Theoret. Chim. Acta (Berl.) 39, 17—24 (1975)

An SCF-MO Study of the Electronic Structure of the [$LiNH_3$] Cation and Related Molecules

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Received November 25, 1974/March 18, 1975

We examine the effect of the charge and degree of protonation of a ligand on its power as a donor. The following molecules are studied $[LiNH_3]^+$, $LiNH_2$, Li_2NH, and Li_3N, which may to a good approximation be regarded as combinations of Li^+ ions with the ligands NH_3, NH_2^-, NH^{-2}, and N^{-3}.

Key word: [$LiNH_3$] cation

1. Introduction

Our objective in this paper is to examine the effect of the charge and degree of protonation of a ligand on its power as a donor. To this end we present the results of *ab initio* Gaussian Molecular Orbital (MO) calculations on $LiNH_3^+$, $LiNH_2$, Li_2NH and Li_3N, since these can be regarded to a good approximation as combinations of Li^+ ions with the ligands NH_3^+, NH_2^-, NH^{2-}, and N^{3-}.

We discuss chiefly population analysis indices and density difference maps for the molecules concerned. All the calculations were performed using the basis sets given by Dunning [1] augmented with polarisation functions (*p* on H and Li with *d* on N) and extra diffuse basis functions for the valence shells, since it is well known that these are necessary for obtaining reliable results for negative ions. The exponents of these diffuse orbitals were chosen so as to continue the approximate geometric progressions shown by the exponents in Dunning's basis sets. In detail, the contraction schemes were; H: $(5, 1)\rightarrow[3, 1]$; Li: $(10, 3)\rightarrow[4, 3]$, and N: $(11, 7, 2)\rightarrow[5, 5, 2]$.

All the calculations were performed on the University of Manchester CDC 7600 computer, and we are grateful to the UMRCC staff for their cooperation.

We discuss firstly any points of interest arising in the calculations on the individual molecules, than give a short general summary.

2. Calculations

2.1. $LiNH_3^+$ and NH_3

Pilot calculations using an *sp*-basis set [1] were performed to find the scale factor for the hydrogen 1*s* orbital which was then kept constant for all further calculations. We found a scale of 2.6 in Dunning's terminology [1]. A partial

Table 1. Variation of energy, dipole moment and population indices with R(Li–N) for $\mathrm{LiNH_3^+}$. The dipole moment is with N as origin, α is defined by the equation $\mu=\mu(\mathrm{NH_3})+\alpha R(\mathrm{N{-}Li})$ and the valence population with respect to N is given in brackets

R(Li–N)/bohr	2.46	3.0	3.5	3.71	4.0	5.0	∞
a) Energy E_{total} (hartree)	−63.3786	0.4917	0.5171	0.5188	0.5172	0.5008	0.4544
b) Dipole Moment							
μ	1.511	1.956	2.396	2.591	2.870	3.908	–
α	0.876	0.867	0.869	0.872	0.878	0.911	1.0
Analysis of μ:							
$\mathrm{Li^+}$ fragment	2.115	2.785	3.238	3.417	3.673	4.656	–
$\mathrm{NH_3}$ fragment	− 1.005	−1.009	−0.917	−0.879	−0.841	−0.785	−0.644
Overlap terms	0.401	0.179	0.074	0.052	0.036	0.035	–
c) Population analysis							
Atomic charges:							
Li	+ 1.058	1.001	0.951	0.937	0.927	0.935	1.0
N	− 0.556	−0.443	−0.367	−0.345	−0.323	−0.288	−0.187
H	+ 0.166	0.147	0.139	0.136	0.132	0.118	0.062
Li–N							
overlap popn.	− 0.203	−0.040	0.078	0.108	0.131	0.122	0
val^c^pop^n^ of H	− 0.267	−0.082	0.014	0.036	0.052	0.051	0
N–H:							
overlap popn.	0.695	0.697	0.701	0.702	0.704	0.711	0.733
val^c^pop^n^ of H	0.558	0.564	0.568	0.569	0.571	0.576	0.594

geometry optimisation gave the N–Li bond length to be 3.72 bohr[1] and the four bonds pointing almost exactly to the corners of a regular tetrahedron. The N–H bond length was assumed to be 1.912 bohr [2] throughout. For the sake of comparison, a calculation was run on $\mathrm{NH_3}$ with the same bond length and tetrahedral geometry giving an energy of −56.218 1 hartree, which compares well with the value −56.226 8 hartree obtained by Rajogopal [3].

