11. *Vibrational Frequencies of Substituted Ammonium Ions.*

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The infrared spectra of some solid secondary and tertiary amine hydrohalides have been measured. Characteristic stretching and deformation vibration frequencies of NH_2^+ and NH^+ have been derived, and the assignments have been substantiated by measurements on the deuterated compounds.

ALTHOUGH much is known about the vibrations of NH_2 and NH groups in primary and and secondary amines, the characteristic vibration frequencies of the substituted ammonium ions $^-NH_3^+$, $>NH_2^+$, and $\geqslant NH^+$ in the amine hydrohalides are still uncertain. Earlier evidence from the infrared absorption spectra was reviewed by Bellamy,[1] by Witkop,[2] and more recently by Heacock and Marion.[3] The last authors measured the spectra of several secondary amine hydrochlorides and derived a value close to 1600 cm.$^{-1}$ for a deformational vibration frequency of the NH_2^+ group.

We have measured the infrared spectra of some solid secondary and tertiary amine hydrohalides, both in potassium chloride discs and in mulls of Nujol and Fluorolube, in order both to assign the characteristic vibration frequencies and also to study the band intensities, since other work on the intensities of NH group vibrations in different secondary amines has revealed interesting correlations with structure.[4] While it has proved impracticable to obtain satisfactory intensity data in these cases owing to difficulties with the disc method and also because of the highly hygroscopic nature of some of the compounds, some new frequency assignments have been deduced which are substantiated by spectral comparisons with the deuterated materials. The greater dispersion which we have used in the region 3—4 μ has also enabled us to disentangle the complex situation arising from the overlapping of the stretching vibration bands of the C–H and N^+–H bonds.

EXPERIMENTAL

The spectra were measured over the range 600—4000 cm.$^{-1}$ on a Perkin-Elmer 21 spectrometer with a rock-salt prisms, and the region 2000—3000 cm.$^{-1}$ was examined further under higher dispersion with a Perkin-Elmer 12 C instrument fitted with a lithium fluoride prism. The potassium chloride used for making the pressed discs was repurified by precipitation from a saturated aqueous solution with hydrochloric acid. It was heated *in vacuo* at about 450° for several days to remove residual water. Additional care was necessary to prevent further adsorption of water vapour by the amine hydrohalides themselves. This adsorbed water was revealed especially by its broad absorption near 3 μ, and it was extremely difficult to obtain records entirely free from it. However, if adequate precautions were taken, the spectral records of the solids in potassium chloride discs were essentially identical with those obtained by using mulls in Nujol or Fluorolube.

The compounds were specially prepared and the following recorded m. p.s indicated satisfactory purity: diethylamine hydrochloride 223·5°, dibenzylamine hydrochloride 255—256°, piperidine hydrochloride 242°, piperazine dihydrochloride 322—323°, morpholine hydrochloride 175—176°, thiazine hydriodide 156—157°, *N*-methylpiperidine hydriodide 121·5°, *N*-benzylpiperidine hydrochloride 176—178°, benzyldimethylamine hydrochloride 173—174°, *N*-ethylmorpholine hydriodide 147—148°, *N*-benzylmorpholine hydrochloride 243—244°, *N*-benzyl-*N'*-methylpiperazine dihydrochloride 257—258°, *N*-benzylpiperazine hydrochloride 167·5—168°.

Deuteration was carried out as follows. The amine hydrohalide was placed in a small glass tube attached to a vacuum line, and adsorbed water was removed by prolonged evacuation. Dry air was then admitted to the line, and 99% deuterium oxide added to the solid from a

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[1] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen, London, 1954.

[2] Witkop, *Experientia*, 1954, **10**, 420.

[3] Heacock and Marion, *Canad. J. Chem.*, 1956, **34**, 1782.

[4] Russell and Thompson, *J.*, 1955, 483; *Proc. Roy. Soc.*, 1956, *A*, **234**, 318.

dropping funnel sealed to the apparatus. After an interval, the heavy water was pumped off; this process was repeated several times. A high degree of deuteration was thus achieved and, although it was incomplete, the marked changes of intensity of certain bands could be used as a guide to the assignments.

RESULTS

In the spectra of the secondary amine hydrohalides there are two regions of particular interest. One includes a complex pattern of bands between 2500 and 3000 cm.$^{-1}$, and the other lies between 600 cm.$^{-1}$ and 1600 cm.$^{-1}$. The former includes the stretching vibrations of the substituted ammonium ion, and the latter its deformational modes in addition to vibrations of the whole skeleton. After deuteration, a new group of bands appears between 1900 cm.$^{-1}$ and 2300 cm.$^{-1}$, in which the N^+-D stretching vibration bands are present, and there are other new bands around 1100 cm.$^{-1}$ and at lower frequencies. Simultaneously with the appearance of these new bands there are changes in the spectra near 3000 cm.$^{-1}$ and 1600 cm.$^{-1}$ as compared with those of the undeuterated compounds. Both before and after deuteration the spectra are very complex, with many of the strongest bands appearing to consist of several components, and it is quite impossible to make many direct assignments of vibration frequencies. There appear to be many combination or difference bands which cannot yet be interpreted. The situation is complicated further by the possibility of hydrogen-bond formation, some of which may arise from the presence of residual water in the solids. However, the results obtained upon deuteration lead to a few definite assignments.

