

Crystallographic and Spectroscopic Evidence for an Asymmetric Proton Potential in a Formally Symmetric System

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Summary The crystal structure of $(\text{benzimidazole}_2\text{H})^+ \text{BF}_4^-$ has been shown to contain a long N-N hydrogen bond [$2.787(4) \text{ \AA}$] with the proton in an asymmetric single minimum; this is consistent with the vibrational spectrum, which also indicates a similar potential in solution.

MANY organic bases form hydrogen bonds with their conjugate cations to give formally symmetric complex cations, $(\text{BHB})^+$.¹ As with the analogous bihalide ions, the form of the proton potential has attracted particular interest. With heterocyclic bases the i.r. spectra typically show a doublet ν_s band in the H-bridged complexes, which has been taken to imply a symmetric double minimum potential² but other features of the vibrational spectra are difficult to reconcile with this model.³ By slowly cooling an equimolar mixture of benzimidazole and benzimidazolium tetrafluoroborate, it has been possible to obtain crystals analysing as $(\text{Bz}_2\text{H})^+ \text{BF}_4^-$ (Bz = benzimidazole). We now report their X-ray crystal structure and vibrational spectra.

Crystals of $(\text{C}_{14}\text{H}_{13}\text{N}_4)^+ \text{BF}_4^-$ are monoclinic, space group $P2_1/n$, $a = 5.797(1)$, $b = 9.231(1)$, $c = 27.480(1) \text{ \AA}$, $\beta = 90.060(5)^\circ$. X-Ray intensity data were collected with Cu-K α radiation on a Siemens four-circle diffractometer.

A total of 2778 independent reflections were measured (to $\theta = 70^\circ$), of which 348 were judged to be unobserved. The structure was solved by direct methods, and refined to a current $R = 0.055$.

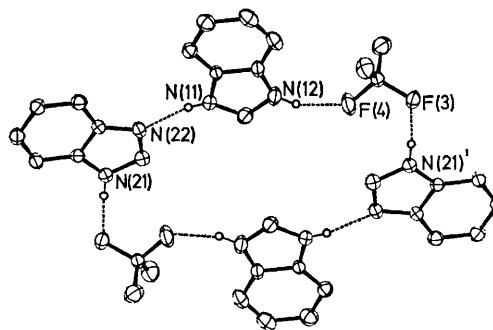


FIGURE 1. Perspective view of one of the sheets of $\text{Bz}_2\text{H}^+\text{BF}_4^-$ looking up the b axis, showing the system of hydrogen bonding.

The structure is made up of discrete columns of parallel sheets inclined at *ca.* 35° to a . Each sheet is separated by a cell translation in a , and is comprised of pairs of $(\text{Bz}_2\text{H})^+$

units related by a crystallographic centre of symmetry. These units are in turn linked by hydrogen bonds, through pairs of the fluoroborate anions related by the same symmetry centre. This forms a complete ring as illustrated in Figure 1. The hydrogen bond distances within the ring are: N(11)-N(22), 2.787(4); N(12)-F(4), 2.870(4); N(21)-F(3), 2.896(3) Å. The hydrogen in the N-N hydrogen bond was

