Intrabridgehead Hydrogen-bonded Ions: Spectroscopic Characteristics and the Question of Single *vs.* Double Minimum Potentials

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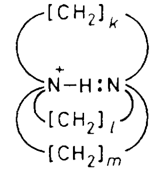
N.m.r. and i.r. data on inside-protonated medium-ring bicyclic diamines are presented and discussed; the $\Delta\delta(^1H,^2H)$ test shows that only the linear $N^+–H:N$ bond within inside-protonated 1,6-diazabicyclo[4.4.4]-tetradecane is of the single minimum type.

We have converted a number of medium-ring bicyclic diamines into inside-protonated ions which possess intrabridgehead $N^+–H:H$ bonds.[1,2] An *X*-ray structure determination[3] of *in*[4.4.4]H^+Cl^- shows it to contain a linear hydrogen bond with the shortest known N,N distance (2.53 Å). We report the varied n.m.r. and i.r. spectroscopic characteristics of the ions in Table 1, all with hydrogen bonds more or less isolated from external influences. A key question is whether any of these ions have a true single minimum potential for the hydrogen bond[4,5] and we use the $\Delta\delta(^1H,^2H)$ test[6] to provide an answer.

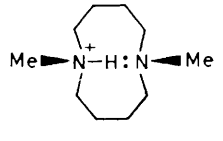
Table 1. Spectroscopic data of the *in*[*k.l.m*]H^+ ions.

	Symmetry[a]	$\delta(^1H)$[b]	$\Delta\delta(^1H,^2H)$[b]	ν_{NH}[e]/ cm^{-1}	ν_{NH}/ν_{ND}
in[5.4.2]H^+		13.5		2450	
in[6.4.2]H^+		10.7		2450	
in[5.5.2]H^+	C_2	12.35		2475	
in[6.3.3]H^+	C_2	17.25	0.76	2200	[f]
in[5.4.3]H^+		17.48	0.53	1400—1900	[f]
in[4.4.4]H^+	D_3	17.40[c]	0.06[c]	1400—1900	[f]
in[6.4.3]H^+		14.62	0.65	2150	1.24
in[5.5.3]H^+	C_s	17.20[d]	0.87[d]	2100	1.26
in[5.4.4]H^+		16.19	0.43	1500—2200	[f]
in[6.5.3]H^+		13.78	0.58	2200	1.25
in[5.5.4]H^+	C_2	15.30	0.92	1500—2300	*ca.* 1
cis-in[4.4.Me_2]H^+[g]	C_2	15.71	0.54	1500—2300	*ca.* 1

[a] Highest symmetry possible assuming no eclipsed C–C bonds (remainder C_1). [b] In $CHCl_3$–$CDCl_3$ unless otherwise stated; shifts are not solvent sensitive except for *in*[5.5.2]H^+ which shifts to δ 13.15 in neat CF_3CO_2H. All spectra were recorded on a JEOL FX200 spectrometer. Shifts are defined as positive if $\delta(^1H) > \delta(^2H)$. [c] Owing to the small quantity of partially *N*-deuteriated material available, ^1H and ^2H spectra were run on the same sample directly from the inside-protonation reaction in 85% aqueous H_2SO_4, CH_3OH and CD_3OH were internal references; $\delta(^1H)$ is the same in this medium as in $CDCl_3$. [d] In H_2O–D_2O. [e] In $CHCl_3$ or CH_2Cl_2 solution, the ν_{NH} position is not solvent sensitive. [f] Not measured, since only partially *N*-deuteriated samples have been made (ref. 2). [g] Prepared as a BF_4^- salt from 1,6-diazabicyclo-[4.4.0]decane by methylation (CH_3I), reductive cleavage (Al–Hg), reductive methylation (CH_2O, $NaBH_3CN$), and protonation. The observation of five ^{13}C lines for this species at −100 °C, coalescing to three lines at higher temperatures, is proof of the *cis* stereochemistry shown.



