted Hartree–Fock[17] level using various versions of the Gaussian series of programs[18] and standard basis sets (e.g., split valence 3-21G,[19] 6-21G,[19] and 6-31G[20];

---

(8) Stull, D. R.; Prophet, H. "JANAF Thermochemical Tables", 2nd ed.; Report NSRDS-NBS 37, 1971. Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttal, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. 2.

(9) Boldyrev, A. I.; Solomonik, V. G.; Zakzhevskii, V. G.; Charkin, O. P. *Chem. Phys. Lett.* **1980**, *73*, 58.

(10) Raghavachari, K. *J. Chem. Phys.* **1982**, *76*, 5421.

(11) Kaufmann, E. Diplomarbeit, Erlangen, Aug 1982. Also see ref 31.

(12) Mootz, D.; Zinnius, A.; Böttcher, B. *Angew. Chem.* **1969**, *81*, 398.

(13) (a) Rogers, R. D.; Atwood, J. L.; Grüning, R. *J. Organomet. Chem.* **1978**, *157*, 229. (b) For the X-ray structure of $[(PhCH_2)_2NLi]_3$, see: Barr, D.; Clegg, W.; Mulvey, R. E.; Snaith, R. *J. Chem. Soc., Chem. Commun.* **1984**, 285.

(14) Lappert, M. F.; Slade, M. J.; Singh, A.; Atwood, J. L.; Rogers, R. D.; Shakir, R. *J. Am. Chem. Soc.* **1983**, *105*, 302. Engelhardt, L. M.; May, A. S.; Raston, C. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1983**, 1671. See ref 13b for the X-ray structures of two dimers based on $[(PhCH_2)_2NLi\cdot Solv]_2$.

(15) Kimura, B. Y.; Brown, T. L. *J. Organomet. Chem.* **1971**, *26*, 57.

(16) Würthwein, E.-U.; Sen, K. D.; Pople, J. A.; Schleyer, P. v. R. *Inorg. Chem.* **1983**, *22*, 496.

(17) Roothaan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69.

(18) GAUSSIAN 76: Binkley, J. S.; Whiteside, R. A.; Hariharan, P. C.; Seeger, R.; Pople, J. A.; Hehre, W. J.; Newton, M. D. *QCPE* **1978**, *14*, 368. GAUSSIAN 80: *Ibid.* 368. GAUSSIAN 82: Binkley, J. S.; Whiteside, R. A.; Raghavachari, K.; Seeger, R.; DeFrees, D. J.; Schlegel, H. B.; Frisch, M. J.; Pople, J. A.; Kahn, L.R., Carnegie-Mellon University. We thank Professor Pople for making a preliminary VAX version of this program available to us. This was adapted to Cyber 173 and 175 computers by A. Sawaryn.

(19) Binkley, J. S.; Pople, J. A.; Hehre, W. J *J. Am. Chem. Soc.* **1980**, *102*, 939. Gordon, M. S.; Binkley, J. S.; Pople, J. A.; Pietro, W. J.; Hehre, W. J. *Ibid.* **1982**, *104*, 2797.

Table III. Calculated Geometries of $LiNH_2$ and Its Dimers and Trimers with Various Basis Sets

	$LiNH_2$ (C_{2v})				$(LiNH_2)_2$ (4, D_{2h})				$(LiNH_2)_2$ (8, D_{2h})			$(LiNH_2)_3$ (5, D_{3h})		$(LiNH_2)_3$ (9, D_{3h})
parameter	3-21G[a]	3-21+G	6-31G	6-31G*[a]	3-21G	3-21+G	6-31G	6-31G*	3-21G	3-21+G	6-31G*	3-21G	6-31G	3-21G
Li-N, Å	1.714	1.759	1.74	1.750	1.908	1.931	1.94	1.943	1.869	1.907	1.910	1.906	1.95	1.850
Li-Li, Å					2.236	2.255	2.28	2.314	2.021	2.061	2.083	2.781	2.94	2.443
N-N, Å					3.093	3.135	3.14	3.122	3.145	3.209	3.201	3.649	3.69	3.629
N-H, Å	1.013	1.013	1.01	1.005	1.016	1.016	1.01	1.007	1.018	1.017	1.007	1.017	1.01	1.019
LiNLi, deg					71.7	71.5	72	73.1	65.4	65.4	66.1	93.7	98	82.6
NLiN, deg					108.3	108.5	108	106.9	114.6	114.6	113.9	146.3	142	157.4
HNH, deg	106.5	107.0	108	105.2	105.9	106.0	106	104.1	102.9	103.2	101.7	105.9	110	102.3
HNLi, deg	126.8	126.5	126	127.4	119.2	119.3	119	119.6	95.8	95.7	96.1	114.4	112	87.6

