718. *Vibration-spectral Band Assignments for the Pyridinium Ion: Pyridine Deuteriochloride and 1-Methylpyridinium Chloride.*

By E. Spinner.

The Raman spectrum of pyridine deuteriochloride and the infrared and Raman spectra of 1-methylpyridinium chloride have yielded new information concerning band assignments. It is concluded that in the pyridinium ion the $^+$NH and the CH bonds do not bend in unison. The 1-methylpyridinium ion strongly resembles toluene as regards " substituent-sensitive " aromatic vibrations.

Extensive vibrational assignments for the pyridinium ion have been proposed by Cook,[1] who determined the infrared spectra of several simple and complex halides of *N*-protonated and *N*-deuteronated pyridine. Several of these assignments, and in particular Cook's conclusion that the $^+$NH and the CH out-of-plane bending motions (but not the in-plane bending motions) occur in unison, seemed sufficiently uncertain to warrant an extension of the study to the Raman spectrum of the *N*-deuterated pyridinium ion, and to the vibrational spectrum of the *N*-methylpyridinium ion.

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[1] Cook, *Canad. J. Chem.*, 1961, **39**, 2009.

Experimental.—1-Methylpyridinium chloride had m. p. 110—112° (from propan-2-ol). Cation concentrations of solutions used for Raman spectra were: pyridine hydrochloride in H_2O, 60%; pyridine deuteriochloride in D_2O–DCl (pyridine in Merck's 35% DCl in D_2O), 42%; 1-methylpyridinium chloride in H_2O, 61%. Infrared and Raman spectra were determined as before [2] (see Table).

Band Nomenclature.—For the numbering of the skeletal aromatic and the CH vibrations, see Lord *et al.*[3] and Spinner,[4] respectively.

Band maxima in vibration spectra.*

Assignment †	$C_5H_5N^+H$ ‡ Raman, in H_2O		$C_5H_5N^+D$ Raman, in D_2O	
8a	1634	16	1626	22
8b	1612	10	1585	19
19b	1487	2	1484	5
14?	1383	2	1372?	3
3	1339	2	1303	10
N^+H ip be	1252	9		
	1242?	1		
9a	1198	15	1202	19
15	1160	4	1162	6
?/N^+D ip be I			1126	6
18a(+ b?)	1057	10	1057	12
12	1026	40	1023	95
1	1009	100	994	100
5?			938?	2 §
	872?	1 ¶		
?/N^+D ip be II			881	5
10a	806?	2	802	3
6b	637	18	634	26
6a	608	10	602	14
	580?	1 §	586	3
16a(+ b?)	393	4	383	6

	1-Methylpyridinium chloride			
Assignment †	Infrared, (solid in KBr)		Raman, in H_2O	
CH st	3015	0·6		
8a	1630	1·1	1637	20
8b	1581	0·15	1586	10
19a	1499	1·5	1499	4
19b	1484	1·7		
Me, CH be	1458	0·2	1446?	1
	1443	0·2		
14?			1417	5
Me, CH be	1383	0·1		
3	1287	0·5	1287	6
	1224	0·1		
9a	1210	0·6	1218	10
S/18a I	1187	1·1	1191	18
15	1141	0·4	1158	4
Me, CH be	1133	0·2	1137	6
(18b?)	1053	0·3		
1 + 12	1023	0·1	1030	100
5?	959	0·1		
S/18a II			799	17
10b	773	1·7		
11	677	1·7		
6b	646	0·02	649	18
6a/S			531	10
16a(+ b?)			393	1
Me op be			218	6

* See footnote * to Table 2, p. 3863. † See footnote † to Table 2, p. 3863; S = C_{Me}–N^+ stretching. ‡ This spectrum, obtained on a more concentrated solution and under better instrumental conditions than before (Spinner, *J.*, 1960, 1226), is more detailed than those reported so far (*loc. cit.* and Evans, personal communication to Cook[1]). § The band actually observed in this position is due, either wholly or mostly, to the frequency 57 ± 1 cm.$^{-1}$ above, excited by the 4347·5 Å Hg line. ¶ There is a corresponding infrared band at 880 cm.$^{-1}$ (Spinner, *loc. cit.*).

Discussion.—Skeletal vibrations. Cook's assignment [1] of the $C_5H_5N^+D$ ion band at 1585 cm.$^{-1}$ to vibration 8b seemed somewhat uncertain in view of its low intensity in the infrared spectrum, but the Raman spectrum of this ion, and the results for the *N*-methylated ion, confirm that this assignment is correct. The similarity of the spectrum of the *N*-deuterated ion to that of the *N*-methylated ion in the range 1450—1650 cm.$^{-1}$ is striking; the Raman-spectral differences near 1000 cm.$^{-1}$ among the three ions examined are unexpected.

CH *and* $^+$NH *Bending vibrations.* The correspondence of the $C_5H_5N^+D$ band at 1300 cm.$^{-1}$ to the $C_5H_5N^+H$ band at 1335 cm.$^{-1}$ (assigned to ν_3) proposed by Cook [1] is confirmed by the Raman spectrum; contrary to an earlier suggestion,[2] ν_3 seems to be essentially a CH bending vibration.

The two very intense infrared bands at 677 and 773 cm.$^{-1}$ in the 1-methylpyridinium ion spectrum undoubtedly correspond to the pyridinium ion bands at 680 and 750 cm.$^{-1}$, the pyridine bands at 700 and 750 cm.$^{-1}$, and the pentadeuteriopyridine bands [5] at 530 and 582 cm.$^{-1}$, respectively. The size of the isotope effect on these frequencies in pentadeuteriopyridine proves that both bands are due to pure CH bending vibrations (*i.e.*, to

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[2] Spinner and White, *J.*, 1962, 3115.

