Proton Double Minimum Potentials in Symmetric Hydrogen Bonds

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Summary A series of hydrogen-bonded cations, $(BHB)^+$ where B is a heterocyclic base, have been characterised spectroscopically, and show evidence for a double minimum proton potential.

THE possibility that the proton potential in the hydrogen bond may have a double minimum has received a great deal of attention. In particular it has been suggested that coupled proton tunnelling in G–C and A–T base pairs can be responsible for mutations and the loss of the genetic code.[1] Although *coupled* proton motions in hydrogen bonds can certainly give rise to a double minimum potential, *e.g.* in liquid water, or acetic acid dimer, none of the evidence, mainly spectroscopic, relating to isolated hydrogen bonds is free from alternative explanations involving only a single minimum potential. In particular the most notable spectroscopic effect, the splitting of the AH stretching mode ν_S in H but not in D bridges, can often be traced to the interaction with other vibrations. Before the occurrence of a d.m. potential is asserted, the effects in other parts of the spectrum must also be considered.

In this connection we have examined an extensive series of hydrogen bonded cations, of the type $(B^1HB^2)^+$, where B^1 and B^2 can be the same, or dissimilar bases. We here summarise our findings on the symmetric cations $(B^1HB^1)^+$, where B^1 is a heterocyclic base. We know of only two previous references to the occurrence of such systems inferred from conductivity studies of the salts in pyridine[2a] or acetonitrile solutions.[2b]

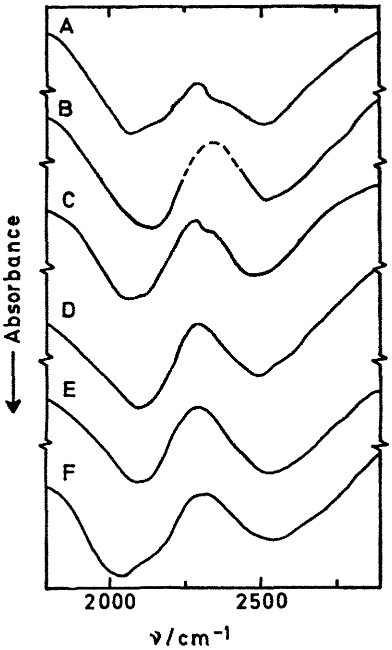

FIGURE 1. ν_S *Bands of* A, $(pyHpy)^+$; B, $([D_5]pyH[D_5]py)^+$; C, $(4\text{-Me-pyH4-Me-py})^+$; D, $(4\text{-Et-pyH4-Et-py})^+$; E, $(3\text{-Cl-pyH3-Cl-py})^+$; F, $(quinHquin)^+$

(1) We confirm that a wide range of heterocyclic bases, *e.g.* pyridine, 4-Me-, 4-Et- and 3-Cl-pyridine, and quinoline form stable complexes, with well characterised vibrational spectra.

(2) Provided the counteranion is not strongly hydrogen bonding, *e.g.* such as Cl^-, the spectra are independent of the anion (which may be BF_4^-, $SbCl_6^-$, PF_6^-, ClO_4^-, or BPh_4^-), and are therefore characteristic of the cation.

(3) Provided the solvent does not enter into a hydrogen bond displacement process, the cation spectra are independent of the solvent, which may be excess of base, or for example acetonitrile or nitromethane. The relative intensity of the cation bands are never observed to change, and we therefore ascribe them to a single species. Job's law type studies confirm the expected $(B_2H)^+$ molecularity.

(4) The ν_S band of the symmetric cations shows a pronounced doublet structure. The appearance of the band changes only slightly with the nature of the base in the systems examined (Figure 1) (Table 1).

TABLE 1

Observed frequencies of ν_S *and* ν_σ *in hydrogen bonded cations* $(B_2H)^+$

Base	ν_S/cm^{-1} $(B_2{}^+H)$	ν_S/cm^{-1} $(B_2\,D)^+$	ν_σ/cm^{-1} $(B_2{}^+H)$	ν_σ/cm^{-1} $(B_2{}^+D)$
Py	2530, 2080	1930	137·5	136
$[D_5]$Py	2530, 2100	1920	135	
4-Me-Py	2500, 2075	1920	123·5	
4-Et-Py	2510, 2105		115	
3-Cl-Py	2545, 2145	1923		
Quin	2532, 2170sh 2055s			

(5) In all the corresponding D bridged complexes examined, the ν_S band has a single maximum (Figure 2). The shoulders and side bands, which vary from system to system, can be accounted for as interactions with internal mode combinations. If ν_H/ν_D is measured from the centroids of the ν_S bands, the ratio is *ca.* 1·2, extremely low even for H-bonds.

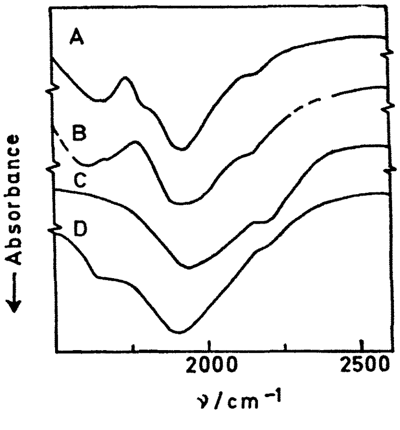

FIGURE 2. ν_S *Bands of* A, $(pyDpy)^+$; B, $([D_5]pyD[D_5]py)^+$; C, $(3\text{-Me-pyD3-Me-py})^+$; D, $(3\text{-Cl-pyD3-Cl-py})^+$

(6) Solutions containing the complex can be chilled to *ca.* 80 K without separation of the simple $\overset{+}{\mathrm{BH}}\,\overset{-}{\mathrm{X}}$ salt, as shown both by the absence of ν_{NH} around 3300 cm^{-1}, and also by monitoring the frequency of certain internal modes of the bases, which are sensitive to the form of association. The small relative intensity change of the ν_S doublet components indicates that the ground states involved in the transition are either the same or at least do not differ greatly in energy.