[a] Whiteside, R. A.; Frisch, M. J.; Binkley, J. S.; DeFrees, D. J.; Schlegel, H. B.; Raghavachari, K.; Pople, J. A. "Carnegie-Mellon Quantum Chemistry Archive", 2nd ed.; Carnegie-Mellon: Pittsburgh, 1981.

Table IV. Comparison of Related Theoretical and Experimental $(LiNR_2)_n$ Geometrical Parameters[a]

	$LiNH_2$	$(LiNR_2)_2$		$(LiNR_2)_3$	
parameter	theor	theor (4)	X-ray (2)	theor (5)	X-ray (1)
N-Li, Å	1.71-1.76[b]	1.91-1.94	1.98-2.06	1.91-1.95	1.91-2.04
NLiN, deg		107-108.5	103-105	142-146	141-147
LiNLi, deg		71.5-73	75-77	94-98	92-95

[a] The average values given for X-ray structures are taken from ref 13 and 14. The theoretical values are from Table III. [b] The 1.965 (4) Å distance in monomeric $\{[(CH_3)_3Si]_2NLi\cdot 12\text{-crown-}4\}$ (Power, P. P.; Xiaojie, X. *J. Chem. Soc., Chem. Commun.* 1984, 358) is lengthened by solvation. For a review of the X-ray structures of lithium compounds, see: Setzer, W.; Schleyer, P. v. R. *Adv. Organomet. Chem.*, in press.

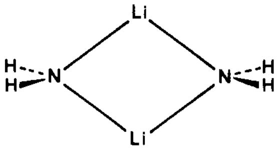
polarization 6-31G*;[20] and diffuse-function augmented 3-21+G[21] and 6-31+G*[21]). The structures were completely optimized within the assumed symmetry constraints by using Davidon–Fletcher–Powell multiparameter search[22] routines with analytically evaluted atomic forces[23] or, in some cases, with the Murtagh–Sargent[24] minimization algorithm. Notations like MP2/6-21G//6-21G designate the levels at which the geometry was optimized (after the "//") and at which single points were calculated (before the "//"). "MP2" indicates Møller–Plesset corrections for electron correlations carried out to second order.[25] Single point calculations with mixed basis sets, 3-21+G/3-21G and 6-31+G*/6-31G*, utilized additional diffuse s and p functions only on nitrogen (exponents 0.0639).[21] The omission of diffuse functions on lithium is expected to change the absolute energies insignificantly.

Table I summarizes the absolute energies of all species calculated at various ab initio levels and includes MNDO heats of formation. Thiel and Clark's parameterization of MNDO for lithium[26] is quite successful as far as the energies of lithium–nitrogen interactions are concerned. This is shown by the comparison of MNDO dimerization and trimerization energies in Table II with the best estimates. The MNDO $\Delta H_f{}^\circ{}_0(LiNH_2)$ = 7.6 kcal/mol is also not far from an ab initio derived estimate (13.8 ± 1.2 kcal/mol).[16]

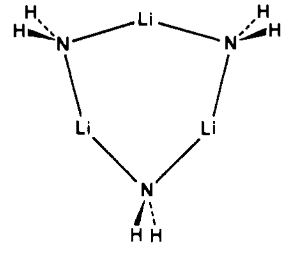
The calculated geometries are summarized in Table III and compared with corresponding experimental parameters in Table IV. The ab initio values are in reasonable agreement with experiment, but MNDO N–Li bond lengths are too short.

Results

Geometries. Although we found $(LiNH_2)_2$ to prefer D_{2h} (**4**) and $(LiNH_2)_3$ to prefer D_{3h} (**5**) symmetries, other structural alternatives were explored. We wished to answer four questions: (1) Are the Li–N distances equal? (2) Are the Li–N rings planar? (3) How well do the calculated and experimental geometries compare? (4) What are the preferred orientations of the NH_2 groups?

