"Symmetrical" and Asymmetrical (NH··· N)⁺ Hydrogen Bonds

Infrared Investigations

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$(N_{(1)}H··· N_{(2)})^+ClO_4^-$ complexes of 5- and 6-membered aromatic rings and of bicyclic non-planar N-base molecules in acetonitrile solutions are investigated by i.r. spectroscopy. Studied are " symmetrical " complexes ($N_{(1)} = N_{(2)}$) and asymmetrical complexes ($N_{(1)} \neq N_{(2)}$). The stability of " symmetrical " complexes increases with increasing pK_a. In the region 2700-1900 cm⁻¹, two broad bands are found with aromatic compounds, but only one with bicyclic ones. It is shown that Fermi resonance and not proton tunnelling is responsible for the band splitting. In this resonance effect the NH⁺ stretching vibration in the hydrogen bonds and a combination vibration, in which the NH⁺ bending vibration and a ring vibration take part, are involved. In addition, a continuous absorption is observed which begins at these bands and extends toward smaller wave numbers. This continuum is also caused by (NH··· N)⁺ bonds and demonstrates that these bonds are easily polarisable, *i.e.*, they have a double minimum energy surface when isolated from their environment. The fact that a continuum as well as the band pair are found in the spectra of solutions with (NH··· N)⁺ hydrogen bonds is explained.

If one partner in an asymmetrical complex is non-planar and the proton is present on this base molecule, only one band is observed in the region 2800-2000 cm⁻¹ instead of the band pair which is observed with complexes formed by two planar N-base molecules. The band splitting with asymmetrical complexes may also be explained by Fermi resonance. The dependence of the relative intensities on the ΔpK_a may also be understood by this assumption. When the ΔpK_a between the two N-base molecules becomes smaller, *i.e.*, the degree of asymmetry of the hydrogen bonds decreases, a continuous absorption occurs, demonstrating that the asymmetrical (NH··· N)⁺ hydrogen bonds may become easily polarisable, too.

Various authors have investigated (NH··· N)⁺ hydrogen bonds by i.r. spectroscopy. These bonds are formed between N-bases when acid, for instance, perchloric acid, is present. Such hydrogen bonds have been studied in acetonitrile and nitromethane solutions by Wood and coworkers,[1-8] in acetonitrile by Pawlak and Sobczyk [9] and Sobczyk [10] and in aqueous solution by Mühlinghaus and Zundel [11] and Sessler and Zundel.[12, 13] (NH··· N)⁺ bonds with adsorbed N-base molecules have been studied by Noller and coworkers.[14] Recently Dean and Wood studied (NH··· N)⁺ bonds in systems without solvents.[15] Furthermore, Szafran and Grech,[16] Quick *et al.*[17] and Głowiak *et al.*[18, 19] investigated such hydrogen bonds in the solid state.

When (NH··· N)⁺ bonds are formed between the same type of N-base molecules, the energy surface of the bonds is symmetrical if they are considered to be isolated from their environment.[8, 20] For the interaction of such hydrogen bonds with their environment it is important that hydrogen bonds with " symmetrical " energy surfaces may be very easily polarisable.[21, 22] When (NH··· N)⁺ bonds are formed

between N-base molecules of different types, the energy surfaces are more or less asymmetrical.

Easily polarisable hydrogen bonds interact strongly with their environment. Due to these interactions the energy levels are more or less strongly shifted since the energy surfaces become more or less strongly deformed [see fig. 5 in ref. (21)]. In solutions the strength of these interactions shows a statistical distribution. Therefore, in solutions with polarisable hydrogen bonds, a continuum is usually observed instead of bands.[12, 21-24] This is especially true with the "symmetrical" $(NH \cdots N)^+$ bonds.[11-14]

In systems with $(NH \cdots N)^+$ bonds, one finds not only the continuum in the whole wave number region below 3000 cm^{-1}, but usually also two broad bands in the region 2700-1900 cm^{-1}. To explain this band splitting, tunnelling of the proton in a double minimum energy surface and Fermi resonance were considered alternatively.[4, 6, 10, 16] The conclusion that the band pair is caused by tunnel effect was, however, contradicted by the fact that easily polarisable $(NH \cdots N)^+$ hydrogen bonds should cause a continuum instead of bands.[21-24] Recently it was indeed demonstrated by crystallographic data that Fermi resonance, not proton tunnelling causes the band splitting.[17] This conclusion is confirmed in the following. Furthermore, an explanation is given why $(NH \cdots N)^+$ bonds in solutions may cause a continuum as well as bands. It is shown that the bands are a component of the continuum.