Table 1 shows the variation of certain quantities with the Li–N distance. The potential energy surface is rather flat, and by a polynominal fit of five of the calculated points we estimate a stretching force constant for the Li–N bond as 0.042 atomic units, giving a frequency of 473 $\mathrm{cm^{-1}}$ for $[\mathrm{Li^7NH_3}]^+$ if interactions between the Li–N and N–H vibrations are neglected.

Section (b) of Table 1 analyses the dipole moment with N as origin. One can write

$$\mu(\mathrm{LiNH_3})=\mu(\mathrm{NH_3})+\alpha R(\mathrm{Li{-}N})\ldots \tag{1}$$

where α would be exactly 1 if no charge transfer or polarisation had taken place. The fact that α is less than 1 suggests that there is charge transfer from N to Li, whilst an examination of the next terms in the Table shows that the approach of the $\mathrm{Li^+}$ also greatly increases the polarity of $\mathrm{NH_3}$. The population analysis indices [4] show

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[1] The atomic system of units is generally used in this paper: hartree = a.u. of energy ≈ 4.359 828 aJ; bohr ≡ a_0 = a.u. of length ≈ 0.529 177 × 10^{-10}m.

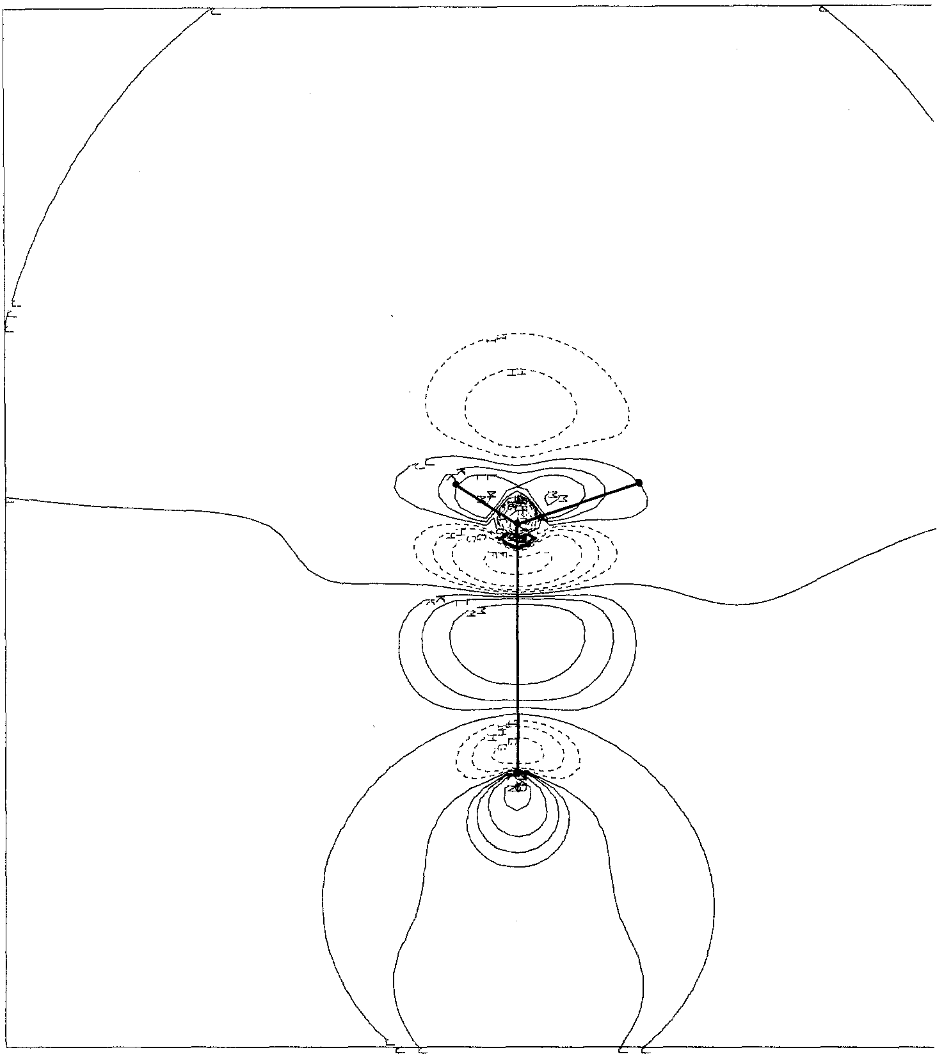

Fig. 1

(a) substantial negative contributions to the overlap population at small values of R(N–Li)

(b) the N–H overlap populations are hardly altered by the approach of the Li^+; it is the net populations of N and H where the polarisation of the NH_3 fragment can be seen.