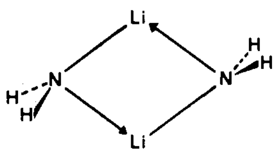


4, D_{2h}

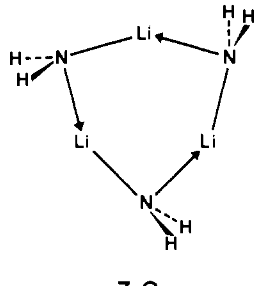


5, D_{3h}

The monomer, $LiNH_2$, is indicated to be planar at high levels of theory.[16] Although NH_3 is pyramidal, electropositive substituents induce planarity. Further, a planar geometry for $LiNH_2$ is favored by whatever p–π delocalization may be present. The simplest dimer (**6**) and trimer (**7**) models would thus involve the interaction of two or three $LiNH_2$ units oriented so that the nitrogen lone-pair orbitals can engage the metal atoms. When C_{2h} and C_{3h} starting geometries corresponding to **6** and **7** were employed, the automatic optimization routines[22-24] led to the more symmetrical forms, **4** (D_{2h}) and **5** (D_{3h}), respectively, with all Li–N distances equal.



6, C_{2h}



7, C_{3h}

The experimental work on the trimer, $[LiN(SiMe_3)_2]_3$, was concerned with the planarity of the Li_3N_3 ring. Our calculations show $(LiNH_2)_3$ to be planar in agreement with the experimental conclusion.[13] In order to probe the freedom of out-of-plane distortions, "boat" and "chair" structures were investigated. In both cases, N1 and Li4 were displaced 10° from the plane of the remaining heavy atoms: in the same direction for the boat and in opposite directions for the chair. The increase in energy due to the "boat" distortion was rela-

---

(20) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213. Dill, J. D.; Pople, J. A. *J. Chem. Phys.* **1975**, *62*, 2921. Francl, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; DeFrees, D. J.; Pople, J. A. *Ibid.* **1982**, *77*, 3654.

(21) Clark, T.; Chandraskhar, J.; Spitznagel, G. W.; Schleyer, P. v. R. *J. Comput. Chem.* **1983**, *4*, 294. See: Spitznagel, G. W.; Clark, T.; Chandrasekhar, J.; Schleyer, P. v. R. *Ibid.* **1982**, *3*, 363. Chandrasekhar, J.; Andrade, J. G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5609.

(22) Davidon, W. C. *Comput. J.* **1968**, *10*, 406. Fletcher, R.; Powell, M. J. D. *Ibid.* **1963**, *6*, 163. Poppinger, D. *Chem. Phys. Lett.* **1975**, *34*, 332.

(23) Schlegel, H. B.; Wolfe, S.; Bernardi, F. *J. Chem. Phys.* **1975**, *63*, 3632.

(24) Murtagh, B. A.; Sargent, R. W. H. *Comput. J.* **1970**, *13*, 185.

(25) Frisch, M. J.; Krishnan, R.; Pople, J. A. *Chem. Phys. Lett.* **1980**, *75*, 66 and references therein.

(26) MNDO: Dewar, M. J. S.; Thiel, W. *J Am. Chem. Soc.* **1977**, *99*, 4899, 4907. Li parameterization: Thiel, W.; Clark, T., to be submitted for publication.

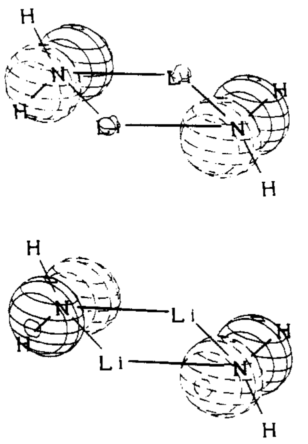


Figure 1. Highest occupied molecular orbitals of the perpendicular $(LiNH_2)_2$ dimer (**4**). The HOMO (MO 12, $2b_{2u}$) is shown at the top, and MO 11 ($1b_{1g}$), underneath. The latter, despite its π^* character, is lower in energy due to the involvement of p orbitals on lithium. Even though the Li p coefficients are significant, these orbitals are diffuse and are not apparent with the contours used in the plot. These orbital representatives, and those of the other figures, were drawn using STO-3G wave functions and Jorgensen's program.[32]