EXPERIMENTAL

Perchlorates of all investigated bases were prepared by addition of an equimolar amount of 70 % aqueous perchloric acid to a solution of the free base in ethanol. **These perchlorates are explosive!** The solvent was removed under reduced pressure and the residue was crystallized from ethanol : acetonitrile solution 5 : 1. The product was checked by elemental analysis.
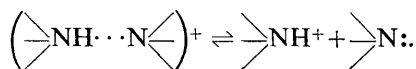
The deuterated compounds were prepared by triple crystallization of the perchlorates from CH_3OD, followed by evaporation of the solvent under reduced pressure.

All bases were recrystallized or redistilled. Acetonitrile for spectroscopy was used and stored over a 4 Å molecular sieve. A dry box was used for all sample preparations.

Infrared spectra in the range 4000-550 cm^{-1} were obtained with a Perkin–Elmer spectrophotometer, model 325. The spectra were taken in CH_3CN-solution (0.5 mol dm^{-3} in a 0.10 mm cell). For salt or base solutions the concentration 0.5 mol dm^{-3} refers to the salt or the base, respectively; for solutions with complexes it refers to 0.5 mol dm^{-3} salt+0.5 mol dm^{-3} base. The absorbance of the solvent acetonitrile was compensated by a cell with pure acetonitrile in the reference beam. The solid state spectra were plotted from suspension in Fluorolube or in Nujol.

RESULTS AND DISCUSSION

Complexes between two N-base molecules and one proton may be obtained in solid state. When these compounds are dissolved in acetonitrile, the following equilibrium is present :

$$\left(\underset{\diagup}{\overset{\diagdown}{}}NH \cdots N\underset{\diagdown}{\overset{\diagup}{}}\right)^+ \rightleftharpoons \underset{\diagup}{\overset{\diagdown}{}}NH^+ + \underset{\diagup}{\overset{\diagdown}{}}N:.$$

The degree of complex formation in the solution can be estimated considering the NH^+ stretching vibration of the non-hydrogen bonded NH^+ groupings. The band of these groupings is observed in the i.r. spectra of, for instance, 4-methylpyridine [fig. 1(a)] at 3250 cm^{-1}. Comparing the intensity of this band in the case of the two N-base molecules + one proton solutions, i.e., in the salt + base solutions (A_k) with the

same band of N-base perchlorate solutions (A_s) one can estimate the degree of non-hydrogen bonded molecules and hence also the % complex formed, as follows:
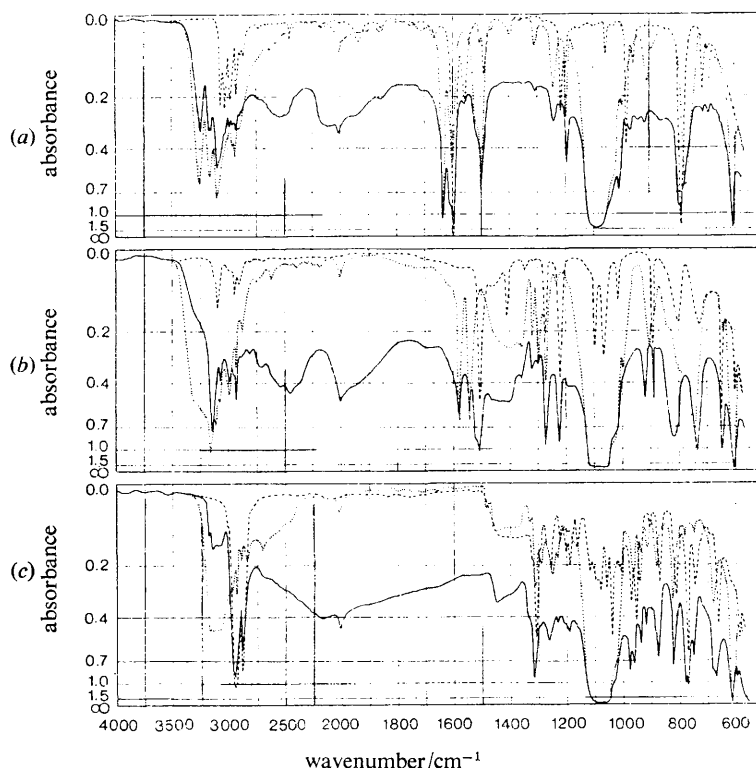
$$\% \text{ complex} = 100(1 - A_k/A_s).$$

FIG. 1.—I.r. spectra of acetonitrile solutions of (a) 4-methylpyridine; (b) N-methylimidazole; (c) 3-chloroquinuclidine; – – – – pure base, ... base perchlorate (salt), ——— base: perchloric acid 2:1 (complex).

