717. *The Vibration Spectra of Some Monosubstituted Pyridines and Pyridinium Ions.*

By E. Spinner.

The infrared and Raman spectra of the monomethyl-, monocyano-, monochloro-, and monobromo-pyridines, and of their hydrochlorides have been determined. The Raman spectrum of a monosubstituted pyridine resembles that of the corresponding monosubstituted benzene and undergoes only minor modifications on cation formation. Within each series of compounds (*i.e.*, 2-, 3-, and 4-substituted, pyridines and pyridinium ions) the nature of the substituent has only a minor effect on the greater part of the spectrum; these effects are summarised. Band assignments are made as far as practicable.

This extension of earlier work [1,2] on the vibration spectra of some substituted pyridinium ions was undertaken in order to ascertain the influence of the mass, and of the electronic effect of the substituent, on the vibration spectrum. The vibration spectra of pyridine and its deuterio-derivatives have been studied in detail [3-5] and band assignments have been made.[3-6] Correlations [7,8] and assignments [8d] are available for the infrared spectra of monosubstituted pyridines; for the methylpyridines,[9a] and the pyridinealdehydes and their ions,[9b] Raman spectra also have been determined. Recent studies of the pyridinium ion [1,10] include a proposed complete vibrational assignment.[10c] Band assignments for monosubstituted benzenes have been widely discussed,[11-16] though without complete agreement.

Experimental.—The methyl-, cyano-, chloro-, and bromo-pyridines used were purified commercial specimens; [17] 4-iodopyridine was obtained as before.[17] Solid hydrochlorides were normally obtained by passing dry hydrogen chloride into ethereal solutions of the pyridines; self-quaternisation by 4-halogenopyridines was avoided by adding the pyridine in ether (or methanol in the case of 4-iodopyridine) dropwise to ether (or methanol) saturated with hydrogen chloride. The structures of the halogenopyridine salts were confirmed by analysis.

The infrared and Raman spectra of the methyl-, chloro-, and bromo-pyridines, and of 2-cyanopyridine, were obtained for the pure liquids. The infrared spectra of 3- and 4-cyano- and 4-iodo-pyridine, and of all the hydrochlorides, were obtained for dispersions of the solids in potassium bromide. The Raman spectrum of 3-cyanopyridine was measured for a 20% aqueous solution, and, for those of the hydrochlorides, solutions of the pyridines in concentrated or saturated aqueous hydrochloric acid were used, the cation concentrations being

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[1] Spinner, *J.*, 1960, 1226.

[2] (*a*) Spinner and White, *J.*, 1962, 3115; Spinner, *J.*, 1962, (*b*) 3119, (*c*) 3127.

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

[4] Andersen, Bak, Broderson, and Rastrup-Andersen, *J. Chem. Phys.*, 1955, **23**, 1047.

[5] (*a*) Wilmhurst and Bernstein, *Canad. J. Chem.*, 1957, **35**, 1183; (*b*) McCullough, Douslin, Messerly, Hossenlopp, Kincheloe, and Waddington, *J. Amer. Chem. Soc.*, 1957, **79**, 4289.

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

[7] Cook and Church, *J. Phys. Chem.*, 1957, **61**, 458.

[8] (*a*) Katritzky and Hands, *J.*, 1958, 2202; (*b*) Katritzky Hands, and Jones, *J.*, 1958, 3165; (*c*) Katritzky and Gardner, *J.*, 1958, 2198; (*d*) Katritzky, *Quart. Rev.*, 1959, **13**, 353.

[9] (*a*) Long, Murfin, Hales, and Kynaston, *Trans. Faraday Soc.*, 1957, **53**, 1171; (*b*) Chiorboli, Mirone, and Lorenzelli, *Ann. Chim.* (*Italy*), 1958, **48**, 355.

[10] (*a*) Greenwood and Wade, *J.*, 1960, 1130; (*b*) Gill, Nuttall, Scaife, and Sharp, *J. Inorg. Nuclear Chem.*, 1961, **18**, 79; (*c*) Cook, *Canad. J. Chem.*, 1961, **39**, 2009.