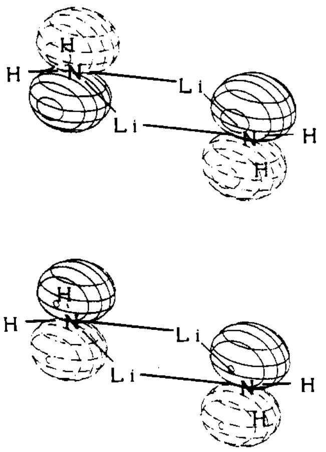


Figure 2. Highest occupied molecular orbitals of the planar $(LiNH_2)_2$ dimer (**8**). Although the HOMO (MO 12, $1b_{2g}$, top) has π^* character, overlap between the nitrogens is negligible and this four-π-electron species cannot be regarded as being "antiaromatic". MO 11 ($1b_{1u}$), shown underneath, benefits from participation of the lithium p orbitals, although this is not apparent from the plot. The symmetry of MO 12 precludes involvement of any Li orbitals (see text).

tively large, but the "chair" deformation only cost about 0.4 kcal/mol. This indicates that rather large amplitudes of movement should be possible.

The calculated geometries of monomeric $LiNH_2$ as well as the dimer, **4**, and the trimer, **5**, at various ab initio theoretical levels are summarized in Table III. The basis set variations are generally within ±0.02 Å for the N–Li distances and ±1° for the angles. The N–Li bonds lengthen by nearly 0.2 Å on going from the monomer to either **4** or **5**. The HNH angle remains constant at about 106°, whereas the HNLi angle closes from about 127° in the trigonal monomer to about 119 or 113° in the tetracoordinate dimer or trimer, respectively.

Calculated nitrogen/lithium parameters are compared in Table IV with the corresponding X-ray values for the amine derivatives. The theoretical N–Li (and other) distances are somewhat shorter, but this can be attributed to the steric and electronic effects of the substituents. The NLiN and LiNLi angles are reproduced within the stated error limits. All in all, there is pleasing agreement of theory with experiment.

In both **4** and **5**, the NH_2 groups are perpendicular to the Li–N ring planes. This allows the nitrogen lone-pair p orbitals to lie in the ring planes and to interact with the lithium atoms (compare Figures 1 and 3 with Figures 2 and 4). To probe the effect of such lone-pair orientations, we calculated fully planar arrangements of the dimer and trimer by imposing D_{2h} (**8**) and D_{3h} (**9**) symmetries. The geometries of **8** and **9** (Table III) show a decrease (0.04–0.05 Å) in the N–Li bond lengths and widening in the NLiN bond angles relative to **4** and **5**.

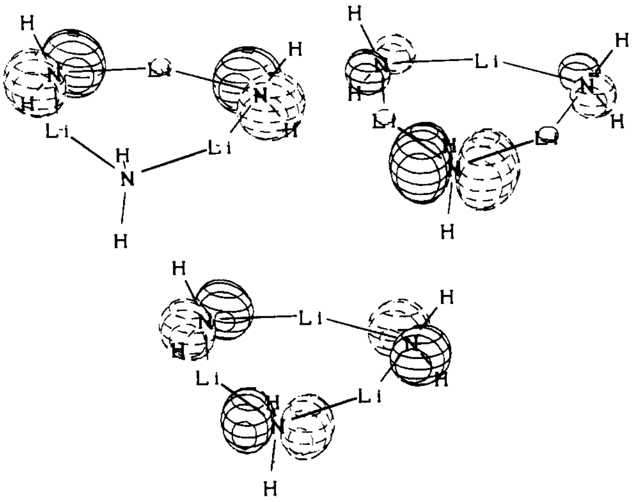


Figure 3. Three highest occupied MO's of the perpendicular $(LiNH_2)_3$ trimer. The degenerate 5e′ HOMO's of **5** are shown at the top; the $1a_2'$ MO (bottom) has nearly the same energy. Because of the diffuse character of the Li p orbitals, these are not apparent in the plots even though the coefficients are significant.

