Proton Transfer from NH_4^+ to NH_3; Floating Spherical Gaussian Orbital Calculations

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Summary Calculations have been made, using Frost's floating spherical Gaussian orbital method, of the hydrogen bond formed between NH_4^+ and NH_3 and of the proton transfer within this hydrogen-bonded system; a contraction in the NN separation in the transition state is obtained, in agreement with other calculations.

Delpuech *et al.*[1] and Merlet *et al.*[2] have carried out SCF–MO calculations for the hydrogen bond between NH_4^+ and NH_3 and the proton transfer from the ion to the molecule. Along with other calculations for reaction paths, we have studied this system (see Figure) using the simple wave function of Frost[3] in which pairs of electrons are assigned to orbitals formed from single Gaussian functions (the method of floating spherical Gaussian orbitals, FSGO). We have performed three sets of calculations. In I, complete minimisation was carried out for the three systems examined: (a) the separated NH_3 and NH_4^+, (b) the system of minimum energy, *i.e.* the hydrogen bonded complex, and (c) the symmetrical transition state for the transfer. Because a poor result is obtained for the HNH angle in NH_3 by the FSGO method, two more sets of calculations were carried out. In II, the angles in NH_3 were fixed at the experimental value of 106·3°. Angles for the other systems were fixed at what seemed to be appropriate values intermediate between this and 109·5°. These are given in the Table. In III, all bond angles were fixed at 109·5°. The results are listed in the Table, the wave functions being summarised in the lower part of the Table. In all calculations the two NH_3 groups were staggered relative to one another. The calculated proton affinities of NH_3 are given in the Table and, for all models, these are of the same order of magnitude as the experimental value.[4]

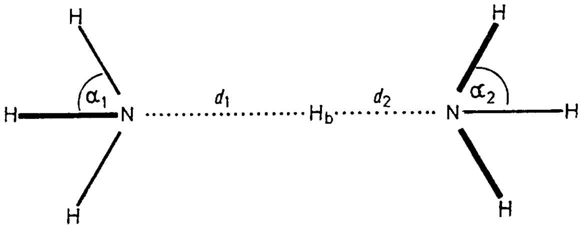

Figure. The conformation of $(H_3NHNH_3)^+$ adopted in these calculations.

Because such a poor value is obtained for the HNH angle in NH_3 by the FSGO method, the results for model I

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TABLE

The structure, properties and wave functions for $(H_3NHNH_3)^+$ in the nine models described in this paper[a]

	I			II			III		
	NH_3+ NH_4^+	Min. energy	Symm. trans. state	NH_3+ NH_4^+	Min. energy	Symm. trans. state	NH_3+ NH_4^+	Min. energy	Symm. trans. state
N–N dist./Å	—	2·80	2·47	—	2·66	2·48	—	2·63	2·48
HNH angles/deg. α_1	87·9	91·7	100·8	(106·3)	(107·0)	(107·9)	(109·5)	(109·5)	(109·5)
α_2	109·5	108·6	100·8	109·5	(108·7)	(107·9)	109·5	(109·5)	(109·5)
NH_b dist./Å d_2	0·99	1·01	1·235	0·99	1·04	1·24	0·99	1·055	1·24
ΔE (rel. to min.)/kcal mol^{-1}	18·7	0	16·8	29·2	0	5·7	34·2	0	2·6
NH_3-Proton affinity (expt. 207 kcal mol^{-1})	208	—	—	235	—	—	249	—	—
Orb. exp.									
N(NH_3)	13·024	13·007	12·992	13·005	12·992	12·989	13·001	12·989	12·988
NH(NH_3)	0·4155	0·4237	0·4444	0·4293	0·4360	0·4479	0·4294	0·4636	0·4478
N(NH_4^+)	12·982	12·984	12·992	12·982	12·986	12·989	12·982	12·986	12·988
NH(NH_4^+)	0·4636	0·4625	0·4444	0·4636	0·4604	0·4479	0·4636	0·4601	0·4478
lone pair (NH_3)	0·3785	0·3815	0·4126	0·3884	0·3891	0·4055	0·3905	0·3906	0·4049
NH_b(NH_4^+)	0·4636	0·4640	0·4126	0·4636	0·4519	0·4055	0·4636	0·4461	0·4049
Dist. of orb. centre[b] from N atom (in a.u.[c])									
lone pair	−0·1440	−0·0360	0·3976	0·1261	0·1886	0·3682	0·1661	0·2246	0·3701
N^+H_b	0·7950	0·7464	0·3976	0·7950	0·6706	0·3682	0·7950	0·6412	0·3701
NH orb. dist. (in a.u.) from									
N(NH_3)	0·8026	0·7845	0·7983	0·8518	0·8120	0·8019	0·8457	0·8068	0·7995
N(NH_4^+)	0·7950	0·8031	0·7983	0·7950	0·8028	0·8019	0·7950	0·8030	0·7995
Angle subt. by NH orbitals at N									
N NH_3	83·5	89·9	100·9	101·2	104·2	107·2	103·9	106·4	108·6
N NH_4^+	109·5	107·9	100·9	109·5	108·4	107·2	109·5	109·2	108·6

[a] Angles in parentheses arbitrarily fixed.

[b] Towards the other N atom is +ve, away from it, −ve. [c] 1 a.u. = 0·5292 × 10^{-10} m.

are of less significance than those from models II and III. The salient features are then: (i) there is a contraction in the NN separation in the transition state compared with the hydrogen-bonded complex (0·18 for II and 0·15 Å for III); (ii) the barrier for proton transfer is much smaller than the energy of the hydrogen bond (5·7 kcal mol^{-1} against 29·2 for II, and 2·6 against 34·2 for III). Using SCF–MO methods, Delpuech *et al.*[1] obtained 0·19 Å for (i), while Merlet *et al.*[2] obtained 0·13 Å. For (ii) Delpuech *et al.*[1] obtained 2·5 and 27·6 kcal mol^{-1} and Merlet *et al.*[2] 2 and 36. All three calculations therefore yield the same general picture: (i) a contraction in the transition state which should show itself in the entropy of activation, and (ii) a low barrier for transfer along with a fairly strong hydrogen bond. For the FSGO calculations, those in II are probably to be preferred. The barrier is rather high and this probably results from the fact that the simple function has limited flexibility. However, the results do show that the FSGO method yields, with a short calculation, results that are correct in form.

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