Infrared Evidence for Complex Hydrogen Bonded Cations

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Summary. The occurrence of a wide range of stable complex cations formed by the hydrogen bonding of two or more non-heterocyclic bases has been demonstrated by vibrational spectroscopy.

Two earlier communications[1,2] report the occurrence of a wide range of stable complex cations, of general formula $(B^1 HB^2)^+$ where B^1 and B^2 are both unifunctional heterocyclic nitrogen bases. We now report the occurrence, of a wide range of complex cations in which at least one of the bases is non heterocyclic, *e.g.* ammonia, aniline, n-butylamine, or trimethylamine. The occurrence of hydrogen bonding between bases of this type and their conjugate acids has been inferred from potentiometric studies.[3] The only spectra previously reported of comparable systems are those of ammonium salts in liquid ammonia.[4] We know of no report of the occurrence of complexes involving differing bases.

Types of complex are exemplified by the following (*a*) Trimethylamine self-complexing: Trimethylamine salts of acids with non-interfering anions, *e.g.* the fluoroborate or perchlorate, form complexes with free trimethylamine. The i.r. spectra are independent of counterion, and display a broad, strong ν_s band centred at *ca.* 2100 cm^{-1}, with no indication of double structure (Figure 1). Since the base

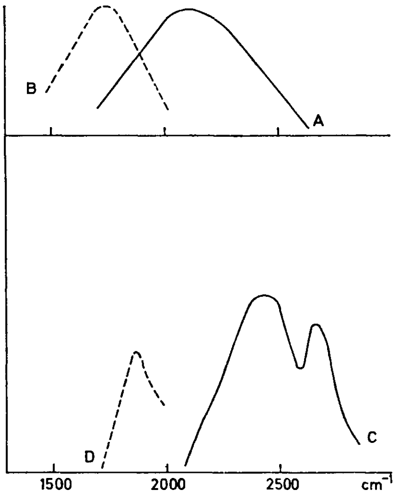

FIGURE 1. (*A*), *The i.r. spectra of trimethylammonium fluoroborate plus trimethylamine in acetonitrile*, (*B*), *Trimethylammonium-*[D_1] *fluoroborate plus trimethylamine in acetonitrile* (*C*), *Trimethylammonium fluoroborate in pyridine*, (*D*), *Trimethylammonium* [D_1] *fluoroborate in pyridine*.

can accept only a single proton in hydrogen bonding and the conjugate acid has only one bonding proton, the molecularity of the cation is inferred to be $(Me_3NHNMe_3)^+$. The ν_S band of the corresponding D bridged cation is at *ca.* 1750 cm^{-1} and notably less broad. The large shift in the ν_S frequency from its value in the free (non H-bonded) Me_3N^+H ion, *viz* 3170 cm^{-1} is indicative of a strong hydrogen bond, as is also the small (ν_H/ν_D) ratio (1·2). The ν_S band shows no evidence of proton tunnelling, so either a single minimum or a high barrier double minimum proton potential is present. In the middle frequency range, only single bands derived from the internal modes of the Me_3N moieties appear in the i.r. spectra, indicative of a single minimum. The far i.r. range has been scanned, but no band is observed below 400 cm^{-1} which can be ascribed to ν_σ. Without placing too great a weight on negative evidence, this also supports a centrosymmetric structure such as occurs in the $(FHF)^-$ ion. (*b*) Me_3N^+H–Pyridine complex: Trimethylammonium cations complex with a range of heterocyclic bases, and the observations with pyridine are typical. Figure 1 shows the ν_S band region displaying a strong, broad band centred around 2450 cm^{-1}, quite distinct from the spectra of either the $(pyHpy)^+$ or $(Me_3NHNMe_3)^+$ complexes. The spectra are independent of counterion, provided this is uncompetitive in H bonding. With excess of pyridine, the spectra indicate that no free Me_3N^+H ions are present. It is apparent that a new complex has been formed, and we infer, since both Me_3N and pyridine are unifunctional in hydrogen bonding, that the molecularity is probably $(Me_3NHpy)^+$.