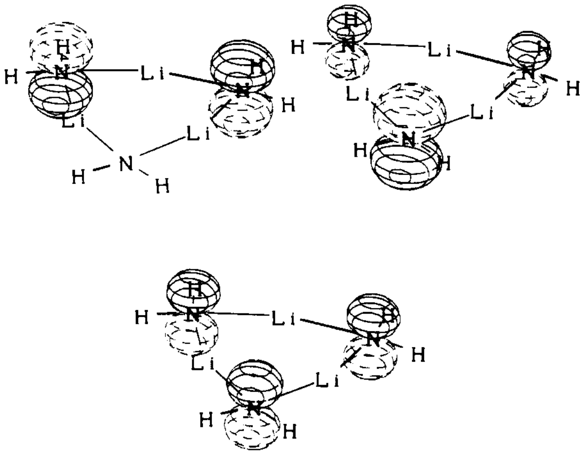
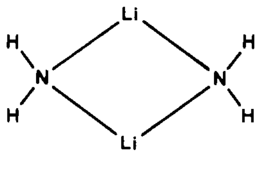
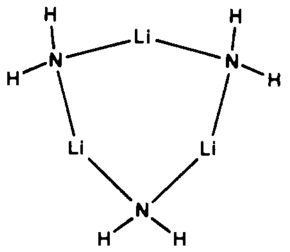


Figure 4. Three highest occupied MO's of the planar $(LiNH_2)_3$ trimer (**9**). The degenerate 1e″ HOMO's are shown at the top; the $1a_2''$ MO (bottom) has nearly the same energy despite cyclopropenium ion like π symmetry. The nitrogen p overlap populations are negligible, and this six-π-electron species has no real "aromatic" character (see text).



8, D_{2h}



9, D_{3h}

At all theoretical levels (Table II), the perpendicular arrangements, **4** and **5**, were considerably more stable than the all-planar alternatives, **8** and **9**. The dimer was studied more extensively with regard to basis set variations. The energy difference between **4** and **8** depended more on the inclusion of diffuse functions than polarization functions, and the smaller 3-21+G basis set performed better than 6-31G* in this respect.

Since **8** has four π and **9** six π electrons, "antiaromatic" vs. "aromatic" behavior is possible. The **4** → **8** energy difference per monomer unit, about 13 kcal/mol by using the best estimates, is almost the same as the **5** → **9** difference, on the same basis. No convincing alternating behavior is found, nor is it really to be expected in such highly ionic systems. As Gimarc has pointed out in similar contexts,[27] the π lone-pair electrons in **8** and **9** are largely localized on the nitrogen atoms, and the 4 + 2 rule does not apply. The Mulliken π-overlap populations in **8** and **9** between N and Li are positive but very small and are nearly zero between nitrogens (see Figures 2 and 4).

The greater stability of the perpendicular (**4** and **5**) over the planar (**8** and **9**) arrangements is due to the more favorable orientation of the nitrogen "lone-pair" orbital toward the two adjacent lithium atoms. The total N–Li overlap populations are significantly higher in **4** and **5** than in **8** and **9**. The highest occupied MO's are compared in Figures 1–4. These MO's for **4** and **5** are suggestive of multicenter covalent bonding involving lithium, although to some extent at least the basis functions on lithium are helping to describe the nitrogen electrons (basis set superposition error (BSSE)).[28] This is shown by the decrease in the energy differences between **4** and **8** and between **5** and **9** as the basis set is improved.

The overlap populations in all four of these species show the Li···Li interactions to be antibonding. The actual values are basis set dependent (and hence are not given), but the trends are consistent at any given theoretical level. The same is true for the charges but those on Li decrease somewhat on going from the dimers, **4** and **8**, to the trimers, **5** and **9**. The Li and N charges are greater in the planar forms, **8** and **9**, than in **4** and **5**, respectively.

The MO energies also lead to the same conclusions. The eigenvalues of the two higher MO's of **4** (MO's 11 and 12, Figure 1) and MO 11 of **8** (Figure 2) all are nearly the same at all basis set levels. Only the b_{2g} HOMO of **8**, which has π^* character and no possible lithium involvement due to symmetry, is higher in energy. In contrast, the corresponding π^*-like orbital of **4** (MO 11, Figure 1) does have lithium p-orbital involvement and actually lies a little below its π-like counterpart (MO 12, Figure 2).

However, the eigenvalues of all the other valence MO's of **8** lie below those of **4**, and the total electronic energy of **8** is much lower. This is overcome by the higher nuclear–nuclear repulsion energy of **8**, and **4** can also said to be more stable on this basis. As can be seen from Table III, most of the heavy-atom separations are greater in **4**. We note that Wannagat proposed a bonding model for **2** in 1969,[29] based on qualitative considerations, which is the semilocalized equivalent of our MO picture.

