963. *Hydrogen Bonding in Alkyl- and Aryl-ammonium Salts.**

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The infrared spectra of a range of alkyl- and aryl-ammonium salts have been studied, particular attention being paid to the N–H stretching and N–H deformation frequencies. In salts where there is no cation–anion hydrogen bonding the N–H stretching frequencies occur well above 3100 cm.$^{-1}$. Except for triphenylammonium fluoroborate, fluoroborates and tetraphenylborates are not hydrogen-bonded.

PREVIOUS infrared studies on alkyl- and aryl-ammonium salts have been largely concerned with their halides.[1-7] The N–H stretching frequencies occur below 3100 cm.$^{-1}$, generally below 2900 cm.$^{-1}$, and it has been concluded that the shift from the normal value for N–H stretching frequencies of 3300 to 3500 cm.$^{-1}$ [8] is because of hydrogen bonding between cation and anion, a conclusion supported by structural studies on this type of salt.[9] It has been suggested [1,2] that in substituted ammonium salts where there is no hydrogen bonding the N–H symmetrical stretching frequencies would occur in the region 3000—3200 cm.$^{-1}$; this paper describes attempts to verify this and to investigate the variation in occurrence of hydrogen bonding with change in anion.

The factors involved in the formation of hydrogen bonds in ammonium salts have been discussed by Chenon and Sandorfy [2] in terms of the ionic and covalent character of the various contributing structures. For an $^+$N–H $\cdots$ X$^-$ bond the major contribution is

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[1] Ebsworth and Sheppard, *Spectrochim. Acta*, 1959, **13**, 261.
[2] Chenon and Sandorfy, *Canad. J. Chem.*, 1958, **36**, 1181.
[3] Brissette and Sandorfy, *Canad. J. Chem.*, 1960, **38**, 34.
[4] Waldron, *J. Chem. Phys.*, 1953, **21**, 734.
[5] Stone, Cymerman-Craig, and Thompson, *J.*, 1958, 52.
[6] Bellanato and Barcelo, *Anales real Soc. españ. Fís. Quím.*, 1956, **52**, *B*, 469.
[7] Heacock and Marion, *Canad. J. Chem.*, 1956, **34**, 1782.
[8] Bellamy, "The Infrared Spectra of Complex Molecules," 2nd edn., Methuen, London, 1958.
[9] Donohue, *J. Phys. Chem.*, 1952, **56**, 502.

from an electrostatic component, $^{+}$N–H $\cdots$ X^{-}. If X is part of a complex anion, *e.g.*, BF_4^{-} or BPh_4^{-}, the charge on X will be relatively small and this term will be correspondingly weak. Contributions such as N $^{+}$H $\cdots$ X^{-} and N H–X, which involve H–X bonds, depend markedly upon the strength of the acid HX. Complex fluoro- and chloro-acids are generally so strong that they do not exist in the absence of bases to solvate the proton; this factor again reduces the strength of hydrogen bonds in ammonium salts of complex acids. On this basis, in a series of substituted ammonium salts, halides, where both electrostatic and covalent terms are favourable, would be expected to show hydrogen bonding, but tetraphenylborates where both terms are unfavourable—free tetraphenyl boric acid immediately decomposes [10]—would be expected not to be hydrogen bonded. Fluoroborates should generally not be hydrogen bonded because of the absence of the covalent term—HF and BF_3 do not interact in normal circumstances [11]—but it is conceivable that with a strongly polarising cation the anion may be distorted into some sort of bonding. Unsubstituted ammonium halides show evidence of hydrogen bonding; the fluoroborate and tetraphenyborate are not hydrogen bonded.[12]

It is difficult to be precise when considering hydrogen bonding but we have used the position of the N–H infrared bands for diagnosis. Where possible, we have used the spectra of tetraphenylborates as standard spectra of unassociated salts. We have not considered in any detail the bands which occur near 2000 cm.$^{-1}$ in the spectra of many of the salts; Chenon and Sandorfy [2] consider that these bands result from a combination between a scissoring mode and an anharmonic vibration near 400 cm.$^{-1}$.