in[*k.l.m*]H^+



cis-in[4.4.Me_2]H^+

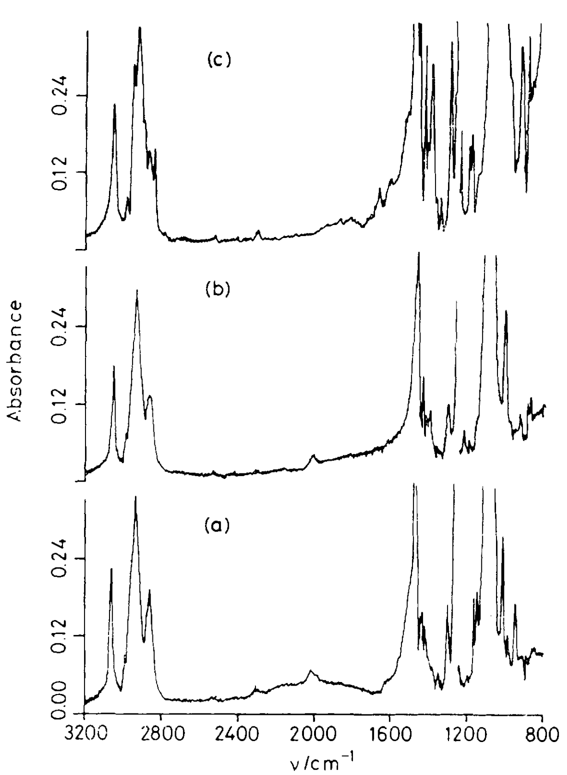


Figure 1. I.r. spectra of (a) *in*[5.5.3]$H^+ClO_4^-$, (b) *in*[5.4.4]H^+-ClO_4^-, and (c) *in*[4.4.4]$H^+BF_4^-$. Spectra were run on 0.16 M solutions in CH_2Cl_2 in 0.1 mm cells, using a Nicolet 7000 Fourier transform i.r. spectrometer. Solvent absorptions have been subtracted. The sharp band near 2000 cm^{-1} in (a) and (b) is probably a ClO_4^- overtone. No broad bands below 1400 cm^{-1}, which might be ascribed to ν_{NH}, are seen in the spectra.

Forsén *et al.*[6] have shown that $\Delta\delta(^1H,^2H)$, the difference between the proton and deuterium chemical shifts, is (a) negligible for weak hydrogen bonds, becomes (b) large and positive (up to 0.72 p.p.m.) for strong hydrogen bonds where there is a low central barrier in a double minimum potential, and becomes (c) zero or weakly negative for a strong bond with a single minimum potential ('symmetrical' hydrogen bond). A semi-quantitative theory of these effects was given, the large, positive $\Delta\delta$ values resulting from the anharmonicity of the double minimum potential. The $\Delta\delta(^1H,^2H)$ values in Table 1 indicate that all the ions we have studied have this double minimum (low central barrier) potential, with one exception: the *in*[4.4.4]H^+ ion which gives a $\Delta\delta(^1H,^2H)$ value consistent with a single minimum potential, in agreement with expectations based on the *X*-ray structure. We suspect that the linearity of this bond is significant; all other single minimum hydrogen bonds are linear or nearly so.

The data on the other ions are notable for their variety. There is no correlation between $\delta(^1H)$ and $\Delta\delta$, and only a very crude one between $\delta(^1H)$ and ν_{NH}. Forsén *et al.*[6] found a correlation of $\delta(^1H)$ with $\Delta\delta$ for O–H:O bonds in a chemically more varied set of compounds. However no-one has examined such a chemically similar, but geometrically diverse set of hydrogen-bonded species before. Each spectroscopic parameter will probably be an individual function of N,N distance and N–H–N angle. Detailed discussion is impossible without more structural information but our set of ions may include ones with N^+–H:N bonds longer than *in*[4.4.4]H^+ but still nearly linear (*in*[5.5.4]H^+ ?) as well as others with short but strongly bent bonds (*in*[5.5.2]H^+ ?). Force field calculations (MM2 program) on the diamines themselves give some idea of the likely non-linearity, though structures will obviously change on protonation. The lone pairs in [6.3.3]diamine make a 30° angle with the N,N axis; in [5.5.2]diamine this angle is 38°. Scheiner[7] has made an *ab initio* study of distortions in the H_3N^+–H:NH_3 system. He found that the barrier to proton transfer increased on lengthening the N,N distance and on distorting the bond from linearity. A single minimum potential was only found for linear bonds of N,N distance <2.5 Å. At 2.73 Å (the minimum energy distance) the barrier was 16 kJ mol^{-1} and was increased by 9 kJ mol^{-1} when the bond was bent such that both lone pairs made a 20° angle with the N,N axis.

