188. *Infrared Spectra and Hydrogen Bonding in Pyridine Derivatives.*

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Some hydrochlorides, mercurichlorides, and carboxylic and sulphonic acids and their sodium salts have been prepared from pyridine and its derivatives. Their infrared spectra are recorded and discussed as evidence for hydrogen bonding.

Chenon and Sandorfy[1] estimated that the N-H stretching frequencies of substituted ammonium ions which were not hydrogen-bonded would fall in the range 3000—3200 cm.$^{-1}$. It has been found[2] that amine tetrachloroborates exhibit bands in the region being considered so that it is possible to obtain the spectrum of a protonated base in which complications due to hydrogen bonding are minimised. Tetrachloroborates are sensitive to moisture and special precautions must therefore be observed. It occurred to us that other complex anions besides tetrachloroborates might be reluctant to form hydrogen bonds with protonated bases, in particular mercurichlorides which are less sensitive to moisture and can be used for the identification and characterisation of bases. In view of this laboratory's interest in pyridine bases, we examined the spectra of the hydrochlorides and mercurichlorides of some pyridine compounds, and of some amphoteric derivatives of pyridine which might be expected to contain a protonated nitrogen atom. The results are given in Table 1.

The spectrum of solid pyridinium chloride shows two weak bands at 3206 and 3134 cm.$^{-1}$, which have been attributed to the presence of a proportion of unbonded NH$^+$ groups perturbed only by crystal forces.[3] This suggestion implies that there may be at least

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[1] Chenon and Sandorfy, *Canad. J. Chem.*, 1958, **36**, 1181.
[2] Kynaston, Larcombe, and Turner, *J.*, 1960, 1772.
[3] Dodd and Stephenson, "Hydrogen Bonding," Pergamon Press, London, 1959, p. 177.

two types of pyridinium cation in the crystal lattice. The NH^+ groups which are hydrogen-bonded to the chloride anions give rise to the very broad intense band around 2500 cm.$^{-1}$. Brissette and Sandorfy[4] assign weak bands at 3000—3200 cm.$^{-1}$ in the spectra of aliphatic primary amine salts to overtone or combination modes of bending vibrations at 1500—1600 cm.$^{-1}$. Nuttall *et al.*[5] have suggested that there is a double minimum in the curve of potential energy against interatomic distance for the hydrogen bond in pyridinium chloride. In the following discussion, we assume that the bands in the 3250—3100 cm.$^{-1}$ region are caused by unbonded NH^+ groups.

TABLE 1.

Frequencies (cm.$^{-1}$) for NH stretching vibrations in pyridine derivatives.

	Unbonded $\geqslant N^+–H$	Bonded $\geqslant N^+–H$ or O–H
Pyridinium chloride	3206w	2500svb
Pyridinium mercurichloride	3225s, 3164s	—
2,6-Lutidinium chloride	3276w	2450svb
2,6-Lutidinium mercurichloride	3285m, 3180w	—
2,6-Di-t-butylpyridinium mercurichloride	3362s	—
2-Ethylpyridinium chloride	—	2619svb
2-Bromopyridinium chloride	—	2273svb, 2033s, 1970s, 1910s
2-Bromopyridinium mercurichloride	3204m, 3188m, 3140m	3000m, 2920m, 2886m, 2852m
Pyridine-2-sulphonic acid	3200w, 3142w	3030s, 2937s, 2870s
Pyridine-3-sulphonic acid	3239w, 3182w, 3127m	2937s, 2800s, 2720s
Pyridine-4-sulphonic acid	3240w, 3135m	3007s, 2910s, 2830s
2,6-Lutidine-3-sulphonic acid	3300vw	2800s, 2746s, 2687s
2,6-Lutidine-4-sulphonic acid	3300vw	2800s, 2700s
2,6-Di-t-butylpyridine-3-sulphonic acid	3374s	—
Toluene-*p*-sulphonic acid[a]	—	2650svb, 2250svb, 1845svb
Picolinic acid[b]	—	2600svb, 2155m, 2070w
Nicotinic acid[b]	—	2450svb, 1880svb ~1700—1600[b]
Isonicotinic acid[b]	—	2400svb, 1970svb ~1700[b]
Dipicolinic acid[a]	—	2870s, 2630s, 2550s

[a] Hydrogen bonding is of the type O—H · · · O. [b] Hydrogen bonding is of the type O—H · · · N.