[11] Kahovec and Reitz, *Monatsh.*, 1936, **69**, 363.

[12] Pitzer and Scott, *J. Amer. Chem. Soc.*, 1943, **65**, 803.

[13] Wilmshurst and Bernstein, *Canad. J. Chem.*, 1957, **35**, 911.

[14] Fuson, Garrigou-Lagrange, and Josien, *Spectrochim. Acta*, 1960, **16**, 106.

[15] Whiffen, *J.*, 1956, 1350; Randle and Whiffen, in "Molecular Spectroscopy," Institute of Petroleum, London, 1955, p. 111.

[16] Green, (*a*) *J.*, 1961, 2236; (*b*) *Spectrochim. Acta*, 1961, **17**, 607; (*c*) *Spectrochim. Acta*, 1962, **18**, 39.

[17] Spinner, preceding paper.

40—50% except for 4-chloro- (33%) and 2- and 4-cyano-pyridine (22%). The 2- and 4-halogenopyridines were dissolved in the hydrochloric acid cautiously and with good cooling, and the solutions obtained were stable. 4-Cyanopyridine in hydrochloric acid, however, slowly undergoes hydrolysis under the conditions used, and 2-cyanopyridine does so more rapidly (half-reaction time, ~8 hr.); the Raman band intensities obtained for these compounds are therefore less accurate. This applies also to 2-bromopyridine, which darkens upon irradiation.

Infrared and Raman spectra were determined as before.[2a] The exciting mercury radiation used for the latter was not entirely monochromatic, but contained, in addition to the main line at 4358 Å (relative intensity, 100), also lines at 4347·5 (~5), 4339 (~2), 4078 (~1), and 4047 Å (~4). Appropriate subtractions from the observed Raman spectra were therefore made at −57, −101, −1578, and −1768 cm.$^{-1}$ from strong Raman bands. (This had not been done in the author's previous work.[1,2,18])

NOTATION AND BAND ASSIGNMENTS

Nomenclature in Description of Vibrations.—α-, β-, and γ-substituted pyridines have the same symmetries as *ortho-*, *meta-*, *and para*-disubstituted benzenes, respectively, and will perform the same CH vibrations as the latter. In the pyridinium ions the symmetries remain unchanged, but coupling is possible between N^+H and CH in-plane bending and conceivable between N^+H and CH out-of-plane bending; where such coupling occurs the vibrations concerned will be essentially like their counterparts in the corresponding monosubstituted benzene.

Various conflicting systems of numbering or lettering are in use for describing the fundamental modes of vibration in monosubstituted[12,14,15] and disubstituted[16,19,20] benzenes. The modes of ring vibration are essentially the same in a substituted benzene or pyridine (or pyridinium ion) as in benzene itself, and, for these, the now almost universally accepted system of numbering the benzene vibrations (due to Wilson[21] and depicted in ref. 6) can be used[6,12,14,16,20] without modification; this will be done here. For the CH and substituent vibrations the numbering system must be modified.

The notation here used for these, which.is shown in Table 1, has been chosen to preserve the maximum similarity between identically numbered vibrations for benzene, its derivatives, pyridines, etc.; symmetry considerations are disregarded (*e.g.*, 2, 3, and 11 always refer to the all-in-phase vibrations). Substituent vibrations are described as such and are *not* allocated redundant vibration numbers * (they have no counterparts in the case of benzene); C_{ar}-substituent stretching will be denoted by " S," for brevity. For 1,3-disubstituted compounds there are two possibilities: (*a*) all four hydrogen atoms vibrate in unison; (*b*) the 4-, 5-, and 6-hydrogen atoms vibrate in unison, but the 2-hydrogen atom vibrates essentially independently; in the present work (*a*) is assumed to be the case.