[3] Lord, Marston, and Miller, *Spectrochim. Acta*, 1957, **9**, 113.

[4] Spinner, *J.*, 1963, 3860.

[5] Corrsin, Fax, and Lord, *J. Chem. Phys.*, 1953, **21**, 1170.

11 and 10b, respectively [5]) and not to mixed CH out-of-plane bending–skeletal out-of-plane bending, 11/4, as proposed * by Cook.[1]

The following $C_5H_5N^+H$ — $C_5H_5N^+D$ band correspondences suggested by Cook [1] seemed partly or wholly suspect because too many frequency ratios near 1·35 are implied: 1245 and 930 cm.$^{-1}$ (assigned by him to vibration 9b); 1000 and 800 cm.$^{-1}$ (5); ~900 and 685 cm.$^{-1}$ (10b); 750 cm.$^{-1}$ and a band below 650 cm.$^{-1}$ (" 4 "); 675 cm.$^{-1}$ and a band predicted to be at 608 cm.$^{-1}$ (" 11 "). Only pure $^+$NH vibrations should have their frequencies lowered by a factor of 1·35 in the *N*-deuteronated compound. For mixed $^+$NH–aromatic vibrations and, even more so, for mainly aromatic vibrations such as Cook's 10b, 5, " 4," and " 11," the factor should be much closer to 1. Further, an inspection of Cook's values suggests that the $C_5H_5N^+D$ ion bands at 930, ~800, and 685 cm.$^{-1}$ are likely to correspond to the $C_5H_5N^+H$ ion bands at ~1000, 750, and 680 cm.$^{-1}$. The results now obtained strongly support the view that this is so.

The fairly prominent $C_5H_5N^+H$ (double) band at 1245 cm.$^{-1}$ disappears on *N*-deuteration from the Raman as well as the infrared spectrum, which confirms Cook's assignment of it [1] to $^+$NH in-plane bending,† but Cook's suggestion that the $C_5H_5N^+D$ band at 930 cm.$^{-1}$ corresponds to it is contradicted by the Raman spectrum, which shows no appreciably intense band there. Presumably $^+$ND in-plane bending mixes with a CH bending vibration of a similar frequency, and the only $C_5H_5N^+D$ bands that are clearly without counterpart in the $C_5H_5N^+H$ spectrum, *i.e.*, the two appreciably intense Raman bands at 1126 and 881 cm.$^{-1}$, are attributed to the mixed vibrations. Which aromatic vibration is involved in the mixing is uncertain. For reasons of symmetry, $^+$ND in-plane bending seems likely to mix with 18b, but on this basis it is puzzling why the two above-mentioned bands do not appear in the infrared spectrum.[1] On the other hand, vibration 17a, which is Raman-active and infrared-inactive, has the right frequency but not the right symmetry to mix with $^+$ND in-plane bending.

The Raman bands near 805 cm.$^{-1}$ are likely to be due to the second infrared-inactive CH out-of-plane bending vibration, 10a.

In X-C_5H_4N and X-$C_5H_4N^+H$ the frequency ratio of X in-plane bending to X out-of-plane bending is close [4] to 1·5. A similar ratio is expected for the $^+$NH bending vibrations in $C_5H_5N^+H$; this leads to a predicted out-of-plane bending frequency near 830 cm.$^{-1}$. Actually the $C_5H_5N^+H$ ion shows an infrared band varying [1] in frequency (in the solid state) from 850 cm.$^{-1}$, when the anion is a very weak hydrogen-bond acceptor, to 940 cm.$^{-1}$ when it is quite strongly hydrogen-bond accepting (chloride, in mull). Such a wide variation is feasible only for an $^+$NH vibration, but not for 10b as suggested by Cook.[1] The absence of this band from the infrared spectrum of 1-methylpyridinium chloride enables one to assign it with confidence to $^+$NH out-of-plane bending.

Corresponding to this, the unperturbed $^+$ND out-of-plane bending frequency in the $C_5H_5N^+D$ ion is expected near 620 cm.$^{-1}$. This vibration might interact for reasons of symmetry with 10b, and also, if hydrogen-bonding were to raise its intrinsic frequency sufficiently, with 11. Hydrogen-bonding effects, though less pronounced in deuteronated than in protonated salts,[1] are still appreciable in the simple halides. The $C_5H_5N^+D$ frequencies found at 680 and 780—800 cm.$^{-1}$ in the complex halides, which are here assigned to ν_{11} and ν_{10b}, respectively, are indeed raised [1] in solid $C_5H_5N^+DCl^-$, to 720 and 812 cm.$^{-1}$, in agreement with expectation.

Substituent-sensitive aromatic vibrations in the 1-*methylpyridinium ion.* Like toluene, the *C*-methylpyridines, and their cations, this ion shows prominent Raman bands, at

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* The vibrations numbered " 11 " and " 4 " by Cook are not identical with those numbered 11 and 4 in Wilson's notation,[3] but are in fact both mixed 11/4 vibrations.

† According to the convention that uses redundant aromatic vibration numbers in Wilson's notation for substituent vibrations, $^+$NH ($^+$ND) in-plane and out-of-plane bending are numbered 9b and 17b, respectively.

1190, 800, and 530 cm.$^{-1}$, which are clearly of the type classed as " X-sensitive " by Whiffen[6] and are interpreted as before.[4] Thus, these vibrations occur irrespective of whether the methyl substituent in the pyridinium ion is attached to a carbon or to the N^+ atom.

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[6] Whiffen, *J.*, 1956, 1350.