Tertiary Ammonium Salts.—*Trimethylammonium salts.* The infrared bands observed for these salts and also for triethylammonium fluoroborate in the range 4000—2000 cm.$^{-1}$ and also the position of the N–H deformation frequency near 1430 cm.$^{-1}$ are given in Table 1. In the 4000—2000 cm.$^{-1}$ region there will be bands due to C–H symmetrical stretching vibrations and also C–H combination and overtone modes in addition to the N–H frequencies. These C–H modes remain at 3030w, 2960s, 2930s, and 2850w cm.$^{-1}$ for

TABLE 1. *Infrared spectra* (cm.$^{-1}$) *of trimethylammonium salts.*

Anion	$\nu_{\text{N–H}}$			$\nu_{\text{C–H}}$			$\nu_{\text{N–H}}$	$\delta_{\text{N–H}}$
Br^{-}	—	—	3010	2965s	2930		2730s	1430
I^{-}	—		3020	2960s	2930		2730s	1420
BPh$_4^{-}$	3130s	3060 *	3030	3000s	—	2720	—	1420
PF$_6^{-}$	3230s	—	—	—	2930s	2860	—	1423
BF$_4^{-}$	3200s	—	—	—	2930s	2850	—	1420
ClO$_4^{-}$	3150s	—	—	—	2930s	2800	—	1418
Et$_3$NHBF$_4$	3150s	—	—	2975s	2942	—	—	1425
Me$_3$NDBF$_4$	—	—	—	—	2930s	—	2450, 2400, 2375	

s = strong.　* This peak also contains contributions from the spectrum of the anion.

salts with different anions and also on *N*-deuteration of trimethylammonium fluoroborate; not all these bands were resolved in all the salts. In salts in which hydrogen bonding is unlikely there is a very strong band at about 3200 cm.$^{-1}$ which we assign to the N–H symmetrical stretching mode. The position of this band varies slightly from one salt to another, but these small shifts are probably due to minor variations in the crystal field at the site of the N–H bond (cf. changes in the N–O frequency of nitrosyl chloride when dissolved in solvents of different dielectric constant [8]). The peak is sharp and well defined, but on deuteration of the fluoroborate the band splits and moves down to about 2400 cm.$^{-1}$ ($\nu_{\text{H}}/\nu_{\text{D}} = 1\cdot33$). A similar splitting has been observed in the spectrum of *N*-deuterotrimethylammonium iodide and was attributed to Fermi interaction between the N–D vibration and overtone and summation bands.[1]

[10] Wittig, Keicher, Rückert, and Raff, *Annalen*, 1949, **563**, 110; Wittig and Raff, *ibid.*, 1951, **573**, 195.
[11] McCaulay and Lien, *J. Amer. Chem. Soc.*, 1951, **73**, 2013.
[12] Waddington, *J.*, 1958, 4340.

The spectra of trimethylammonium bromide and iodide show no peaks at 3200 cm.$^{-1}$, but instead there is a strong peak at 2730 cm.$^{-1}$; this band has been recorded at even lower frequencies in the spectra of trimethylammonium chloride [13] and other trialkylammonium chlorides.[2]   There is a very weak band at 2720 cm.$^{-1}$ in the spectrum of trimethylammonium tetraphenylborate but this is probably a combination band.

The N–H deformation frequency occurs near 1420 cm.$^{-1}$ in the spectra of all the salts studied; it does not appear to be sensitive to the presence of hydrogen bonding.   On deuteration of trimethylammonium fluoroborate this band moves under the strong fluoroborate absorption at 1050 cm.$^{-1}$.

We conclude that these spectra are in agreement with the presence of strong hydrogen bonding in the trimethylammonium halides but not in the other trimethylammonium salts studied.