A simple extension of the electrostatic model[11,30,31] also can explain the observed energy differences between perpendicular and planar forms. If full positive and negative charges are centered on the 3-21G optimized lithium and nitrogen positions, the calculated gain in Coulombic energy on going from the monomer to the dimer is nearly the same for **4** as for **8** (about 53 kcal/mol).[11,31] However, if one assumes that half of the charge at nitrogen resides in each of the two lobes of the π orbital, the perpendicular form (**4**) becomes more favorable electrostatically whereas the energy of the planar form (**8**) increases. If a distance of 0.6 Å between the nucleus and the half-electrons (partial negative charges) in the π-orbital lobes is assumed in the monomer as well as in both dimers, "Coulombic dimerization energies" of −76.6 (**4**) and −44.5 kcal/mol (**8**) are calculated. These values are in reasonable agreement with the data in Table II. Hence, the assumption of fully ionic N–Li bonds also is consistent with our data.

Green et al.[33] found $[(CH_3)_3Si]_2NLi$ to be a dimer in the gas phase by mass spectrometry. The PE spectrum showed groups of bands, A–G. Our MNDO calculations on this dimer suggest a minor modification of the assignments made by these authors. While band A is due to the N π electrons, as assigned, the N lone pairs described as "σ" are split between bands B and C. The assignments of bands C + D to combinations of Si–N and Si–C ionizations is confirmed. Although the calculated values are generally 0.6 eV too high, there is reasonable qualitative agreement between the experimental and MNDO binding energies.

Association Energies

The $LiNH_2$ dimerization (to **4**) and trimerization (to **5**) energies (Table II) are sensitive to the level of theory employed and, due to BSSE,[28] are overestimated by inadequate basis sets. The same is true for energy differences between perpendicular (**4** and **5**) and planar (**8** and **9**) geometries (Table I). Split-valence basis sets, such as 3-21G and 6-31G, do not have enough flexibility to describe the nitrogen lone pairs in the NH_2Li monomer adequately.[30] In the dimer or trimer, this problem is alleviated by the basis functions on the additional lithium in the vicinity. With larger basis sets, the nitrogen lone pair in $LiNH_2$ is represented satisfactorily; lower, more accurate association energies are calculated. The perpendicular nitrogen p orbitals in **8** and **9** are affected much less by lithium functions (BSSE is negligible or small), and the association energies involving these structures are much less dependent on the basis set. Diffuse functions are needed to help describe the nitrogen lone pairs in the perpendicular geometries **4** and **5** and are more effective than polarization functions for this purpose.[21] Polarization and diffuse functions together give the best results.

Judging from the MP2/6-21G vs. 6-21G differences, electron correlation corrections are unimportant in **4** and have only a modest effect in **8**. This behavior is typical for molecules with high ionic character. Zero-point energy corrections are also small.

While electrostatic interactions between nitrogen and lithium (also facilitated in the planar conformations) dominate the situation,[11,30] we believe a smaller covalent contribution is present. We analyze the situation in greater detail elsewhere[31] but note here that the experimental dimerization energies of LiF and of LiOH (61.4 ± 8 and 62.4 ± 12 kcal/mol, respectively)[8] are about the same as our best value for $(LiNH_2)_2$ (Table II). The calculated dimerization energy of CH_3Li, 42 kcal/mol,[7] is much less. Both fluorine and oxygen are more electronegative than nitrogen, and a marked trend in the dimerization energies, LiF > LiOH > $LiNH_2$ > $LiCH_3$ is expected on a purely electrostatic basis.[11,31] The involvement of the nitrogen (and to some extent the oxygen) lone pairs in

---

(27) Gimarc, B. M.; Trinajstić, N. *Pure Appl. Chem.* **1980**, *52*, 1443.

(28) Boys, S. F.; Bernardi, F. *Mol. Phys.* **1970**, *19*, 553. Carsky, P.; Urban, M. "Ab Initio Calculations, Methods and Applications in Chemistry"; Springer-Verlag: Berlin, 1980; p 176–177. See also ref 30.

(29) Wannagat, U. *Pure Appl. Chem.* **1969**, *19*, 329. Wannagat, U.; Niederprüm, H. *Chem. Ber.* **1961**, *94*, 1540.