Figures 1 and 2 give respectively the density difference summed over all MO's of a_1 symmetry, and the density difference for the e_xMO of $[LiNH_3]^+$ compared with Li^+ and NH_3. In Fig. 1 the Li cation is polarised away from N. There appear to be two distinct regions in the NH_3 fragment where electron density has been redistributed; one on each side of the N nucleus. In each, electron density is moved directly towards the Li. The charge appears to affect the N electrons only, the H

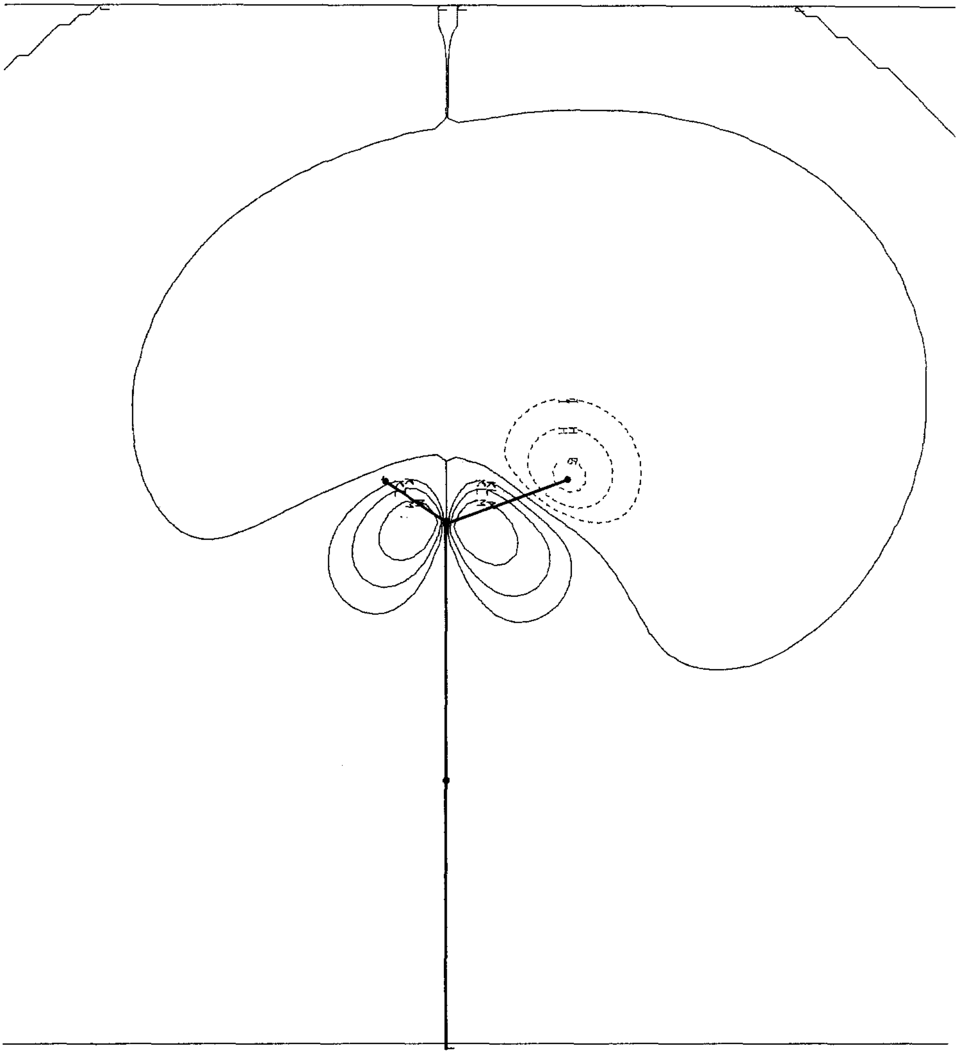

Fig. 2

nuclei lying very close to the zero contour line. Figure 2 in contrast shows how the electron density is transferred from close to the H nucleus into a forwardly polarised p_x orbital on H.

2.2. $LiNH_2$

A geometry search revealed an energy minimum corresponding to a planar molecule with $H\hat{N}H$ angle 110° and an N–Li bond length 3.368 bohr. This is much shorter than the average distance in the crystal (4.03 bohr [5]) and also rather shorter than the Li–N distance in $LiNH_3^+$. The N–H bond length was again assumed to be 1.912 bohr.