The corresponding D bridged complex has the ν_S band at *ca.* 1850 cm^{-1} (Figure 1). Again the band is much sharpened. The ν_H/ν_D ratio (1·325) is greater than in the Me_3N self complex, and typical of a 'normal' hydrogen bond. The shift of ν_S by 720 cm^{-1} from its value in the free trimethylammonium ion also indicates a weaker bond than in the Me_3N self complex. The only indication of abnormality is the pronounced secondary maximum at *ca.* 2650 cm^{-1} on the ν_S band of the H bridged cation. However, this is of quite different appearance to the doublet structures of the heterocyclic base systems, and a Fermi resonance origin cannot be excluded. A very similar ν_S band structure occurs in several other Me_3N^+H–heterocyclic base complexes which have been examined. If we are dealing with a normal asymmetric single minimum proton potential in these complexes, the pK_a difference would suggest that the proton was closer to the Me_3N base. In this case we would expect the Fermi resonance structure to be characteristic of Me_3N, but almost independent of the proton acceptor,^{5} in conformity with the observed behaviour. (*c*) Aniline complexes: Provided the counterion is inert, aniline enters into a wide range of complex hydrogen bonded cations, involving bases of both larger and smaller pK_a, as well as self-complexing. Figure 2 illustrates three possibilities. The ν_S band in self-associated aniline, shown in B, differs markedly from the type typical of heterocyclic bases. The shift of ν_S from free anilinium ion† (3250 cm^{-1}) indicates that all these ions are hydrogen bonded, the smallness of the shift indicating weaker bridging than in any of the previous complexes. Although the ν_S band displays a quite pronounced doublet structure with maxima at *ca.* 2560 and *ca.* 2860 cm^{-1} origins alternative to proton tunnelling are possible. In particular the possibility of multiple hydrogen bonding arises for the first time in this system. Figure 2A shows the ν_S band of the 2,6-dimethylpyridine–aniline complex cation. 2,6-Dimethylpyridine does not self-complex, and the band is quite distinctive from that of the aniline self complex. It is inferred that a new complex is present. 2,6-Dimethylpyridine is a stronger base than aniline and can be expected to attract preferentially the proton, and act as the proton donor. As aniline has only a single acceptor function, this suggests the molecularity (2,6-dimethyl pyridine–H-aniline)$^+$ The shift of ν_S indicates weaker H bonding than in trimethylamine or entirely heterocyclic complexes, and present evidence gives no indication of proton tunnelling.

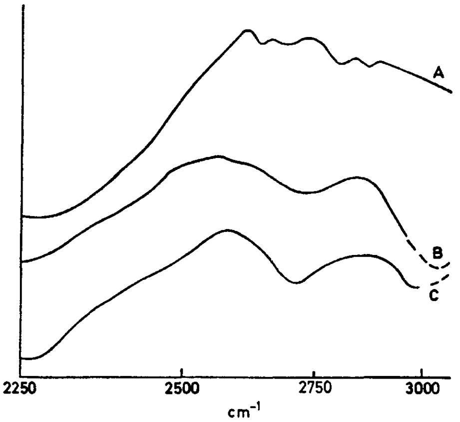

FIGURE 2. *I.r. spectra of* (*A*), ca. 2M *2,6-dimethylpyridinium perchlorate in aniline;* (*B*), ca. 2M *anilium fluoroborate in aniline;* (*C*), ca. 1·5M *anilinium perchlorate in 3-chloropyridine.*

Spectroscopic evidence indicates that aniline also forms complex cations involving weaker bases. Figure 2C show the ν_S band in association with 3Clpy, keeping $[\overset{+}{H}]$ = [Aniline] and using an inert counterion. The spectra show that no free aniline is present. Consequently if any aniline self-complexing occurs, forming $[(\text{Aniline})_x\text{H}]^+$ with $x \geqslant 2$, at least an equal amount of $[3(\text{Clpy})\cdot\text{H}\cdot3(\text{Clpy})]^+$ will be present. This complex has its strongest ν_S component at 2145 cm^{-1}, and is certainly not present in this proportion here. Thus, despite the similarities in the ν_S band contours of aniline self-complex and aniline $\overset{+}{H}$-3Clpy, a new "asymmetric" complex appears to be present, involving relatively weak hydrogen bonding.

Many other aliphatic bases, *e.g.* n-butylamine and triethylenediamine also give i.r. spectroscopic evidence of forming hydrogen bonded complex cations.

The occurrence of these stable complexes, linking a wide variety of bases by hydrogen bonds, has many chemical consequences. The possibility of their occurrence must be taken into account in accurate potentiometric determinations of base strengths, and in the interpretation of conducti-

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† Caution: Anilinium perchlorate, involved in the preparation of some anilinium complexes, is explosive.

metric titrations in non aqueous solvents.[3] They are also possible intermediates in many proton transfer reactions including those in enzyme systems (the biochemically important imidazole group forms a wide variety of complexes of the present type). The indications of comformational restriction about the hydrogen bond introduce interesting structural considerations. Steric restrictions could account for nearly all cases where it has not so far been possible to obtain a complex. A connection between the conformation, the N–N distance, and hence the form of the proton potential, which appears to display wide variations, is expected.

(*Received*, *October 4th*, 1971; *Com.* 1722.)

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