(30) See: Collins, J. B.; Streitwieser, A., Jr. *J. Comput Chem.* **1980**, *1*, 81. Klein, J.; Kost, D.; Schriver, W. G.; Streitwieser, A., Jr. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 3922. Streitwieser, A., Jr., private communication.

(31) For a short report on the detailed study of ref 11, see: Schleyer, P. v. R. *Pure Appl. Chem.* **1983**, *55*, 355. Kaufmann, E.; Clark, T.; Schleyer, P. v. R., in press.

(32) Jorgensen, W. L. *QCPE* **1977**, *14*, 340. See: Jorgensen, W. L.; Salem, L. "The Organic Chemist's Book of Orbitals"; Academic Press: New York, 1973.

(33) Green, J. C.; Payne, M.; Seddon, E. A.; Andersen, R. A. *J. Chem. Soc., Dalton Trans.* **1982**, 887.

multicenter bonding is responsible for the extra stabilization that leads to the observed order of dimerization energies[11,31] LiF ~ LiOH ~ $LiNH_2$ >> $LiCH_3$.

The estimated $LiNH_2$ trimerization energy, about −120 kcal/mol, also is quite high and may even exceed the energy gain on $(LiF)_3$ formation (−116.8 ± 12 kcal/mol).[8] The calculated trimerization energy of $(CH_3Li)_3$ is much less, about −82 kcal/mol.[7]

The disproportion energy of $3(LiNH_2)_2 \rightarrow 2(LiNH_2)_3$ (−54.1 kcal/mol at 3-21G//3-21G) clearly favors the trimer over the dimer. The experimental observation of both dimers and trimers of $(Me_3Si)_2NLi$ can be attributed to steric effects of the bulky groups and possible solvation energy differences.

In agreement with experiment,[14] recent calculations of Raghavachari[34] on $(LiNH_2)_4$ indicate a planar eight-membered ring (D_{4h} symmetry) to be preferred over a tetrahedral arrangement (D_{2d} symmetry). The disproportion energy, $4(LiNH_2)_3 \rightarrow 3(LiNH_2)_4$, also is negative, but to a lesser extent (−25.9 kcal/mol, also at 3-21G/3-21G).

Acknowledgment. We thank Professor J. Atwood for his interest and information prior to publication, U. Fischbach for preliminary calculations on the lithium amide dimer, and A. Sawaryn for his contributions to the program used at Erlangen. Support was provided by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft.

Registry No. **4**, 89043-68-5; **5**, 88656-96-6.

---

(34) Raghavachari, K., unpublished calculations privately communicated.

Contribution from the Department of Chemistry,
University of New Orleans, New Orleans, Louisiana 70148

Investigation of ^{67}Zn Coordination Effects on the ^{15}N NMR Spectra of Coordinated Ligands[1]

BRAD P. BAMMEL and R. F. EVILIA*

Received July 26, 1983

A new method for the assignment of zinc(II)–nitrogen coordination schemes is reported. In this method ^{15}N NMR spectra are acquired of complexes enriched in zinc-67 and complexes at natural abundance. Resonances due to nitrogens coordinated to the zinc are broadened by scalar interaction of the nitrogen with the coordinated quadrupolar isotope while uncoordinated nitrogens show no effect from the isotopic enrichment. The method is tested with bis(diethylenetriamine) and bis(histidine) complexes. Solvent and temperature conditions are reported that repress rapid chemical exchange and allow observation of the broadening in even simple ligand systems.

The unambiguous identification of binding sites utilized by potentially polydentate ligands to coordinate to metals has been a topic of considerable interest to chemists for many years. A large group of biologically significant macromolecules are metalloenzymes that coordinate transition metals at their active site in their biologically active forms. Because of the importance of such molecules, a great many studies of the coordination details have been reported.[2-20] Within this class of compounds, zinc-containing metalloenzymes have proven to be especially difficult to study because of the lack of a good spectroscopic "handle" for the metal.

This paper reports the investigation of a new method for the assignment of coordination details in compounds containing zinc–nitrogen bonds. This method relies on the enhancement of ^{15}N T_2 relaxation by scalar coupling to a high-spin nucleus.[21] It is the purpose of this paper to demonstrate that significant ^{15}N T_2 relaxation enhancement by ^{67}Zn is observed in model compounds of known bonding. The experimental conditions under which chemical exchange is repressed and the desired behavior is observed are reported.