With the change from pyridinium chloride to pyridinium mercurichloride, the broad intense band around 2500 cm.$^{-1}$ disappears and two very strong sharp bands appear at 3225 and 3164 cm.$^{-1}$. A similar result is obtained with pyridinium tetrachloroborate,[2] and we conclude that hydrogen bonding is absent in the mercurichloride and that the strong bands around 3200 cm.$^{-1}$ are due to unbonded NH^+ groups, perturbed only by crystal forces. There is strong hydrogen bonding in 2,6-lutidinium chloride, causing a very broad strong band at 2450 cm.$^{-1}$. However, the two methyl groups must hinder the approach of the chloride ion towards the NH^+ of the cation since the intensity of the N–H stretching band at 3276 cm.$^{-1}$ is greater than that of the corresponding band in pyridinium chloride. In the spectrum of 2,6-lutidinium mercurichloride, hydrogen bonding is no longer apparent. The band due to N–H stretching of unbonded NH^+ appears at a higher frequency than does the corresponding band in pyridinium mercurichloride, which is again believed to result from the shielding effect of the two methyl groups in the α-positions of the pyridine nucleus. In support of this hypothesis, the N–H stretching band of unbonded NH^+ appears at a still higher frequency (3362 cm.$^{-1}$) in the spectrum of 2,6-di-t-butylpyridinium mercurichloride which is in accord with the greater shielding effect to be expected from alkyl groups larger than methyl.

The steric effect of one group α to the pyridine nitrogen atom seems to be insufficient to cause a noticeable diminution in hydrogen bonding. Thus we were unable to detect weak NH stretching bands above 3100 cm.$^{-1}$ in the spectra of 2-ethyl- and 2-bromopyridinium chlorides although the very broad strong bands due to hydrogen bonding of the type $N^+–H \cdots Cl$ appeared at 2619 and 2273 cm.$^{-1}$ respectively. In 2-bromopyridinium mercurichloride, the unbonded NH^+ stretching vibration appears as three

[4] Brissette and Sandorfy, *Canad. J. Chem.*, 1960, **38**, 34.

[5] Nuttall, Sharp, and Waddington, *J.*, 1960, 4965.

medium strong bands at 3204, 3188, and 3140 cm.$^{-1}$, and in addition four new bands of medium intensity appear at 3000—2850 cm.$^{-1}$. The latter may result from the NH stretching of NH^+ hydrogen-bonded to the covalent bromine atom of a second 2-bromopyridine molecule, since hydrogen bonding with the mercurichloride anion seems unlikely in view of the results obtained with other mercurichlorides, while hydrogen bonding with the bromine atom of the same molecule involves formation of a four-membered ring.

In Table 2 are collected the frequencies of the strongest band in the C–H out-of-plane vibration region for the spectra of the alkylpyridinium salts. In this region the spectra resemble those of the corresponding benzene hydrocarbons having the same number of unsubstituted hydrogen atoms on the aromatic nucleus, *i.e.*, a Cannon–Sutherland type of correlation applies, and for comparison of spectra the NH^+ in pyridinium salts can be regarded as if it were a substituent.[6]

TABLE 2.

Frequencies (cm.$^{-1}$) for C–H out-of-plane vibrations.

Pyridine derivative		Benzene derivative	
Pyridine	743	Benzene	674
Pyridinium chloride	756	Toluene	729
Pyridinium mercurichloride	741		
2-Ethylpyridinium chloride	795, 770	*o*-Ethyltoluene	794, 755, 728
2,6-Lutidinium chloride	801	1,2,3-Trimethylbenzene	766
2,6-Lutidinium mercurichloride	794	1-Ethyl-2,3-dimethylbenzene	776
2,6-Di-t-butylpyridinium mercurichloride	821, 737		

The infrared spectra of the three pyridinemonocarboxylic acids have a strong, fairly sharp, C=O band at 1715—1710 cm.$^{-1}$, indicating that the carbonyl group is present as such in the solid. Hydrogen bonding involving the carboxylic acid group is considerable and causes very broad bands centred near 2450, 1880, and 1700—1600 cm.$^{-1}$ for nicotinic acid, at 2400, 1970, and 1700 cm.$^{-1}$ for isonicotinic acid, and at 2600, 2155, and 2070 cm.$^{-1}$ for picolinic acid. These bands are absent in the spectra of the corresponding sodium salts. The differences between the spectra of nicotinic and isonicotinic acid on the one hand and that of picolinic acid on the other support the suggestion that hydrogen bonding is intermolecular in the first two compounds and intramolecular (and weaker) in the third.[7,8]

The spectrum of dipicolinic acid shows strong, broad bands centred at 2869, 2630, and 2550 cm.$^{-1}$ but has no strong bands between 2550 and 1800 cm.$^{-1}$. In this region, therefore, the spectrum resembles that of an aromatic carboxylic acid which is associated with dimeric hydrogen-bonded carboxyl units.[9] The spectrum also shows a strong, sharp C=O band at 1692 cm.$^{-1}$. Hence, the hydrogen bonding in dipicolinic acid is probably of the O–H $\cdots$ O type and not of the O–H $\cdots$ N type of the pyridinemonocarboxylic acids.

