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Factors Influencing the Stability of Cations (Amine-H-amine)$^+$ and Related Ions

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The existence of the hydrogen-bonded cations $(L{-}H{-}L)^+$ where L represents pyridine or a substituted pyridine, was first suggested for salts of lanthanoid chelates $L_2H{\cdot}Ln(hfaa)_4$ (Ln = lanthanoid; hfaa = $CF_3COCHCOCF_3$) and tetraphenyl borates $L_2H{\cdot}BPh_4$ [1]. This suggestion was not supported by definitive evidence, although ESCA data indicate a difference between the nitrogen environments in 4-Mepy·HCl (4-Mepy = 4-methylpyridine) and in $4\text{-MepyHBPh}_4{\cdot}4\text{-Mepy}$: the N (1s) binding energy in the tetraphenyl borate is 399.6(1) eV, mid-way between the values in 4-Mepy, 398.1(1) eV and 4-Mepy·HCl, 400.2(1) eV. Proof of the existence of such a cation was provided by an X-ray analysis of $(4\text{-Mepy})_2H^+BPh_4^-$ [2] which revealed a strongly hydrogen-bonded planar cation lying across a crystallographic centre of inversion with a very short N···N distance of 2.610(15) Å, and having the unique hydrogen located at the centre of symmetry. This finding has prompted a further study of the factors which influence the stability of cations of this type, no other examples of which appear to be known: it may be noted here that no evidence was obtained [1] for the persistence of these cations in solution.

We consider first the nature of the counter-ion X^-: for the decomposition of a crystalline salt (LHL)X into crystalline (LH)X and liquid (or gaseous) L, we may write, from a Born–Haber cycle:

$$\Delta H^{\phi} = +D(LH^+ - L) - \Delta H^{\phi}_{L} - \\ - [U(LH{\cdot}X) - U(LHL{\cdot}X)]$$

where $D(LH^+ - L)$ represents the gas-phase dissociation enthalpy of LHL^+ in LH^+ and L; ΔH^{ϕ}_{L} represents the enthalpy of vaporisation of liquid L; if L is a gas in its standard state (*e.g.* if L = NH_3) ΔH^{ϕ}_{L} will be set equal to zero; U(LH·X) and U(LHL·X) represent the lattice energies of LH·X and LHL·X respectively.

Unless L is a gas in its standard state $\Delta S^{\phi} \cong 0$, so that $\Delta G^{\phi} \cong \Delta H^{\phi}$.

Since LH^+ is always smaller than LHL^+, the term $\Delta U = [U(LH{\cdot}X) - U(LHL{\cdot}X)]$ is always positive; hence the only contribution which can make ΔH^{ϕ} positive, and hence ΔG^{ϕ} positive, thereby stabilising the salt (LHL)X is $D(LH^+ - L)$. ΔH^{ϕ}_{L} is small, and for a given value of $D(LH^+ - L)$ the stability is maximised if ΔU is minimised.

Introducing Kapunstinskii's approximation for the lattice energy [3], we may write

$$\Delta U = 2k\left[\frac{1}{r(LH) + r(X)} - \frac{1}{r(LHL) + r(X)}\right]$$

where k ≅ 1050 kJ mol^{-1}, and the r represent thermochemical radii [4].

Hence,

$$\Delta U = 2k\left[\frac{r(LHL) - r(LH)}{(r(LH) + r(X))(r(LHL) + r(X))}\right]$$

We now introduce the further approximation that the radius ratio of the cations LHL^+ and LH^+ is constant, *i.e.*

$$r(LHL) = p{\cdot}r(LH)$$

where p is a constant greater than unity.

So that

$$\Delta U = \frac{2k(p-1)r(LH)}{= p[r(LH)]^2 + (p+1)r(LH)r(X) + [r(X)]^2}$$

Now ΔU is a minimum when $\partial(\Delta U)/\partial r(LH)$ is zero, that is when $[r(X)]^2 = p{\cdot}[r(LH)]^2$: re-introducing $p = r(LHL)/r(LH)$ leads to the condition for minimisation of ΔU that

$$r(LHL){\cdot}r(LH) = [r(X)]^2$$

Hence to minimise ΔU, large LH^+ and LHL^+ require a large counter-ion X^-, and small LH^+, LHL^+ require a small X^-, in all cases such that r(X) is the geometric mean of r(LH) and r(LHL).