(7) The cations have a well defined absorption band in the far i.r. [*e.g.* 137·5 cm^{-1} for $\mathrm{py_2H^+}$ (Table 1)] which decreases only slightly in frequency on deuteriation. This shows decisively that it is not ν_τ, the tunnelling inversion. The frequency generally depends directly on the mass of the base, and the band can be assigned with confidence to the *inter*-molecular mode ν_σ. The band exhibits no doublet structure, and the width is not appreciably changed in the D bonded system. The frequency and profile is independent of counter-ion.

(8) Several of the internal modes of the bases shift substantially (in some cases by over 20 cm^{-1}) on complexing. Although each base mode produces two modes in the complex, never more than one i.r. band is seen. Some base modes can also be seen in the Raman spectrum. Again they are singlets, which frequently do *not* coincide with the corresponding i.r. bands. In bases of symmetry C_{2v}, *e.g.* pyridine and 4-Me-pyridine, the a_2 modes are still unobservable in the complexes.

(9) The NH in-plane bending δ_{NH} can be located in $(\mathrm{py_2H})^+$ at 1255 cm^{-1} in the i.r., not far removed from its frequency in the $\mathrm{py\overset{+}{H}}$ ion (1249 cm^{-1}).[3]

(10) No symmetric complex is formed by 2,6-lutidine or 2,4,6-collidine. Models show that provided the complexes are planar, steric hindrance between the methyl groups in these cases would require an N–N distance of $\geqslant$3·5 Å. However, twisting the rings would relax this restriction. In this connection it is interesting that the asymmetric complex of 2,6-lutidine with pyridine does form. Here, again provided the complex is planar, a model indicates the N–N distance as $\geqslant$ *ca.* 2·55 Å. This suggests that the rings are coplanar, and the N–N distance is in the range 2·55—3·5 Å.

(11) We have been unable to observe either ν_σ or ν_S in the Raman spectrum.

From these observations we can make the following inferences: (*A*) The ν_S band doubling is not due to Fermi resonance effects[4,5] arising from ring modes, as the latter vary widely, while ν_S is unaffected. (*B*) The ν_S band doubling is not due to combinations involving ν_σ for this frequency also varies while ν_S is unaffected. (*C*) It is more difficult to reject 2 × δ_{NH}, which would be near 2500 cm^{-1} in all the systems, as the origin of the upper band. This overtone can indeed be greatly intensified in hydrogen-bonded systems.[6] Although not impossible, this origin is unlikely for the following reasons. (i) The upper component develops continuously into the single ν_S band as the system becomes asymmetric. (ii) Its contour is always similar to, and the intensity proportional to, that of the lower component. (iii) It is never observed in D systems, (although special arguments to suit each case can account for this). (iv) If the lower component is taken to represent ν_S, then $\Delta\nu_S$ is *ca.* 1200 cm^{-1}, much greater than in the more strongly bonded hydrochloride salt. The shift of the corresponding D salt however, is similar to that of the hydrochloride (Table 2). Proton tunnelling is thus left as the most plausible origin for the ν_S band behaviour. (*D*) The theory relating the appearance of the internal modes of the bases due to interaction with the proton tunnelling motion has been developed. This extends quantitatively an idea of Cardwell, Dunitz, and Orgel[7] and provides a new method for determining the proton barrier parameters. Briefly, if ν_r is the frequency of a base internal mode characteristic of B, and ν_r' the counterpart in $\mathrm{B\overset{+}{H}}$ when $\nu_\tau \ll (\nu_r - \nu_r')$, (high barrier) each base mode should display two i.r. active bands in the complex. When $\nu_\tau \approx (\nu_r - \nu_r')$, four bands should derive from each internal mode. As ν_τ becomes greater than $(\nu_r - \nu_r')$ (progress towards a single minimum) only a single member of the quartet survives. The latter is observed and implies a single Raman band, which may only accidentally coincide with the i.r. band as is consistent with the Raman observations. The spectra thus indicate that ν_τ is at least greater than $(\nu_r - \nu_r')$, which can be up to 10 cm^{-1}. Thus the possibility of a deep double minimum is strongly ruled out.

TABLE 2

Comparison of frequencies of ν_s *in pyridinium salts*

$\mathrm{Py\overset{+}{H}BF_4^-}$	3290	$\mathrm{Py\overset{+}{D}BF_4^-}$	2454 2412	No H-bond
$\mathrm{Py\overset{+}{H}Cl^-}$	2439 2375	$\mathrm{Py\overset{+}{D}Cl^-}$	1985 1915	Strong H-bond
$\mathrm{Py\overset{+}{H}Py}$	2530 2080	$\mathrm{Py\overset{+}{D}Py}$	1920	

(*E*) The preservation of δ_{NH} argues against a centrally located proton, as does also the i.r. activity of ν_σ. A bent structure seems unlikely, in view of the inactivity of the a_2 modes, the closeness of ν_σ in the $\mathrm{py_2\overset{+}{H}}$ and $\mathrm{py_2{}^+D}$, and the insensitivity of any bands to the nature of the counterion.

Thus the weight of evidence favours a linear complex with a shallow double minimum potential, and rapid proton tunnelling. Although the expected splitting of the i.r. ν_σ band has not shown up, the components may be of very unequal intensity[8] and the objections to the high barrier and single minimum alternatives are more decisive. It is hoped that current n.m.r. and inelastic neutron scattering measurements will serve to check these conclusions.

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