"SYMMETRICAL" $(NH \cdot \cdot N)^+$ COMPLEXES

In fig. 2 the % complex formed in the acetonitrile solutions, as calculated with the above formula, i.e., the degree of $(NH \cdot \cdot N)^+$ hydrogen bonding, is plotted dependent on the pK_a of the N-base present. With increasing pK_a of the N-base the degree of hydrogen bonding increases. With increasing pK_a the hydrogen bond acceptor property of the lone pair of the N-base increases. The hydrogen bond donor property, however, decreases. Hence the observed dependence of the degree of the $(NH \cdot \cdot N)^+$ bond formation on the pK_a demonstrates that the acceptor property of the lone pair is of main importance for the relation between pK_a and degree of hydrogen bonding in these systems.

Fig. 1(a) and 1(b) show that with "symmetrical" $(NH \cdot \cdot N)^+$ complexes formed by two 4-methylpyridine or two N-methylimidazole molecules in acetonitrile a band pair is found in the region 2700-1900 cm^{-1} as well as a continuum which begins at this band pair and extends toward smaller wave numbers. With all other investigated 5- and 6-membered N-bases with planar rings the same results are obtained [fig. 3(a) and 3(b)]. Furthermore, fig. 1(c) illustrates that the $(NH \cdot \cdot N)^+$ complexes between

two 3-chloroquinuclidine molecules possess only one band at about 2160 cm^{-1} apart from a continuum. The same is observed with quinuclidine, triethylenediamine and with hexamethylenetetramine [fig. 3(c)], *i.e.*, with bicyclic compounds which have non-planar rings.
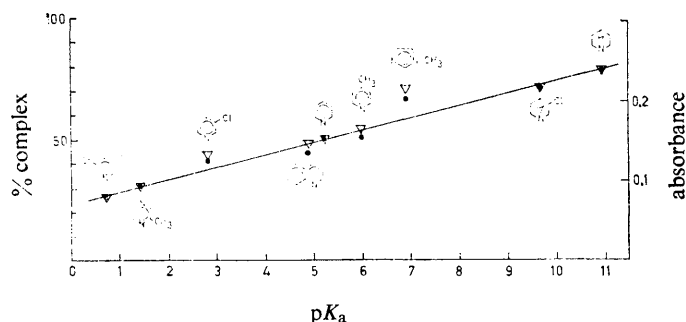

FIG. 2.— % (NH···N)$^+$ complex (·) and absorbance of the continuum at 1750 cm^{-1} ($\triangledown$) as a function of the pK_a of the N-base. (The solutions are 1 mol dm^{-3} relative to the N-base present.)
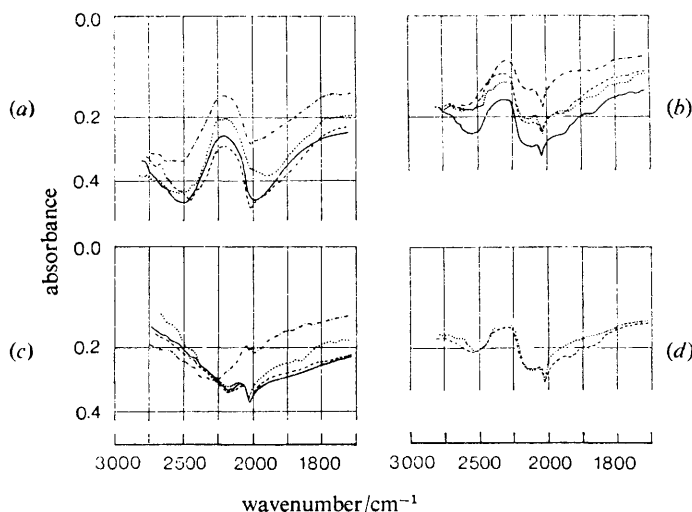

FIG. 3.—I.r. spectra of acetonitrile solution of base : perchloric acid 2 : 1 (complex). (*a*) *N*-bases with 5-membered rings ; ——— 2-ethylimidazole ; – – – – *N*-methylimidazole ; . . . . benzimidazole ; – · – · – 1,2,4-triazole. (*b*) *N*-bases with 6-membered rings ; ——— 4-methylpyridine ; – – – – 2-methylpyrazine ; . . . . 3-chloropyridine ; – · – · – 3,5-dichloropyridine. (*c*) bicyclic *N*-bases ; ——— quinuclidine ; – – – – 3-chloroquinuclidine ; . . . . triethylenediamine ; – · – · – hexamethylenetetramine (in solid state). (*d*) – – – – pyridine ; . . . . [^{2}H$_5$] pyridine.