The ν_{NH} band ($\equiv \nu_{as}$ for a single minimum potential) does seem to vary in an explicable way with gross structure. The three diaminoethane derivatives have ν_{NH} = *ca.* 2450 cm^{-1}; here the N,N distance is probably short and the N–H–N angle acute. Four of the five ions with an >N–$[CH_2]_3$–N< fragment have ν_{NH} = *ca.* 2150 cm^{-1} and ν_{NH}/ν_{ND} *ca.* 1.25, well below the classical limit.[4,8] In all these ions the band shape is quite normal, Figure 1(a). Next come three >N–$[CH_2]_4$–N< derivatives *in*[5.4.4]H^+, *in*[5.5.4]H^+, and *in*[4.4.Me_2]H^+, which show, Figure 1(b), more or less steadily rising absorption from 2500 to 1500 cm^{-1}; in these cases deuteriation changes the band shape without causing any clear overall shift. Finally, the band for *in*[5.4.3]H^+ and *in*[4.4.4]H^+ is complex and of low intensity, Figure 1(c). Perhaps the latter feature is associated with very restricted proton motion in these tight cages?

We intend to gather more structural information and to use these ions as a test-bed for comparing the results from the fascinating variety of experimental methods now available[9–13] for probing the single/double minimum question.

We thank the S.E.R.C. for a grant and a Research Studentship (to R. E. M.) and Dr. Peter Goggin for help with Fourier transform i.r. spectra.

Received, 1st June 1983; Com. 706

References

1 R. W. Alder, A. Casson, and R. B. Sessions, *J. Am. Chem. Soc.*, 1979, **101**, 3652.

2 R. W. Alder, R. E. Moss, and R. B. Sessions, *J. Chem. Soc., Chem. Commun.*, 1983, 997, accompanying communication.

3 R. W. Alder, A. G. Orpen, and R. B. Sessions, *J. Chem. Soc., Chem. Commun.*, 1983, preceding communication.

4 J. Emsley, *Chem. Soc. Rev.*, 1980, **9**, 91, provides a recent review of strong hydrogen bonding.

5 It has been pointed out that the crucial point comes when the central maximum in a double minimum potential becomes lower than the zero point energy level: M. M. Kreevoy and T. M. Liang, *J. Am. Chem. Soc.*, 1980, **102**, 3315.

6 G. Gunnarsson, H. Wennerström, W. Egan, and S. Forsén, *Chem. Phys. Lett.*, 1976, **38**, 96; L. J. Altman, D. Laungani, G. Gunnarsson, H. Wennerström, and S. Forsén, *J. Am. Chem. Soc.*, 1978, **100**, 8264.

7 S. Scheiner, *J. Phys. Chem.*, 1982, **86**, 376.

8 R. Clements, F. N. Masri, and J. L. Wood, *Chem. Commun.*, 1971, 1530 report similar numbers for the linear Me_3N^+–H : NMe_3 complex; we suspect the similarity is accidental.

9 Neutron diffraction, see *e.g.* J. Roziere, C. Belin, and M. S. Lehman, *J. Chem. Soc., Chem. Commun.*, 1982, 388.

10 E.s.c.a.: E. Haselbach, A. Hendriksson, F. Jachimowicz, and J. Wirz, *Helv. Chim. Acta*, 1972, **55**, 1757; R. S. Brown, *J. Am. Chem. Soc.*, 1977, **99**, 5497; R. S. Brown, A. Tse, T. Nakashima, and R. C. Haddon, *J. Am. Chem. Soc.*, 1979, **101**, 3157.

11 Deuterium quadrupole relaxation times: W. Egan, G. Gunnarsson, T. E. Bull, and S. Forsén, *J. Am. Chem. Soc.*, 1977, **99**, 4568; L. M. Jackman, J. C. Trewella, and R. C. Haddon, *J. Am. Chem. Soc.*, 1980, **102**, 2519.

12 The isotopic perturbation method: M. Saunders and M. R. Kates, *J. Am. Chem. Soc.*, 1980, **102**, 6867 and references therein.

13 Isotopic fractionation factors: ref. 5 and M. M. Kreevoy and B. A. Ridl, *J. Phys. Chem.*, 1981, **85**, 914.