The spectra of the three pyridinemonosulphonic acids exhibited weak NH stretching bands around 3200 cm.$^{-1}$. Hydrogen bonding caused strong bands at 3030—2870 cm.$^{-1}$ for the 2-sulphonic acid but at slightly lower frequencies for its 3- and 4-isomers. It was concluded that the 3- and 4-acids were more strongly hydrogen-bonded than the 2-acid. The bands in question are weaker in, or absent from, the sodium salts and arise from $O^- \cdots H{-}N^+$ bonding since the spectra are different from that of toluene-*p*-sulphonic acid, in which O–H $\cdots$ O bonding occurs. As expected, the shielding effect of the two α-methyl groups moves the N–H stretching frequency of the lutidinesulphonic acids to higher frequencies but there is still strong hydrogen bonding. Finally, in the spectrum of 2,6-di-t-butylpyridine-3-sulphonic acid, no hydrogen bonding is apparent and the

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[6] Podall, *Analyt. Chem.*, 1957, **29**, 1423.

[7] Cantwell and Brown, *J. Amer. Chem. Soc.*, 1952, **74**, 5967.

[8] Yoshida and Asai, *Pharm. Bull. (Japan)*, 1959, **7**, 162; *Chem. Abs.*, 1960, **54**, 22,008.

[9] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 1960, p. 161.

N–H stretching frequency of unbonded NH^+, which appears at **3374** cm.$^{-1}$, disappears when the acid is converted into its sodium salt.

EXPERIMENTAL

Pyridinium chlorides were prepared by saturating an ether–ethanol solution of the base with dry hydrogen chloride and filtering off the precipitate. With 2-bromopyridine, an ether–methanol solution was used, evaporated to dryness, and the residue stored over phosphorus pentoxide. 2-*Bromopyridinium chloride* had m. p. 198—200° (Found: C, 30·2; H, 2·7; N, 6·8. C_5H_5BrClN requires C, 30·8; H, 2·6; N, 7·2%).

The mercurichlorides were prepared by addition of pyridine base (0·01 mole), in ethanol acidified with concentrated hydrochloric acid (2 ml.) [or saturated with hydrogen chloride (2-bromo-compound)], to mercuric chloride (0·01 mole) in methanol, followed by crystallisation from methanol. The following were prepared: *pyridinium mercurichloride*, m. p. 140·5—145·0° (Found: C, 15·5; H, 2·3; Cl, 27·1; N, 3·7. $C_5H_6Cl_3HgN$ requires C, 15·5; H, 1·6; Cl, 27·5; N, 3·6%); 2,6-lutidinium mercurichloride, m. p. 190—192·5° (lit.,[10] m. p. 186°) (Found: N, 3·6. Calc. for $C_7H_{10}Cl_3HgN$: N, 3·4%); 2-*bromopyridinium mercurichloride*, m. p. 118—122° (Found: C, 12·9; H, 1·1; N, 3·2. $C_5H_5BrCl_3HgN$ requires C, 12·9; H, 1·1; N, 3·0%).

Pyridinecarboxylic acids were prepared by oxidation of the corresponding picolines and 2,6-lutidine, which were at least 99 moles % pure, with potassium permanganate in hot aqueous solution according to the method of Black *et al.*[11] Specimens of 2,6-di-t-butylpyridinium mercurichloride and various pyridinesulphonic acids were prepared in connection with a programme on dissociation constants.[12]

The sodium salts of the carboxylic and sulphonic acids were prepared by titration of aqueous solutions of the acids with aqueous sodium hydroxide to a phenolphthalein end-point. The aqueous solutions were evaporated at 100°/20 mm., the residue was crystallised from ether–methylated spirit and then dried (P_2O_5) to constant weight *in vacuo* at 100°. The sodium salts of the lutidinesulphonic acids required a temperature of 198° for complete dehydration, and were very hygroscopic. In most cases the infrared spectra were measured for potassium chloride discs. With the sodium 2,6-lutidinesulphonates, mulls in hexachlorobutadiene were prepared in a dry box. All spectra were measured on a double-beam recording grating spectrometer designed and constructed in this laboratory.[13]

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[10] Ladenburg, *Annalen*, 1888, **247**, 30.

[11] Black, Depp, and Corson, *J. Org. Chem.*, 1949, **14**, 14.

[12] Evans and Brown, *J. Org. Chem.*, in the press.

[13] Hales, *J. Sci. Instr.*, 1959, **36**, 264.