THE TWO BROAD BANDS IN THE REGION 2700-1900 cm^{-1}

Fig. 3 shows the following results :

(i) The two bands are similar in the cases of all 6-membered *N*-bases. They are also similar with all planar 5-membered *N*-bases.

(ii) The distance between the two bands is different with 5-membered compared with 6-membered planar *N*-base molecules. With 5-membered *N*-bases the bands are shifted slightly toward smaller wave numbers.

(iii) In contrast to the results with planar N-bases, only one band is observed with the bicyclic compounds, which have non-planar rings [fig. 3(c)]. The maximum of this band is found in the region between the maxima of the two bands observed with the planar compounds. Analogous results with regard to systems with planar and non-planar rings are obtained with compounds in the solid state (fig. 4).

(iv) The two broad bands are almost independent of the pK_a of the special N-base molecules. This is true of the 6-membered as well as the 5-membered N-bases. The position of the one broad band observed with bicyclic N-bases is also almost independent of the pK_a of the special N-base molecules [the spectrum in fig. 3(c) with the band at larger wave numbers is the spectrum of hexamethylenetetramine in the solid state]. This demonstrates that position and band splitting depend on the fact whether the rings are 5- or 6-membered or bicyclic with non-planar rings. The bands are, however, largely independent of the number of N-atoms in the rings, of the substituents and especially of the pK_a of the special N-base molecules.
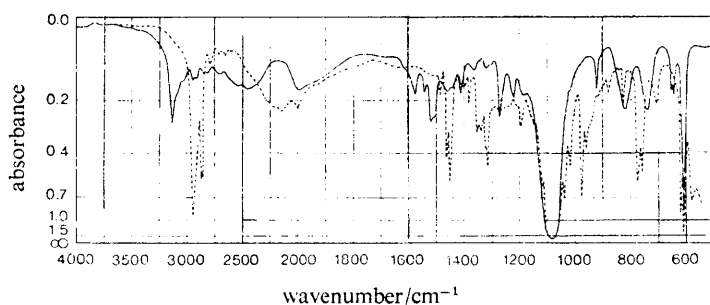

FIG. 4.—I.r. spectra of symmetrical complexes formed by 2 N-base molecules with 1 HClO$_4$ molecule in nujol and fluorolube. —— N-methylimidazole; – – – – quinuclidine.

The fact that two bands are only observed with molecules having planar rings and not with molecules having non-planar rings, although both have similar pK_a values, cannot be understood supposing that tunnelling of the proton in the $(NH\cdots N)^+$ bond causes the band splitting. Such substances with comparable pK_a values are, for instance, 2-ethylimidazole $pK_a = 8.05$ (planar) and triethylenediamine $pK_a = 8.20$ (non-planar). When the pK_a is similar, energy surfaces and bond lengths should also be much the same. Therefore, no different distinctive features of the spectra can be caused by different proton tunnelling. The fact that the $(NH\cdots N)^+$ bond length is similar with all these $(NH\cdots N)^+$ bonds was shown by crystallographic data. With planar N-bases, for instance, with benzimidazole the $(NH\cdots N)^+$ bond length is 2.787Å,[17] with pyrazine 2.853 Å [18]; and with the non-planar N-base triethylenediamine this bond length is 2.84 Å.[19] Hence the length of $(NH\cdots N)^+$ bonds in planar and non-planar compounds is similar.*

The conclusion that tunnelling is not the reason for the observed band splitting is confirmed by the fact that the degree of band splitting is dependent on the size of the N-base ring, but independent of the pK_a of the special N-base. If proton tunnelling were the reason for the observed band splitting it should decrease with increasing barriers between the minima of the energy surface, $i.e.$, the band splitting should be

* Dean and Wood [15] explained the different features with regard to band splitting in the region 2700-1900 cm^{-1} observed with planar and non-planar N-bases in terms of different $(NH\cdots N)^+$ bond lengths. They postulated with triethylenediamine a $(NH\cdots N)^+$ bond length of only 2.5 Å. This is in contradiction to the crystallographic result.[19] The explanation given in ref. (15b) for the different spectra of planar and non-planar N-bases can not, therefore, be correct.

dependent on the pK_a of the bases.   The energy surface in the $(NH \cdots N)^+$ bonds can, however, not be completely independent of the pK_a.