Pyridinium salts.   The infrared peaks which occur between 4000 and 2000 cm.$^{-1}$ in the spectra of the salts studied are given in Table 2.   The peaks between 3080 and 2850 cm.$^{-1}$

TABLE 2.   *Infrared spectra* (cm.$^{-1}$) *of pyridinium salts.*

Anion	$\nu_{\text{N-H}}$			$\nu_{\text{C-H}}$			$\nu_{\text{N-H}}$
Cl⁻	3200w	—	3120sh	3045m	2925s	2840s	2450s
Br⁻	3210w	3180w	—	3040m	2930s	2860w	2650b
I⁻	3210w	3160w	3100w	3060m	3020s	2950s	2870b
NO₃⁻	3230w	3170w	3100w	3070m	2960s		2730b
HF₂⁻	3230w	3180w	—	3080m	—		2800b
CH₃·SO₃⁻ ...	3220w	3160sh	—	3080m	2920s	2850w	2700b
PbCl₆²⁻	3230s	3160s	3110s	3080m	3050s		—
ClO₄⁻	3255s	3180s	3110s	3080m	2980s	2930s	—
BPh₄⁻	3230s	3178s	3130s	3058m	3010s	2930s	2860w
BF₄⁻	3250w	3160s	3120s	3080m	2900s		2827w
BCl₄⁻	3240s	3130s	3100s	3090m	2960s	2930s	2800w
PF₆⁻	3230s	3190s	3110s	—	2920s		2870w
pyDBF₄	—	—	—	3080m	2900s	2827w	2450s, 2405s, 2325s

w = weak, m = medium, s = strong, sh = shoulder, b = broad, py = pyridine.

are due to C–H modes.[8]   Three peaks due to N–H vibrations occur above 3100 cm.$^{-1}$ in the spectra of all salts studied, whether hydrogen bonded or not; these peaks are of very low intensity in salts which might be expected to be hydrogen bonded but are of high intensity in the tetraphenylborate and other salts in which the tendency to hydrogen bonding should be small.   On deuteration of pyridinium fluoroborate these bands shift to about 2400 cm.$^{-1}$ ($\nu_{\text{H}}/\nu_{\text{D}}$ = 1·32, 1·32, and 1·29 for the 3250, 3160, and 3120 cm.$^{-1}$ band, respectively).   In the halides and other salts where hydrogen bonding can be expected there is an additional, intense, broad band well below 3000 cm.$^{-1}$.   The infrared spectra of pyridinium salts below 2000 cm.$^{-1}$ are complex and will be discussed separately.[14]

From the spectra, the presence of the strong band below 3000 cm.$^{-1}$ being taken as diagnostic of hydrogen bonding, we conclude that pyridinium halides, nitrate, bifluoride, and methanesulphonate are hydrogen bonded but that the other salts that we have studied do not have this type of cation–anion interaction.   The presence of N–H peaks above 3100 cm.$^{-1}$ in the spectra of salts in which there is hydrogen bonding suggests that either there are some non-associated cations in these salts or, more likely, that there is a double-well effect in the potential energy–interatomic distance curve for the hydrogen bonds in these compounds (cf. ref. 15).

Triarylammonium salts.   The infrared spectra from 4000 to 2000 cm.$^{-1}$ of the salts studied are recorded in Table 3.   There is a series of peaks near 3000 cm.$^{-1}$ which are assigned to C–H vibrations and the N–H peaks are widely split and occur between 2850 and

[13] Lord and Merrifield, *J. Chem. Phys.*, 1953, **21**, 166.
[14] Gill, Nuttall, Scaife, and Sharp, *J. Inorg. Nuclear Chem.*, in the press.
[15] McKinney and Barrow, *J. Chem. Phys.*, 1959, **31**, 294; Bell and Barrow, *ibid.*, pp. 300, 1158.