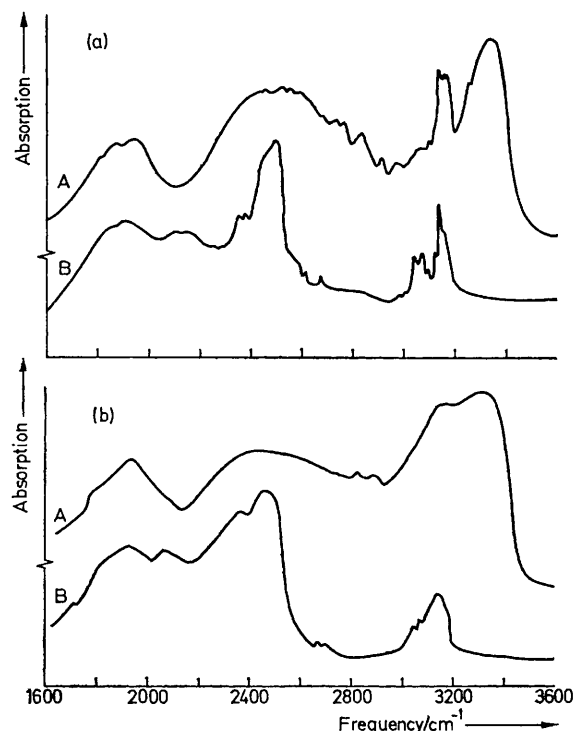


FIGURE 2. (a) I. r. spectra in the solid state, (hexachlorobutadiene mulls), of (A) $(\text{Bz}_2\text{H}^+)\text{BF}_4^-$ and (B) $(\text{Bz}_2\text{D}^+)\text{BF}_4^-$; where Bz = benzimidazole, $\text{Bz}' = [^2\text{H}_1]\text{benzimidazole}$. (b) The spectra of the above salts in (A) acetonitrile, and (B) $[^2\text{H}_3]\text{acetonitrile}$ respectively.

found unambiguously to be asymmetric and attached to N(11). This asymmetry is also reflected in corresponding differences in the bond lengths in the two imidazole rings.

¹ C. R. Witschonke and C. A. Kraus, *J. Amer. Chem. Soc.*, 1947, **69**, 2472; I. M. Kolthoff, D. Stocesoca, and T. S. Lee, *ibid.*, 1953, **75**, 1834; D. Feakins, W. A. Last, and R. A. Shaw, *J. Chem. Soc.*, 1964, 2387; J. F. Coetzee, G. R. Padmanabhan, and G. P. Cunningham, *Talanta*, 1964, **11**, 93.

² G. Zundel and J. Mühlinghaus, *Z. Naturforsch.*, 1971, **26b**, 546; W. Sessler and G. Zundel, *Z. Phys. Chem. (Frankfurt)*, 1972, 180; R. Clements, R. L. Dean, T. R. Singh, and J. L. Wood, *Chem. Comm.*, 1971, 1125.

³ R. Clements and J. L. Wood, *J. Mol. Struct.*, 1973, **17**, 265, 283; J. L. Wood, *ibid.*, p. 307.

Figure 2(a) shows the higher frequency range of the i.r. spectra of the solid complex salt, and also that in which the hydrogen bonding H atoms have been exchanged by D. Comparison with the spectra of similar $(\text{BHB})^+$ complex cations shows that the characteristic pair of peaks at ca. 2500 and 1900 cm^{-1} arise from the $\text{NH}\cdots\text{N}$ grouping, while the band at ca. 3330 cm^{-1} is due to the $\text{NH}\cdots\text{F}$ group. In the deuteriated salt, the broad absorption around 2000 cm^{-1} is due to $\text{ND}\cdots\text{N}$, and the $\text{ND}\cdots\text{F}$ group gives the band at 2460 cm^{-1} . From the crystal structure it is clear that the bands at 2500 and 1900 cm^{-1} cannot arise from the $0_+ \rightarrow 1_-$ and $0_- \rightarrow 1_+$ transitions of a symmetric double minimum potential. The 2500 cm^{-1} band, which evolves into the only component in the spectra of cations with bases of differing strength, most probably is the primary ν_8 (NH stretching) band, while 1900 cm^{-1} arises by Fermi resonance of an overtone or combination mode with ν_8 . In the middle frequency range, bands characteristic of both the donor and acceptor base can be distinguished. All these features are retained in solution, (Figure 2b) suggesting that here, too, the $\text{NH}\cdots\text{N}$ bond has an asymmetric single minimum potential.

Many other $(\text{BHB})^+$ complex cations involving heterocyclic bases, e.g. pyridine, quinoline, *N*-methylimidazole, or thiazole, have very similar vibrational spectra to the present ones, both in solution, and also in those cases when solid complexes can be obtained. In particular, they also display a pronounced doublet in the ν_8 band in H-bridged systems, which is replaced by a single band in the D-bridged analogues. It is therefore very probable that in these systems too the ν_8 doublet is not indicative of proton tunnelling in a symmetric double minimum potential, but is due to Fermi resonance, the potential again being of an asymmetric single minimum type.

The asymmetry producing the spectral features is only necessary on a short time scale, and can arise from the location of the counterion, the solvation, or the relative orientation of the bases. On a time scale long compared to molecular vibrations one expects the donor and acceptor bases not to retain their roles, in solution, so that on this time scale the cations become formally symmetric.

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