Thus the band splitting cannot be explained by tunnelling.   It can, however, be understood assuming Fermi resonance, as recently postulated by Wood and co-workers.[15, 17]
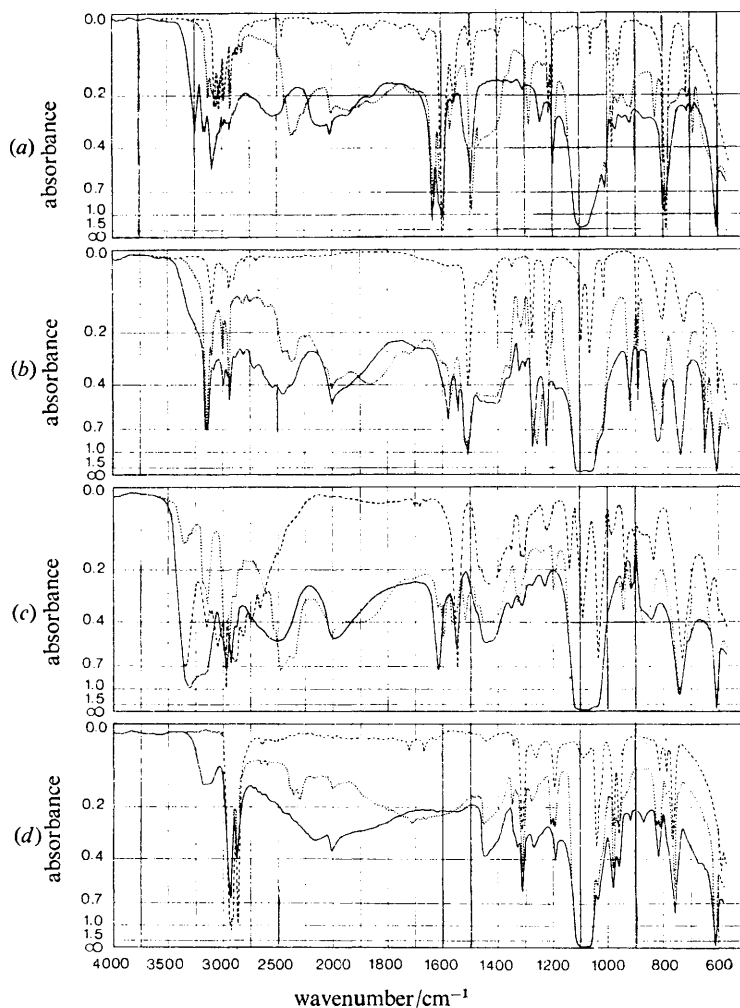

FIG. 5.—I.r. spectra of acetonitrile solutions: (a) 4-methylpyridine; (b) N-methylimidazole; (c) 2-ethylimidazole; (d) quinuclidine.   – – – – pure base; ——— $(NH \cdots N)^+$ complex; .... $(ND \cdots N)^+$ complex.

In fig. 5 changes with N-deuteration are illustrated.   With N-deuteration of quinuclidine a band of non-hydrogen bonded ND^+ groups is found at 2350 cm^{-1}. The maximum of the broad band is shifted from 2160 cm^{-1} to 1650 cm^{-1} [isotope factor 1.31, fig. 5(d)].   This broad band is caused by the NH^+ or ND^+ stretching vibration, respectively, in hydrogen bonded groups.

With the planar N-bases the band of the non-hydrogen bonded ND^+ groups is found at about 2350 cm^{-1} [fig. 5(a) and (b)].   With N-deuteration the two broad bands

caused by the $(NH \cdots N)^+$ associates vanish, and only one broad intense band is observed at smaller wave numbers, sometimes together with one or two weak bands. In the case of N-methylimidazole, for instance, the large wave number band shifts from 2450 to 1862 cm^{-1} (isotope factor 1.32). This band is caused by the NH$^+$ or ND$^+$ groups in the hydrogen bonds, and has a considerable NH$^+$ or ND$^+$ stretching vibration character. The second vibration involved in the formation of the band pair with the non-deuterated samples may be an overtone or combination vibration as discussed for other compounds by various authors.[15, 25-28] Instead of this band, however, only weak bands are observed after deuteration at the slope of the strong band towards smaller wave numbers. With 4-methylpyridine two weak bands are found at 1850 and at 1718 cm^{-1}. With N-methylimidazole one weak band is observed at 1720 cm^{-1} [fig. 5(b)] and finally, with 2-ethylimidazole no band appears in this region [fig. 5(c)].