The potential well for the variation of energy with N–Li distance is also rather deeper than that of LiNH$_3^+$. From the value of $\partial^2 E/\partial R^2$ at the minimum we estimate a stretching frequency of 800 cm^{-1} for LiNH. In many respects the quantities shown in Table 1 vary in the same way for LiNH$_2$ as for LiNH$_3^+$ (and so need not be given): thus the contribution of the NH$_2$ fragment to the component of dipole moment along the N–Li bond becomes more negative as the Li cation approaches, whilst the overlap term increases. However, there are some significant differences.

(a) The charge on the H atoms hardly change as the Li$^+$ cation approaches. Apparently it is the electron density directly associated with the N atom, rather than the N–H bonds, which is polarised by the Li$^+$ cation.

(b) The overlap population is almost equally shared at its maximum value.

(c) Maximum charge transfer to Li, as measured by the atomic charges, occurs beyond 5 bohr.

2.3. LiNH *and* LiN

A geometry search gave energy minima with N–Li bond lengths 3.365 bohr and 3.300 bohr for Li$_2$NH and Li$_3$N respectively (an X-ray study of the Li–N distance in solid Li$_2$NH gives 4.14 bohr), and again the molecules are predicted to be planar. The Li$\hat{N}$Li angle was calculated to be 146° and again the N–H bond length was taken to be 1.912 bohr.

For purposes of comparison, a calculation was also run on the N^{3-} ion. The total energy fits well the sequence obtained by Clementi and McLean [7] for N, N$^-$ and N^{2-} ions.

An examination of the density difference map (not shown) between Li$_3$N and its ions shows that all the outer regions of the molecule are in a negative contour region: the N^{3-} ion has apparently contracted greatly in forming the molecule. There is in addition a large build-up of charge between the N and Li nuclei, rather towards the N end of the bond: there is an almost equal build-up of charge on the far side of the N nucleus, and a heavy depletion in a direction at right angles which illustrates the finding of Bader *et al.* [8] that atoms bonding through *p*-electrons, such as N, experience a "quadrupole polarisation" whatever the symmetry of the applied field.

3. Discussion

Table 2 assembles the calculated and estimated energies for the molecules and ions studied. Section 1 of Table 3 combines the SCF total energies with correlation energies after Clementi [10] to estimate the successive electron affinities of N. The first two affinities agree moderately well with the estimate by Baughan [11] who used Glockler's technique [12] of extrapolating ionisation potentials along an isoelectronic series. The remainder of the Table computes the enthalpy of formation of LiNH$_3^+$, LiNH$_2$, Li$_2$NH, and Li$_3$N from their ions. For comparison we give a rough estimate from the ionic model [13]. For LiNH$_3^+$

Table 2. Calculated SCF energies for certain molecules and ions

Species	Present calculations E/hartree	Literature E/hartree
$[LiNH_3]^+$	−63.51883	
$LiNH_2$	−63.07778	
Li_2NH	−69.91335	
Li_3N	−76.75398	
NH_3	−56.21815	−56.2268 [3]
		−56.1812 [9]
NH_2^-	−55.54562	−55.5009 [9]
NH^{2-}	−54.66332	−54.5076 [9]
N^{3-}	−53.68831	−53.2117 [9]
$N(^4S)$		−54.40091 [7]
$N^-(^3P)$		−54.32189 [7]
$N^{2-}(^2P)$		−54.02903 [7]

Table 3. Calculated standard enthalpies/kJmol^{-1} for certain processes, all assumed gas-phase

Process	SCF kJmol^{-1}	SCF+ correlation [10]	Other estimates
1. $N+e=N^-$	+207 [7]	+26	+58[11] −5±10[14] −54[15]
$N^-+e=N^{2-}$	+769 [7]	+596	+800 [11]
$N^{2-}+e=N^{3-}$	+895	+667±50	+1293 [11]
$N+3e=N^{3-}$	+1872	+1289±50	+2151 [11]
2. $Li^++NH_3=LiNH_3^+$	−169		−82[a]
3. $Li^++NH_2^-=LiNH_2$	−3092		−650[a]
4. $2Li^++NH^{2-}=Li_2NH$	−2041		−2201[a]
5. $3Li^++N^{3-}=Li_3N$	−3562		−4653[a]

[a] Calculated by the ionic model, Eqs. (2) and (3) of text.

the binding energy of a point charge e and a point dipole μ is

$$\Delta H = -\left(1-\frac{2}{n}\right)\mu R_{eq}^{-2}\ldots \tag{2}$$

where R_{eq} is the equilibrium Li–N distance and the appropriate value for the repulsive exponent n is 6. For the other molecules the energy is

$$\Delta H = -\left(1-\frac{1}{n}\right)A R_{eq}^{-1}\ldots \tag{3}$$

where the Madelung constant A depends on the geometry and charges of the ions (1.0, 3.388, and 7.163 for $LiNH_2$, Li_2NH, and Li_3N respectively).