Band Assignments.—In the spectra assembled in Table 2 many bands are readily assigned, at least by analogy with the vibration spectra of related compounds; others are assigned tentatively, the assignments made by Lord, Marston, and Miller[6] for the deuteriopyridines being assumed to be correct. No assignments are attempted for CH stretching vibrations.

High-frequency Skeletal Stretching Vibrations.—For both neutral pyridines and ions, vibration 8a is readily located by its high intensity in the Raman spectrum. It has been assumed that the frequency of 19a is always higher than that of 19b, but the evidence on this point is not conclusive. ν_{14} has been placed[6] near 1350 cm.$^{-1}$ for the deuteriopyridines but cannot be located for the substituted derivatives. The 2-substituted pyridinium

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* This avoids confusion; *e.g.*, the C–D stretching vibration has been numbered[6] 20a, 7b, and 13 in 2-, 3-, and 4-deuteriopyridine, respectively.

[18] Spinner, *J.*, 1960, 1232.

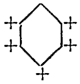
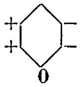
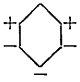
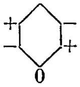
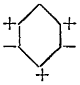
[19] Stojiljkovic and Whiffen, *Spectrochim. Acta*, 1958, **12**, 47, 57.

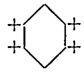
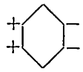
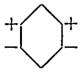
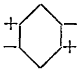
[20] Garrigou-Lagrange, Lebas, and Josien, *Spectrochim. Acta*, 1958, **12**, 305.

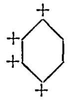
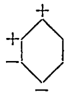
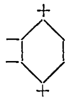
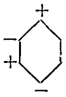
[21] Wilson, *Phys. Rev.*, 1934, **45**, 706.

TABLE 1.

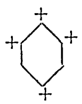
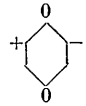
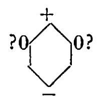
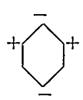
System adopted for numbering the CH vibrations in mono- and di-substituted benzenes and related compounds.*

Mono Vibration †						Redundant
CH st	2	20b	20a	7b	13	7a
CH ip be	3	18a	18b	9a	15	9b
CH op be	11	10a	10b	17a	5	17b

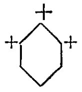
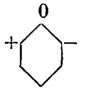
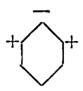
1,4-*Di*					Redundant	
CH st	2	20b	13	7b	7a	20a
CH ip be	3	18a	15	9a	9b	18b
CH op be	11	10a	5	17a	17b	10b

1,2-*Di*- ‡					Redundant	
CH st	2	20a	7a	13	20b	7b
CH ip be	3	18b	9b	15	18a	9a
CH op be	11	10b	17b	5	10a	17a

1,3-*Di*: All four hydrogen atoms move in concert.

							Redundant
CH st	2	20b ≡ 7b	20a		13	7a	
CH ip be	3	18a ≡ 9a	18b	or §	15	9b	Choice arbitrary
CH op be	11	10a ≡ 17a	10b		5	17b	

1,3-*Di*: The 4-, 5-, and 6-hydrogen atoms only move in concert.

				Redundant automatically	Redundant by choice	
CH st	2	20b ≡ 7b	13 ≡ 7a	20a	20b	7a
CH ip be	3	18a ≡ 9a	15 ≡ 9b	18b	18a	9b
CH op be	11	10a ≡ 17a	5 ≡ 17b	10b	10a	17b

* This system resembles that used by Lord *et al.*[6] for the diazabenzenes (but not for the mono-deuteriopyridines). † ++ denotes in-phase motion, +− out-of-phase motion, etc., 0 denotes no motion. (N.B. The + and − signs here do not refer solely to out-of-plane bending motions.) st = stretching; ip be = in-plane bending; op be = out-of-plane bending. ‡ The vibrations here designated " a " actually possess symmetry " b," and *vice versa* (for pyridazine Lord *et al.*[6] use the reversed designations.) § Neither description is very close, but the set 20a, 18b, and 10b presumably gives the more correct one.

ions show five reasonably intense infrared bands in the range 1630—1370 cm.$^{-1}$, and that near 1390 cm.$^{-1}$ is tentatively assigned to ν_{14}, as is the band found in the same position for the 4-substituted ions.