All these weak bands have nothing to do with the strong Fermi resonance causing the two intense bands with the non-deuterated compounds. In the following, this is demonstrated with N-methylimidazole. With the non-deuterated compound the separation of the intense bands amounts to 450 cm^{-1}, with the deuterated compound the distance between the strong and the weak band, however, amounts only to 120 cm^{-1}. Although the distance between the bands is smaller with the deuterated compound, the intensity exchange is smaller. This cannot be true if with non-deuterated and deuterated compounds Fermi resonance between analogous vibrations were to exist. Thus the strong Fermi resonance observed with the non-deuterated compound is not observed after deuteration. The observed weak bands are probably caused by weak coupling between the stretching vibration of the ND$^+$ groups in the hydrogen bonds and other vibrations. The fact that the strong Fermi resonance is no longer observed after deuteration becomes understandable when one considers the character of the second vibration which participates in the band pair of the non-deuterated compounds. As already mentioned this vibration has the character of a combination

TABLE 1.—A SUGGESTION OF A COMBINATION VIBRATION TO EXPLAIN ONE OF THE COMPONENTS OF THE BAND PAIR IN THE REGION 2500–2000 cm^{-1}

	six-membered ring				five-membered ring		
compound salts of	ring breathing/ cm^{-1}	δ_{NH^+}/ cm^{-1}	combination/ cm^{-1}	compound	ring breathing/ cm^{-1}	δ_{NH^+}/ cm^{-1}	combination/ cm^{-1}
4-methylpyridine	1011 [6]	1259 [6]	2270	pyrazole	1037 [35]	1168 [36]	2205
3-chloropyridine	1028 [6]	1251 [6]	2279	imidazole	1053 [37]	1185 [36]	2238
pyridine	1027 [5]	1249 [5]	2279	N-methylimidazole	1037 [38]	1178 [36]	2215
2-methylpyrazine	1022 [33]	1251 [33]	2273	1,2,3-triazole	1003 [39]	1222 [40]	2225
quinoline	1014 [34]	1256 [34]	2270	tetrazole	1054 [41]	1167 [41]	2221

vibration or of an overtone. Dean and Wood [15] demonstrated that the NH$^+$ bending vibration is involved. The facts that the band pair is dependent on the size of the ring [see result (i)] and especially that the band splitting vanishes with the non-planar compounds [see result (iii)] demonstrate that a ring vibration is involved.* With deuteartion this vibration shows no shift or only a smaller shift than the NH$^+$ stretching vibration. Thus, after deuteration, the resonance condition is no longer fulfilled and strong Fermi resonance is no longer observed. Table 1 shows that the combination of the NH$^+$ bending vibration and the ring breathing vibration leads to similar results : imidazole compounds at about 2220 cm^{-1}, pyridine compounds at about 2275 cm^{-1}.

* A CH bending vibration does not participate in these vibrations since for [$^2H_5$]pyridine the same band pair is observed as with pyridine (fig. 3).

This is in good agreement with the results shown in fig. 3.   With five-membered rings the low wave number component is observed at smaller wave numbers than with six-membered compounds.   Hence this combination could be the reason for the low wave number component of the band pair.

In summary we can state : The band pair observed with planar N-bases associated via $(NH\cdots N)^+$ bonds is caused by Fermi resonance between the NH^+ stretching vibration and combination vibration in which the NH^+ bending vibration and a ring vibration are involved.

CONTINUOUS ABSORPTION

When $(NH\cdots N)^+$ bonds are present a continuum is found.   It begins at the bands which we have discussed and extends toward smaller wave numbers (fig. 1).   This continuum demonstrates that the $(NH\cdots N)^+$ bonds are easily polarisable.   As expected,[29] this continuum is considerably less intense with $(ND\cdots N)^+$ bonds (fig. 5).

Fig. 2 shows that the absorbance of the continuum increases with increasing concentration of the $(NH\cdots N)^+$ bonds.   The absorbance of the continuum per $(NH\cdots N)^+$ bond is, however, almost independent of the pK_a of the N-bases.   Concentration of the associates and absorbance of the continuum increase to the same extent.