2400 cm.$^{-1}$.   Since triarylamines are such weak bases,[16] it is possible that the N–H bond in triarylammonium salts is excessively weak and that the frequencies fall in the observed region without the necessity of invoking hydrogen bonding.   Triarylammonium tetraphenylborates have not been prepared, so a direct test of this cannot be made but, since

TABLE 3.   *Infrared spectra* (cm.$^{-1}$) *of triphenylammonium salts.*

Anion	ν_{C-H}				ν_{N-H}					δ_{N-H}
BF$_4$⁻	3070	3015		2930	2842		2738	*2655*		1391
SbCl$_4$⁻	3062	3038		2888		2795		*2702*		1380
SnCl$_6$²⁻	3085	3060	3038	2920	2850	2805	2710	*2602*	*2540*	1380
AlCl$_4$⁻	3047			2883		2800	2705		*2483*	1390, 1375
SnBr$_5$⁻	3030			2855		2790	2700	*2580*	*2503*	1378
SbBr$_4$⁻	3034			2882		2811	2710	*2592*	*2522*	1385
Ph$_3$NDBF$_4$ ...	3050	3045	2910				*2240*	*2165*	*2065*	—

All peaks of approximately equal intensity.   The most intense peak in the N–H region is italicised.

these spectra are broadened in the manner of known hydrogen-bonded ammonium salts, and since the frequency of the vibrations is influenced by the anion, we consider that these spectra imply the existence of strong hydrogen bonds in all the triarylammonium salts that we have studied.   If the position of the principal band is taken as a measure of the strength of the hydrogen bonding, the fluoroborate and the chloroantimonite are the least strongly associated.   In *N*-deuterotriphenylammonium fluoroborate the N–H peaks have shifted to about 2100 cm.$^{-1}$ ($\nu_H/\nu_D = 1\cdot28$, $1\cdot26$, and $1\cdot27$ for the 2842, 2738, and 2655 cm.$^{-1}$ peak, respectively).   The N–H deformation frequency at 1391 cm.$^{-1}$ moves under the fluoroborate band at 1050 cm.$^{-1}$ on deuteration.

Secondary and Primary Ammonium Salts.—The infrared spectra over the range 4000—2000 cm.$^{-1}$ of the salts studied are recorded in Table 4.   Anilinium and *p*-toluidinium

TABLE 4.   *Infrared spectra* (cm.$^{-1}$) *of primary and secondary ammonium salts.*

Me$_2$NH$_2$BF$_4$	3257s, 3010, 2935, 2860, 2790, 2450
Me$_2$NH$_2$BPh$_4$	3140s, 3045, 2995, 2760
MeNH$_3$BF$_4$	3275, 2926, 2854, 2772, 2560, 2470
MeNH$_3$BPh$_4$	3175, 3130, 3043, 2955, 2915, 2875, 2775, 2556
Ph$_2$NH$_2$BF$_4$	3175, 3075, 2925, 2845, 2583, 2485
PhNH$_3$BF$_4$	3215, 2923, 2850, 2600, 2325
C$_6$H$_4$Me·NH$_3$BF$_4$	3195, 3070, 3010, 2920, 2845, 2620

tetraphenylborates were precipitated from solution as hydrates and, as there would certainly be hydrogen bonding between the ammonium ions and water, these cannot be used as spectra of non-hydrogen bonded salts.   The isolated ions should give two N–H frequencies near 3000 cm.$^{-1}$.[1]   Previous work on the alkylammonium halides has placed these frequencies at 3080 and 2980 cm.$^{-1}$ in methylammonium chloride,[4] at 2965 and 2745 cm.$^{-1}$ in dimethylammonium chloride,[1] and at even lower frequencies for other alkyl- and aryl-ammonium halides.[2,3]   By analogy with previous assignments we consider that the N–H vibrations in dimethylammonium fluoroborate absorb at 3257 and 2790 cm.$^{-1}$ (3140 and 2760 cm.$^{-1}$ in the tetraphenylborate) (values in parentheses throughout this section refer to the tetraphenylborates), the bands at 3010 (3045), 2935 (2995), and 2860 cm.$^{-1}$ being C–H modes.   In the spectrum of methylammonium fluoroborate only the 3275 (3175) cm.$^{-1}$ band has been definitely assigned to an N–H vibration; the second N–H vibration may have become accidentally degenerate with the first or, more probably, is under one of the C–H bands which occur at 2926 and 2854 (3050, 2990) cm.$^{-1}$.   The spectra of all the salts considered in this section contain weak bands below 2800 cm.$^{-1}$.   These bands are not as strong or as broad as those observed in the spectra of hydrogen-bonded salts, and it is very probable that they are combination and overtone frequencies as are observed in this region of the spectra of many hydrocarbon derivatives.[1,8]