The Strong Raman Bands at 980—1070 cm.$^{-1}$.—The band near 1000 cm.$^{-1}$ in 2- and 4- and near 1040 cm.$^{-1}$ in 3-substituted pyridines and pyridinium ions is assigned to ring-breathing ν_1, that near 1040 cm.$^{-1}$ in 2-, near 1030 cm.$^{-1}$ in 3-, and near 1060 cm.$^{-1}$ in 4-substituted compounds to ring deformation ν_{12}. The last band could, instead, be attributed to in-plane CH bending ν_{18a} in 4-, ν_{18b} in 2-, and $\nu_{18a} = \nu_{9a}$ in 3-substituted compounds; however, this band is observed, not only for monosubstituted benzenes and pyridines, but also for pyridine where it is assigned[3] to vibration 12; it should be assigned to the same vibration throughout.

CH *Out-of-plane Bending Bands.*—2-, 3-, and 4-Substituted pyridines show a strong infrared band due to vibration 11 within the ranges [22] expected for 1,2-, 1,3-, and 1,4-disubstituted benzenes, respectively, but in the cations some of these bands are displaced outside these ranges. 3-Substituted pyridines, like 1,3-disubstituted benzenes,[22] show a

TABLE 2.

Band maxima in vibration spectra.*

Assignment †	4-Methylpyridine				4-Cyanopyridine				4-Chloropyridine				4-Bromopyridine			
	Infrared		Raman		Infrared		Raman		Infrared		Raman		Infrared		Raman	
8a	1607	1·6	1603	30	1595	0·85			1565	1·5	1567	59	1561	1·5	1561	33
8b	1561	0·5	1563	12	1546	0·75			1565	1·5	1567	59	1561	1·5	1561	33
19a	1497	0·4	1495	11	1499	0·5			1481	0·8	1479	7	1479	0·8	1479	3
19b	1414	0·9	1411	6	1415	1·3			1404	0·9	1403	7	1404	0·85	1404	4
3?	1289	0·01	1281	9					1316	0·2	1314	12	1313	0·2	1316	7
S/18a I	1226	0·5	1220	46	1193	0·3										
					1239	0·45										
9a	1212	0·2			1205	0·5			{1218	0·3	1217	40	1217	0·5	1216	31
									{1211							
					1111	0·2			1130	0·4	1128	25				
18a/S									1102	0·6	1101	69	1091	0·7	1092	53
12	1071	0·2	1069	9	1083	0·7			1062	0·5	1061	22	1061	0·7	1063	21
	1040	0·3	1041	4												
1	996	0·6	995	100	991	0·7					995	100	992	0·1	993	100
	971	0·1	973	6					982	0·3	983	81				
S/18a II			801	70	777	1·0										
11	800	1·6			828	1·4			809	1·0	811	3	803	1·1		
	725	0·3											718	0·2	723	2
S/6a I									706	1·3	709	45	676	1·5	678	25
6b			669	29							699	51			660	27
6a/S			515	25												
16b			487	8							493	7			485	4
S/6a II											414	59			314	70
16a											387	5				
X ip be			345	5							299	22			254	13
X op be			214	13							194	32			180	28