As Table 3 shows, this simple ionic model rather underestimates the enthalpy of formation of $LiNH_3^+$ and $LiNH_2$ but agrees quite well with the SCF value for Li_2NH and Li_3N. It is certainly not always true (as Baughan suggests) that the lattice energy of the "ideal" ionic lattice is less negative than for the real lattice.

Table 4. Population analysis for the various Li complexes at geometries corresponding to their energy minima (see text). For each Li (or H) the valence population of Li (or H) with respect to N is given in brackets, and for $LiNH_3^+$ the terms "σ" and "π" are applied in the loose sense of with respect to rotations about the Li–N bonds

	NH_3	$[LiNH_3]^+$	$LiNH_2$	Li_2NH	Li_3N
a) Overall indices					
Li–N overlap population					
Total		0.108(0.036)	0.290(0.082)	0.165(−0.059)	0.030(−0.119)
σ		0.102(0.034)	0.191(0.038)	0.036(−0.122)	−0.114(−0.156)
π		0.006(0.003)	0.099(0.004)	0.129(0.063)	0.144(0.037)
N–H overlap population	0.733(0.594)	0.702(0.569)	0.714(0.606)	0.693(0.628)	
N net population	6.769	6.874	7.444	8.361	9.196
N valence population	0.418	0.471	0.423	0.513	0.655
N charge	−0.187	−0.345	−0.867	−1.875	−2.850
Li net population		2.029	2.070	2.106	2.139
Li valence population		0.034	0.077	−0.059	−0.114
Li charge		0.937	0.853	0.952	0.975
H net population	0.372	0.315	0.409	0.416	
H valence population	0.566	0.549	0.584	0.614	
H charge	0.062	0.136	0.007	−0.030	
b) Gross populations					
N *s*	3.546	3.574	3.553	3.660	3.752
N *p*	3.634	3.769	4.174	5.048	5.911
N *d*	0.007	0.003	0.139	0.167	0.188
Li		2.013	2.016	1.896	1.833
Li *p*		0.046	0.131	0.151	0.192
H *s*	0.914	0.841	0.964	0.997	
H *p*	0.024	0.024	0.030	0.033	
c) Bond dipoles					
$\mu(N^- – H^+)$	0.144	0.280	0.028	0.001	
$\mu(N^- – Li^+)$		3.484	2.830	2.503	2.207
$[\mu(N–Li)/R(N–Li)]$		0.939	0.840	0.743	0.669

The results of a population analysis [4] are shown in Table 4. What is perhaps surprising is the way the Li–N overlap population breaks down into "σ" and "π" contributions (referring to symmetry with respect to rotations about the Li-N bond in the case of $LiNH_3^+$). The π contribution increases steadily whilst the σ population rises slightly from $[LiNH_3]^+$ to $LiNH_2$, then falls to Li_3N; it becomes rather more equally shared along the series. A partial explanation may be that (according to the gross populations) the occupancy of the N 2*s* orbitals increases relatively little from $[LiNH_3]^+$ to Li_3N, that of the 2*p* orbitals several times more; hence the electron affinity of the 2*p* orbitals will decrease faster, making them better donors. This still does not explain why N $2p_\sigma$ to Li overlap does not increase; but granted the power of Li as a π acceptor the increase in the π overlap population is certainly to be expected.

4. Conclusions

This paper has surveyed a variety of Li–N bonds from the weak bond in $[LiNH_3]^+$ with its slight degree of charge transfer, to the much more "covalent" bond in Li_3N with its strong p_π-p_π interaction. Indeed if the gross populations on Li are a reliable guide, Li_3N and Li_2NH are far removed from the ionic ideal. The large electron density rearrangements in Li_3N bear this out. Further evidence has been obtained for the "quadrupole polarisation" of Bader *et al.* [8] which persists even in the three-fold symmetry assumed for Li_3N.

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