

2x signal than of the 5n. Interpretation of other signals and couplings was verified by double resonance experiments, and comparing them with the NMR data of norbornadiols^{10,13} and norbornatriols.^{11,12} The results are presented in Figs. 1 and 2.

The mass spectra of IIIA and IVA (C₅H₁₃ClO) were quite similar; M⁺ peaks at *m/e* 160 and 162 were detected. The base peak at *m/e* 66 can be attributed to the cyclopentadienyl cation (C₅H₅⁺), as in the case of starting compound (I). The other characteristic peaks in the mass spectrum of IIIA and IVA were at *m/e* 124, 93, 92, 91, 79, 58, 45, and 36. M⁺ peaks were at *m/e* 161 and 163 in the mass spectra of IIIB and IVB. In each case the base peak was at *m/e* 67 and was due to the cation (C₅H₅D⁺). The other characteristic peaks in mass spectra of IIIB and IVB were at *m/e* 125, 94, 93, 92, 80, 67, 58, 45, and 36 (run with a Perkin-Elmer gas chromatograph mass spectrometer Model 270).

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A Comparison of *ab initio* and Semi-empirical Calculations on Li⁺(NH₃)

AE STØGARD

Department of Chemistry, University of Bergen, N-5014 Bergen, Norway

The comparison between the *ab initio* and CNDO/2 method on the hydration of Li⁺ is reported in a separate paper.¹ The ammonia molecule is now substituted for the water molecule to investigate whether the *ab initio* calculations on Li⁺(NH₃) compared to the CNDO/2 method gives results similar to those found for the Li⁺(H₂O) and Li⁺(H₂O)₂ systems.

During the calculations the geometry of the ammonia molecule was kept constant at the experimental values: $R_{\text{N-H}} = 1.01$ Å and $\angle \text{HNH} = 107^\circ$. The three hydrogens lie in the *xy*-plane and N-Li lies on a line perpendicular to the *xy*-plane.

For the *ab initio* calculations the program IBMOL^{2,3} was used. This program uses gaussian type functions

$$g = Nx^l y^m z^n e^{-ar^2} \quad (1)$$

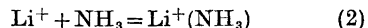
where α is the orbital exponent and N is a normalisation constant. The calculations were performed with the following basis set:

$$\begin{aligned} & \langle \text{H}|4 \rangle \text{ contracted to } \langle \text{H}|2 \rangle \\ & \langle \text{N}|7,3 \rangle \text{ contracted to } \langle \text{N}|4,2 \rangle \\ & \langle \text{Li}|7,2 \rangle \text{ contracted to } \langle \text{Li}|4,2 \rangle \end{aligned}$$

Orbital exponents and contraction coefficients are tabulated in Table 1. $R_{\text{Li-N}}$ was varied to find the distance corresponding to minimum energy.

The semi-empirical calculations are based on the CNDO theory as developed by Pople and co-workers.⁴⁻⁶ The computations were performed with the QCPE program.⁷ All parameters were taken from the original papers without any modification.

The results are given in Table 2. The calculated ammoniation energies (ΔE) for the reaction



are also listed here.

The ΔE for the CNDO/2 calculation is much greater than for the *ab initio*. The ΔE for *ab initio* calculation is sensitive to the basis set.¹ No experimental ΔE value is available for the Li⁺(NH₃) system.

Table 1. Contracted Gaussian basis set for $\text{Li}^+(\text{NH}_3)$.

Atom	Type	Function No.	Coefficients C	Exponents α
H	s	1	0.01906	16.7019
			0.13424	2.51663
			0.47449	0.567196
			1.0	0.154146
N	s	1	0.004479	2038.41
			0.034581	301.689
			0.164263	66.4630
			0.453898	17.8081
			1.0	5.30452
			1.0	0.764993
			1.0	0.234424
			1.0	0.234424
	p	1	0.119664	5.9546
			0.474629	1.23293
			1.0	0.286752
			1.0	0.286752
Li	s	1	0.005889	284.399
			0.044471	42.3482
			0.194745	9.37924
			0.474138	2.50578
			1.0	0.733345
			1.0	0.073733
	p	1	1.0	0.039787
			1.0	0.154
			1.0	0.154
			1.0	0.057

Table 2. Equilibrium distances and ΔE 's for $\text{Li}^+(\text{NH}_3)$.

	NH_3 $-E$ (a.u.)	Li^+ $-E$ (a.u.)	Li^+NH_3 $-E$ (a.u.)	$-\Delta E$ (kcal/mol)	$R_{\text{Li}-\text{N}}$ (Å)
<i>ab initio</i>	56.098647	7.233138	63.417165	53.6	1.98
CNDO/2	13.87307		14.01947	91.9	2.19

Experimental Li-N distances in four-coordinated lithium compounds are reported for $\text{Li}(\text{NH}_3)_4$ ⁸ where $R_{\text{Li}-\text{N}} = 1.94$ Å, and for LiCN ⁹ with $R_{\text{Li}-\text{N}} = 2.06$ Å. The *ab initio* result is closer to the experimental data than the CNDO/2 calculation. The same was found for the $\text{Li}^+(\text{H}_2\text{O})$ and $\text{Li}^+(\text{H}_2\text{O})_2$ systems,¹ but for these the differences between the equilibrium distances of the *ab initio* and the CNDO/2 method were greater.

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