As already mentioned in the introduction, such continua are caused by the interaction of easily polarisable hydrogen bonds with their environment.[12, 21-24]

When isolated from their environment $(NH\cdots N)^+$ bonds have a symmetrical double minimum energy surface.   The barrier of this energy surface is much higher than the barrier of the energy surface observed with $(OH\cdots O)^+$ bonds,[21] since the length of $(NH\cdots N)^+$ hydrogen bonds is about 2.8 Å.[17-19]   Hence these bonds are substantially longer than $(OH\cdots O)^+$ bonds usually are, as, for instance, in $H_5O_2^+$, hence the barriers in these bonds are larger.   The larger the barrier, the smaller is the splitting of the two lowest levels.   With decreasing splitting of the lowest levels the polarisability increases strongly.[21, 24]   Thus the polarisability of the $(NH\cdots N)^+$ bonds is usually larger than that of $(OH\cdots O)^+$ bonds.   Therefore, the energy surfaces in the $(NH\cdots N)^+$ bonds become particularly strongly deformed by interactions with their environment, whereby the polarisability decreases [see fig. 15.14 and 15.15 in ref. (24)].

The absorbance of the continuum and the absorbance of the bands in the region 2700-1900 cm^{-1} show the same dependence on the $(NH\cdots N)^+$ concentration.   This demonstrates that the same $(NH\cdots N)^+$ bonds cause the formation of a continuum as well as bands.   This seemingly surprising fact can be understood since the $(NH\cdots N)^+$ bonds are much longer than $(OH\cdots O)^+$ bonds usually are.   It was shown by SCF calculations that with increasing bond length the transitions 10-20, 00-20 and 00-30 become dominating in the region 2000-2500 cm^{-1} [see fig. 6 in ref. (22)].   When electrical fields of 10^6-10^7 V cm^{-1} are present at the hydrogen bonds these transitions are strongly mixed due to Fermi resonance, since with increasing field strength the energy levels approach each other for field strengths in the region $10^6 - 2.5 \times 10^7$ V cm^{-1} [see fig. 5 in ref. (22)].   From the transition moments given in ref. (22) i.r. spectra were calculated.   In solution, a broad distribution of the length of the hydrogen bonds occurs, as demonstrated by neutron scattering experiments,[30] as well as a broad distribution of the strength of local electrical fields.   Both were taken into account in these calculated spectra [31, 32] which demonstrate that with increasing bond length a band-like structure with maximum in the region 2000-2500 cm^{-1} is superposed on the continuum.   This band-like structure of the continuum is caused by the transitions mentioned above.   These transitions may couple with the combination vibration causing the observed band splitting.   Thus the observed bands are a structure of the continuum which may occur with relatively long easily polarisable hydrogen bonds, as,

for instance, with the $(NH\cdots N)^+$ bonds studied. With regard to the broad distribution of the length of these easily polarisable hydrogen bonds in solution the relatively long bonds of this distribution contribute preferentially to the band-like structure and the shorter ones preferentially to the continuous absorption extending toward smaller wave numbers, as illustrated by fig. 6 in ref. (22) and the calculations.[31, 32]

The fact that Dean and Wood [15a] observed an asymmetrical single minimum energy surface with $(NH\cdots N)^+$ bonds in crystals can be understood easily since the $(NH\cdots N)^+$ bonds are polarised due to the crystal field [with regard to these effects, *i.e.*, easily polarisable H-bonds in crystals, see ref. (24), p. 747].

ASYMMETRICAL $(N_1H\cdots N_2)^+$ BONDS

Fig. 6 shows i.r. spectra of asymmetrical $(N_1H\cdots N_2)^+$ complexes in acetonitrile solutions. In all complexes one N-base is 3-chloroquinuclidine, the other is an N-base with planar ring. With these complexes, only one broad band is observed in the region 2800-2000 cm^{-1}. In contrast to this when both N-bases are planar, Clements, Dean and Wood [2, 15] observed two broad bands. Our findings can be understood, since with regard to the pK_a values of the compounds in these complexes the deeper well of the energy surface in the $(N_1H\cdots N_2)^+$ bonds is at the 3-chloroquinuclidine molecule, *i.e.*, the proton is preferentially present on this molecule. From our investigations with " symmetrical " $(NH\cdots N)^+$ complexes it is, however, known that when the proton is present at the non-planar base the NH$^+$ stretching vibration cannot couple with other vibrations, as with " symmetrical " complexes formed by non-planar N-bases no band pair is observed.
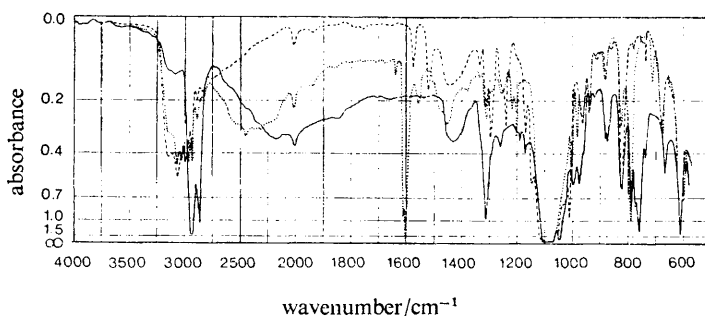

FIG. 6.—I.r. spectra of acetonitrile solution of asymmetrical $(N_1H\cdots N_2)^+$ complexes: 3-chloroquinuclidine plus —— triethylenediamine 1:1; .... 4-methylpyridine 1:1; ---- 2-methylpyrazine 1:1.