We turn now to the term $D(LH^+ - L)$, representing the enthalpy change of the gas-phase reaction

$$LHL^+_{(g)} \rightarrow LH^+_{(g)} + L_{(g)}$$

We have calculated ΔH^{ϕ}_{f} values, using the MNDO method [5, 6] with full geometry optimisation, for L, LH^+ and LHL^+ for a selection of bases, L, and ΔH^{ϕ}_{f} values together with $d(L - H^+)$ and $D(LH^+ - L)$ values, calculated using $\Delta H^{\phi}_{f}(H^+)$ = 1528.0 kJ mol^{-1} [7] are given in Table I. As expected the values of $D(L - H^+)$ indicate that NF_3 is a much weaker base than the remaining amines: the ordering of the

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TABLE I. Molecular Energies for LH^+ and LHL^+ (All values in kJ mol^{-1}).

L	$\Delta H_f^{\phi}(L)$	$\Delta H_f^{\phi}(LH^+)$	$\Delta H_f^{\phi}(LHL^+)$	$D(L - H^+)$	$D(LH^+ - L)$
NH_3	−26.3[a]	+689.2	+644.5	+812.5	+18.4
NF_3	−143.1[b]	+1018.8	+943.9	+366.1	−68.2
py	+120.2[c]	+785.7	+912.3	+862.5	−6.4
4-Mepy	+86.9	+747.0	+840.5	+867.9	−6.6
Me_3N	−11.6[d]	+728.5	+822.1	+787.9	−105.2
H_2NCHCH_2	+58.7	+769.4	[e]	+817.3	

[a] Experimental value, −45.6 [8]. [b] Experimental value, −124.7 [9]. [c] Experimental value, +144.8 [8]. [d] Experimental value −23.8 [8]. [e] Dissociates.

other values has to be viewed in the light of the probable errors in the two calculated values, $\Delta H_f^{\phi}(L)$ and $\Delta H_f^{\phi}(LH^+)$, since the differences between the several values of $D(L - H^+)$ are fairly small: where experimental values of $\Delta H_f^{\phi}(L)$ are available, they indicate typical calculated errors in the range ±20 kJ mol^{-1}. This means that the calculated values of $D(LH^+ - L)$, each of which is the small difference between two large quantities, may be qualitatively in error if they are close to zero. The value of $D(LH^+ - L)$ for NH_3 is positive as expected [10], while that for NF_3 is large and negative, indicative of the very low basicity of this amine: however the calculated values of py and 4-Mepy are small and negative whereas they are expected to be small and positive. For small values of $D(LH^+ - L)$, it is unlikely that any computational technique at present available can make reliable predictions of the sign of this term.

The calculated structures of $(NH_3)_2H^+$ and $(NF_3)_2H^+$ both had exact D_{3d} symmetry in which the N–H distances were 1.277 Å and 1.381 Å respectively: the symmetric N–H–N fragment is found also in $(4\text{-Mepy})_2H^+$, where the N–H distance is 1.269 Å, but in py_2H^+ there is an unsymmetric minimum in which the two N–H distances are 1.296 Å and 1.246 Å, giving an overall N···N distance of 2.544 Å, virtually identical with the 2.538 Å found in $(4\text{-Mepy})_2H^+$. For both of these aromatic cations, the isolated ion is calculated to have the two rings perpendicular, presumably due to repulsions between *ortho* hydrogens, with a barrier to planarity in the 4-methyl compound calculated as 5.7 kJ mol^{-1}, so that this is easily overcome in the crystal to give the observed planar cation.

Somewhat analogous to these cations are species $(L–X–L)^+$ where X = halogen, several salts of which have been structurally characterised [11–14] for X = Br or I. Although MNDO calculations are not yet possible for species containing bromine or iodine, we have made calculations for some species $(LX)^+$ and $(LXL)^+$ for X = Cl: in general, calculations with X = F failed to achieve self-consistence. The resulting molecular energies are given in Table II: these data indicate that the cations $(LClL)^+$ are more robust than $(LHL)^+$. Since our limited data indicate also that the dissociation energy is higher for $(LClL)^+$ than for $(LFL)^+$, it is possible that the energies in $(LBrL)^+$ and $(LIL)^+$ are higher still: it is noteworthy that ions of type $(LIL)^+$ persist in solution and so presumably have high dissociation energies.

TABLE II. Molecular Energies for LCl^+ and $LClL^+$ (All values in kJ mol^{-1}).

L	$\Delta H_f^{\phi}(L)$	$\Delta H_f^{\phi}(LCl^+)$	$\Delta H_f^{\phi}(LClL^+)$	$D(LCl^+ - L)$
NH_3	−26.3	+840.1	+666.7	+147.1
NF_3	−143.1	+1167.0	+1009.9	+14.0
py	+120.2	+917.1	+928.5	+108.8
Me_3N	−11.6	+893.0	+863.4	+18.0

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