[16] Kemmitt, Nuttall, and Sharp, *J.*, 1960, 46.

The spectra of aryl-substituted secondary and primary ammonium salts look more complex because of the presence of broad, moderately strong bands below 2800 cm.$^{-1}$. The spectra of the fluoroborates show a strong band above 3100 cm.$^{-1}$ which we assign to one of the N–H vibrations. The other N–H frequency has not definitely been identified but probably occurs below 2900 cm.$^{-1}$ and is responsible for exciting combination modes and overtones to give moderately strong peaks in this region. Since all the salts have a strong band above 3150 cm.$^{-1}$ we conclude that there is no evidence for hydrogen bonding in any of the primary or secondary ammonium fluoroborates.

EXPERIMENTAL

Infrared spectra were measured in hexachlorobutadiene or Nujol mulls by using a Perkin–Elmer model 21 spectrophotometer fitted with rock-salt or fluorite optics.

Fluoroborates were generally prepared from the parent amine and aqueous fluoroboric acid, followed by recrystallisation from ethanol (Found, for trimethylammonium fluoroborate: C, 24·7; H, 6·9. Calc. for $C_3H_{10}NBF_4$: C, 24·5; H, 6·8. Found, for triethylammonium fluoroborate: C, 38·2; H, 8·4. Calc. for $C_6H_{16}NBF_4$: C, 38·1; H, 8·5. Found, for diphenylammonium fluoroborate: C, 55·5; H, 4·6. Calc. for $C_{12}H_{12}NBF_4$: C, 56·0; H, 4·7. Found, for anilinium fluoroborate: C, 39·8; H, 4·7. Calc. for $C_6H_8NBF_4$: C, 39·9; H, 4·5. Found for *p*-tolylammonium fluoroborate: C, 40·8; H, 5·5. Calc. for $C_7H_{10}NBF_4$: C, 42·4; H, 5·1%). Deuterations were effected by crystallisation from 99% D_2O.

Dimethylammonium fluoroborate was prepared from dimethylamine and fluoroboric acid. It was recrystallised from dry ethanol and subsequently handled in the " dry-box." Since it is extremely deliquescent, analysis was not attempted; the infrared spectrum showed no traces of water or other impurities.

Pyridinium fluoroborate was prepared by hydrolysis of pyridine–boron trifluoride in 95% ethanol [17] (Found: C, 36·0; H, 3·6. Calc. for $C_5H_6NBF_4$: C, 36·0; H, 3·6%). Triphenylammonium fluoroborate and all other triarylammonium salts were the samples prepared and analysed previously.[16,18]