First, with the secondary amine hydrohalides containing the $>NH_2^+$ ion, there are two N–H stretching vibration bands, the symmetric and antisymmetric vibrations, at about 2800 cm.$^{-1}$ and 2920 cm.$^{-1}$ respectively, which decrease in intensity upon deuteration. Two new bands then appear, near 2120 cm.$^{-1}$ and 2200 cm.$^{-1}$. The results are given in Table 1, and the positions quoted for the bands should be regarded as correct to within 10 cm.$^{-1}$, but cannot be fixed more precisely because of their broad nature and overlap with other bands. In the case of piperazine dihydrochloride the assignments are doubtful, owing to an unusual complexity which was also noted by Heacock and Marion.[3]

TABLE 1. $>NH_2^+$ *stretching vibrations.*

	Asymmetric			Symmetric		
	ν(H)	ν(D)	Ratio	ν(H)	ν(D)	Ratio
Diethylamine hydrochloride	2915	2195	1·33	2824	2100	1·34
Dibenzylamine ,,	2920	2212	1·32	2789	2112	1·32
Piperidine ,,	2920	2170	1·35	2844	2117	1·35
Morpholine ,,	2920	2220	1·32	2780	2108	1·32
Thiazine hydriodide	2920	2223	1·32	2820	2164	1·30
Piperazine dihydrochloride	2950?	2281?	(1·29)	2840?	2093	(1·36)

Table 1 includes the frequency ratios for the isotopic species. If the N^+-H link is regarded as the vibrating molecule, the ratio should be close to 1·37, and Edsall [5] found values of about 1·36 for the vibrational frequencies of the NH_3^+ ion from Raman spectral measurements on methylamine and hydrazine hydrochlorides. The ratios now observed therefore support the assignments suggested.

Near 1600 cm.$^{-1}$ there is another sharp band of the secondary amine hydrohalides which is replaced by another around 1200 cm.$^{-1}$ after deuteration. The results are given in Table 2. This band is clearly due to a deformational mode of the ion and supports the assignments made by Heacock and Marion. Indeed, the band of amino-acid hydrochlorides in this region discovered earlier by Randall *et al.*[6] can now be definitely associated with the $>NH_2^+$ group deformation. The new point to note is that its exact location

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[5] Edsall, *J. Chem. Phys.*, 1940, **8**, 520.

[6] Randall, Fowler, Fuson, and Dangl, "Infra-red Determination of Organic Structures," van Nostrand, New York, 1949.

depends upon the particular residues attached to this group. There is in fact a rough correspondence between the value of this frequency and the σ^* values of the attached groups, discussed by Taft.[7] As σ^* increases, the frequency is lowered. Thus with the hydrochlorides of *N*-phenylglycine, diphenylamine, dibenzylamine, *N*-ethylaniline, dimethylamine, and diethylamine, for which $\sigma^* = 1{\cdot}65$ 1·20, 0·45, 0·50, 0, and −0·2, the frequencies are 1560, 1572, 1572, 1589, 1600, and 1600 cm.$^{-1}$ respectively.

TABLE 2. $>NH_2^+$ *Deformational mode.*

	ν(H)	ν(D)	Ratio
Diethylamine hydrochloride	1600	1178	1·36
Dibenzylamine ,, ...	1572	1160	1·36
Piperidine ,, ...	1598	1240	1·29
Morpholine ,, ...	1580	1275	1·24
Thiazine hydriodide	1560	1140	1·37
Piperazine dihydrochloride	1591	—	—
N-Benzylpiperidine hydrochloride	1597	—	—

In the spectra of the secondary amine hydrohalides there are two other prominent bands near 2500 cm.$^{-1}$ and 2400 cm.$^{-1}$, which decrease in intensity after deuteration. These must be connected in some way with the $>NH_2^+$ group, and as Table 3 shows there is a regular relation between these bands and those assigned above to the stretching vibrations of this group. The interpretation of this pair of bands is uncertain. They could arise as difference bands caused by absorption from a low-frequency fundamental near 400 cm.$^{-1}$, or alternatively as vibrations of the $>NH_2^+$ group lowered by hydrogen bonding either with other similar groups or even with residual water in the solid.

TABLE 3.

	ν_a	ν_{sym}	Δ	ν_b	$\nu_{antisym}$	Δ
Diethylamine hydrochloride	2390	2824	434	2483	2915	432
Piperidine ,, ...	2427	2844	417	2496	2920	434
Morpholine ,, ...	2461	2780	329	2605	2920	315
Thiazine hydriodide	2400	2820	420	2484	2920	436
Piperazine dihydrochloride	2426	2840	424	2515	2950	435

With the tertiary amine hydrohalides, an assignment of the $\geqslant NH^+$ group stretching vibration has been made as given in Table 4. The frequency ratio for the isotopic species is between 1·25 and 1·30. These results agree with earlier suggestions by Lord and Merrifield[8] for triethylamine hydrochloride and pyridine hydrochloride, also included in Table 4.

TABLE 4. $\geqslant NH^+$ *Stretching vibration.*

	ν(H)	ν(D)	Ratio
N-Methylpiperidine hydrochloride	*ca.* 2680	*ca.* 2068	1·30
N-Ethyl morpholine ,, ...	2665	2046	1·30
Benzyldimethylamine ,, ...	2630	2023	1·30
N-Benzylpiperidine ,, ...	2512	1962	1·28
N-Benzylmorpholine ,, ...	2480	1980	1·25
N-Benzyl-*N'*-methylpiperazine dihydrochloride	2330	1850	1·26
Triethylamine hydrochloride	2540	1965	1·29
Pyridine ,, ...	2425	1880	1·29

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[7] See Newman, " Steric Effects in Organic Chemistry," Wiley, New York, 1956.
[8] Lord and Merrifield, *J. Chem. Phys.*, 1953, **21**, 166.