Clements, Dean and Wood [2, 15] studied similar asymmetrical $(N_1H\cdots N_2)^+$ complexes between planar N-bases. With these planar N-bases a band pair is found [see fig. 1 in ref. (2)]. With increasing asymmetry of these complexes, the intensity of the band at smaller wave numbers decreases and that at higher wave numbers increases. This result can probably also be understood using the assumption of Fermi resonance, since with increasing asymmetry of the $(N_1H\cdots N_2)^+$ bond the anharmonicity of the NH$^+$ stretching vibration decreases. With decreasing anharmonicity, coupling due to Fermi resonance decreases more and more. Thus the intensity of one of the two bands should increase at the cost of the other, as observed.

In fig. 7 the wave numbers of the maximum of the broad band observed in the region 2800-2000 cm^{-1} are plotted against the pK_a of the planar N-base of the complex. From fig. 6 and 7 the following result is obtained. The maximum of the broad

band in the region 2800-2000 cm^{-1} is shifted towards smaller wave numbers with increasing pK_a of the planar base and increases in intensity. The pK_a of 3-chloro-quinuclidine is 9.7. Hence with increasing pK_a of the planar N-base the pK_a difference between the N-base in the $(N_1H \cdots N_2)^+$ complex decreases, $i.e.$, the symmetry increases. Thus with increasing symmetry of the energy surface in the $(N_1H \cdots N_2)^+$ bond the NH stretching vibration shifts towards smaller wave numbers and gains more and more in intensity.
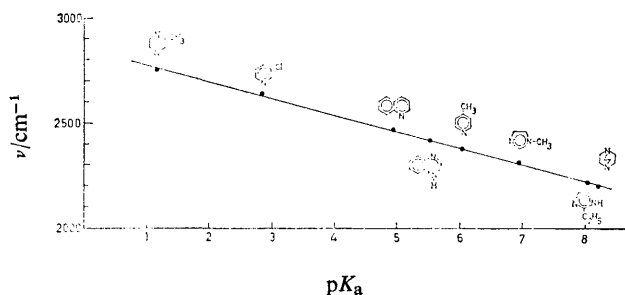

FIG. 7.—Maximum of the broad band in the region 2800-2000 cm^{-1} of the asymmetrical $(N_1H \cdots N_2)^+$ complexes with 3-chloroquinuclidine as a function of the pK_a of the second N-base.

Regarding the continuous absorption, fig. 6 shows the following. When the pK_a difference (ΔpK_a) between 3-chloroquinuclidine and the planar N-base is small, as, for instance, with the system 3-chloroquinuclidine + triethylenediamine, ΔpK_a = 1.5, a continuum is observed just as with " symmetrical " hydrogen bonds. This continuum begins at the broad band and extends toward smaller wave numbers. When the pK_a difference becomes larger, as, for instance, with the system 3-chloroquinuclidine + 4-methylpyridine, ΔpK_a = 3.7, the continuum also begins at the broad band but only extends up about 1000 cm^{-1}. With further increase of the ΔpK_a the continuum vanishes more and more; with the system 3-chloroquinuclidine + 2-methyl-pyrazine, ΔpK_a = 8.2 it is no longer found.

All these results can easily be understood. If with asymmetrical $(N_1H \cdots N_2)^+$ bonds the ΔpK_a is small, the energy surface is largely symmetrical when isolated from its environment, the hydrogen bonds are easily polarisable and a continuum is observed. If, however, the ΔpK_a becomes larger, the energy surface becomes more and more asymmetrical and the polarisability decreases. With more or less symmetrical hydrogen bonds the energy surface is the same as the energy surface of " symmetrical " hydrogen bonds which are in an electrical field.[21] This demonstrates that with asymmetrical hydrogen bonds no low wave number transitions are present [see fig. 5 in ref. (21)]. Hence the continuum does not extend toward small wave numbers, as observed. With further increasing asymmetry the polarisability and hence the continuity of the energy level differences vanishes.

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