Tetraphenylborates were prepared by precipitation from aqueous solutions of the amine hydrochloride and sodium tetraphenylborate (Found, for trimethylammonium tetraphenylborate: C, 85·8; H, 8·2. Calc. for Me_3NHBPh_4: C, 85·6; H, 8·0. Found, for pyridinium tetraphenylborate: C, 87·2; H, 6·9. Calc. for $C_5H_5NHBPh_4$: C, 87·3; H, 6·6. Found, for dimethylammonium tetraphenylborate: C, 86·0; H, 8·0. Calc. for $Me_2NH_2BPh_4$: C, 85·7; H, 7·8. Found, for methylammonium tetraphenylborate: C, 86·0; H, 7·9. Calc. for $MeNH_3BPh_4$: C, 85·7; H, 7·5%). Anilinium and *p*-toluidinium tetraphenylborates were precipitated as hydrates and were not studied further. Di- and tri-phenylammonium tetraphenylborates could not be prepared. Perchlorates were prepared from solutions of the amine in aqueous perchloric acid. After decomposition with sodium hydroxide, perchlorate was estimated by precipitation as the tetraphenylarsonium salt (Found, for trimethylammonium perchlorate: ClO_4, 61·8. Calc. for $C_3H_{10}NClO_4$: ClO_4, 62·2. Found, for pyridinium perchlorate: ClO_4, 55·6. Calc. for $C_5H_6NClO_4$: ClO_4, 55·4%). An aqueous solution of hexafluorophosphoric acid was prepared by passing a solution of the sodium salt over a cation-exchange resin. Hexafluorophosphates were prepared from solutions of the amine in the acid (Found, for trimethylammonium hexafluorophosphate: C, 18·0; H, 5·2; N, 6·5. Calc. for $C_3H_{10}NPF_6$: C, 17·6; H, 4·9; N, 6·8. Found, for pyridinium hexafluorophosphate: C, 27·5; H, 2·65; N, 6·5. Calc. for $C_5H_6NPF_6$: C, 26·7; H, 2·7; N, 6·2%). Trimethylammonium chloride and bromide were prepared by freeze-drying aqueous solutions which had been made from the amine and free acid [Found, for trimethylammonium chloride: Cl, 37·4. Calc. for $C_3H_{10}NCl$: Cl, 37·1. Found, for trimethylammonium bromide: Br, 60·3. Calc. for $C_3H_{10}NBr$: Br, 56·8% (this sample contained a slight excess of hydrogen bromide)]. The trimethylammonium iodide was a commercial sample. Pyridinium nitrate was prepared by freeze-drying an aqueous solution of the salt (Found: N, 19·0. Calc. for $C_5H_6N_2O_3$: N, 19·7%). Pyridinium hydrogen fluoride was obtained by dissolving pyridine in an excess of aqueous hydrofluoric acid, evaporation, and drying at 120°. Fluorine was estimated gravimetrically as PbClF (Found: F, 32·4. Calc. for $C_5H_6NHF_2$: F, 31·8%). Pyridinium methanesulphonate was prepared

[17] Van der Meulen and Heller, *J. Amer. Chem. Soc.*, 1932, **54**, 4404.
[18] Sharp, *Chem. and Ind.*, 1958, 1235.

7 X

from a solution of pyridine in the acid (Found: C, 40·7; H, 5·5; N, 7·6. Calc. for $C_5H_6NSO_3CH_3$: C, 41·1; H, 5·2; N, 8·0%). Pyridinium hexachloroplumbate was made as described by Palmer [19] [Found: C, 20·6; H, 2·3; N, 4·9%; M, 578. Calc. for $(C_5H_6N)_2PbCl_6$: C, 20·7; H, 2·1; N, 4·8%; M, 580]. Pyridinium chloride, bromide, and iodide were made by condensing excess of the dry hydrogen halide on to anhydrous pyridine at liquid-nitrogen temperatures and allowing the solids to warm very slowly. In the case of the chloride the pyridinium hydrogen dichloride formed initially was decomposed by heating *in vacuo* to 100° (Found, for pyridinium chloride: Cl, 30·4. Calc. for C_5H_6NCl: Cl, 30·7. Found, for pyridinium bromide: Br, 49·3. Calc. for C_5H_6NBr: Br, 49·8%. Found, for pyridinium iodide: I, 61·9. Calc. for C_5H_6NI: I, 61·4%). Pyridinium tetrachloroborate was prepared from pyridine, hydrogen chloride, and boron trichloride, the hydrogen chloride being used as a solvent [20] (Found: Cl, 60·1. Calc. for $C_5H_6NBCl_4$: Cl, 60·9%).

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