Experimental Section

All chemicals, except as specifically noted below, were obtained from commercial sources in the highest available purity and were used without further purification. ^{67}Zn was obtained from Oak Ridge National Laboratories as 89.68% isotopically pure zinc oxide. Diethylenetriamine was distilled at reduced pressure and stored under nitrogen in the dark until used.

All NMR spectra were recorded on a JEOL FX90Q spectrometer employing 10-mm NMR tubes. A 1.7-mm capillary containing deuterium oxide or acetone-d_6 was used for the lock signal. Neat formamide in a second capillary held alongside the lock capillary provided the ^{15}N reference signal when a nitrogen reference was desired. Temperature control was provided by the JEOL NM-VTS variable-temperature control unit calibrated with methanol.

---

(1) Presented in part at 184th National Meeting of the American Chemical Society, Kansas City, MO, Sept 12–17, 1982. Submitted in partial fulfillment of Ph.D. degree (B.P.B.) at the University of New Orleans, Oct 1983. Financial assistance from the National Science foundation for the purchase of the FT NMR instrument through Grant CHE 78-02081, from a Merck foundation faculty development grant (R.F.E.), and from the Cancer Association of Greater New Orleans (B.P.B.) is acknowledged.

(2) Dabrowiak, J. C.; Greenaway, F. T.; Grulich, R. *Biochemistry* **1978**, *17*, 4090–5.

(3) Williamson, K. L.; Williams, R. J. P. *Biochemistry* **1979**, *18*, 5966–72.

(4) Oppenheimer, N. J.; Rodriguez, L. O.; Hecht, S. M. *Biochemistry* **1979**, *18*, 3439–45.

(5) Dabrowiak, J. C.; Tsukayama, M. J. *J. Am. Chem. Soc.* **1981**, *103*, 7543–50.

(6) Lenkinski, R. E.; Dallas, J. L. *J. Am. Chem. Soc.* **1979**, *101*, 5902–6.

(7) Dabrowiak, J. C.; Greenaway, F. T.; Longa, W. E.; Van Husen, M.; Croake, S. T. *Biochim. Biophys. Acta* **1978**, *517*, 517–26.

(8) Kessler, H.; Hehlein, W.; Schuch, R. *J. Am. Chem. Soc.* **1982**, *104*, 4534–40.

(9) Naganawa, H.; Takita, T.; Umezawa, H.; Hull, W. E. *J. Antiobiot.* **1979**, *32*, 539–41.

(10) Gust, D.; Moon, R. B.; Roberts, J. D. *Proc. Natl. Acad. Sci. U.S.A.* **1975**, *72*, 4696–700.

(11) Mantsch, H. H.; Saito, H.; Smith, I. C. P. *Prog. Nucl. Magn. Reson. Spectrosc.* **1977**, *11*, 211–72.

(12) Chlebowski, J. F.; Coleman, J. E. "Metal Ions in Biological Systems"; Marcel Dekker: New York, 1974; Vol. 6, Chapter 1.

(13) Zegzhde, G. D.; Gulya, A. P.; Neikaoskii, S. I.; Trilyupa, F. M. *Koord. Khim.* **1976**, *2*, 1031–5.

(14) Albert, A. *Biochem. J.* **1952**, *50*, 690–8.

(15) Evans, W. P.; Monk, C. B. *Trans. Faraday Soc.* **1955**, 1244–50.

(16) Li, C.; Chen, M. C. M. *J. Am. Chem. Soc.* **1958**, 80, 5678–80.

(17) Perrin, D. D.; Soyce, I. G. *J. Chem. Soc. A* **1968**, 53–7.

(18) Fabray, M. E.; Koenig, S. H.; Shillinger, W. D. *J. Biol. Chem.* **1970**, *45*, 4256–62.

(19) Haffner, P. H.; Goodsaid-Zalduondo, F.; Colman, J. E. *J. Biol. Chem.* **1974**, *249*, 6693–5.

(20) Armitage, I. M.; Uiterkamp, A. J. M.; Chlebowski, J. F.; Coleman, J. E. *J. Magn. Reson.* **1978**, *29*, 375–96.

(21) Pople, J. A. *Mol. Phys.* **1958**, *1*, 168–74.