Assignment	4-Methylpyridine hydrochloride				4-Cyanopyridine hydrochloride				4-Chloropyridine hydrochloride				4-Bromopyridine hydrochloride			
	Infrared		Raman		Infrared		Raman		Infrared		Raman		Infrared		Raman	
8a	1633	0·55	1638	65	1631	0·55	1639	79	1621	0·9	1624	61	1620	1·0	1620	63
8b	1611	0·4	1610	9	1594	0·75	1587	12	1608	0·8			1604	0·7		
19a	1504	0·35	1507	5			1508	17	1511	0·2	1517	5	1508	0·3	1517	5
19b	1504	0·35	1507	5	1496	1·4			1480	1·0	1489	5	1474	0·7	1483	5
14?	{1377	0·2	1308	36	1362	0·15	1358	17	1364	0·3	1374	9	1357	0·5	1369	10
	{1366	0·2														
3	1311	0·4	1326	9	1335	0·45			1327	0·2	1321	7	1320	0·3	1327	7
					1299	0·6										
N+H ip be	1259	0·1	1258	18	1245	0·15	1246	21	1244	0·3	1251	28	1243	0·3	1250	31
S/18a I	1220	0·05	1227	62	1187	0·1	1198	92								
9a	1200	0·3	1205	22	1232	0·4			1204	0·2	1204	12	1201	0·2	1204	16
									1137	0·1	1151	7				
18a/S									1103	0·9	1114	72	1086	1·0	1093	82
					1086	0·2										
12	1069	0·1	1064	22	1056	0·2	1062	8	1052	0·1	1061	20	1051	0·2	1063	23
	1033	0·2			1044	0·2										
1	1007	0·1	1011	100	1005	0·4	1007	100	1008	0·5	1010	100	1007	0·1	1009	100
					995	0·15										
S/18a II			806	36			776	17								
11	793	1·0	797	16	822	1·1			802	1·8			798	1·9		
S/6a I									721	0·2	725	24			689	12
6b			651	42			652	29			645	35			644	30
6a/S			521	29			463	17								
16b			477	7			549	17			488	6			475	4
S/6a II											427	18			328	16
X ip be			351	7							305	14			257	12
X op be			222	12							203	12			193	12

* Wave numbers are in cm.$^{-1}$; concerning relative band intensities within each spectrum, see footnote *a*, *J.*, 1962, 3116. (N.B.: these intensities possess no absolute significance.)

† See ref. 6 and Table 1 for the numbering of ring and CH vibrations, respectively; st = stretching, be = bending, op = out-of-plane, ip = in-plane; X = substituent; S = C_{ar}–X stretching.

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[22] Cannon and Sutherland, *Spectrochim. Acta*, 1951, **4**, 373; McMurry and Thornton, *Analyt. Chem.*, 1952, **24**, 318.

TABLE 2. (*Continued.*)

Assignment	3-Methylpyridine				3-Cyanopyridine				3-Chloropyridine				3-Bromopyridine			
	Infrared		Raman		Infrared		Raman ‡		Infrared		Raman		Infrared		Raman	
8a	1598	0·2	1594	26	1589	1·1	1591	100	1563	0·3	1565	19	1560	0·15	1557	22
8b	1579	0·55	1575	14	1565	0·8			1572	0·7	*1569*		1571	0·35	1571	9
19a	1481	0·6	1476	6	1475	0·55			1468	1·0	1467	3	1463	0·5	1464	3
19b	1414	0·5	1408	5	1421	1·3			1415	1·1	1415	3	1414	0·65	1413	4
					1405	0·2			1320	0·2	1318	4	1319	0·2	1320	1
S/9a I	1228	0·1	1228	20	1214	0·3	1215	40								
3?	1193	0·3	1190	16	1188	0·5	1192	40	1190	0·2	1191	8	1190	0·1	1190	9
18b?	1126	0·2	1127	3					1155	0·2			1116	0·15	1118	2
9b?	1104	0·25	1103	2					1093	0·5	1094	11	1095 1086	0·55	1086	14
9a/S									1106	1·2	1107	12				
1	1043	0·2	1041	100	1035	0·25	1037	60			1038	100	1023	0·2	1035	100
12	1031	0·45	1029	29	1024	0·8	1031	50			1038	100	1023	0·2	1035	100
									1016	0·3	1018	4	1007	0·7	1007	2
	994	0·1														
S/9a II			805 797	23 25	780	0·2	785	20								
10b	788	0·6			810	1·45			795	1·0	802	1	791	0·55	797	1
S/6a I									727	0·8	729	20			705	20
11	709	0·7	713	1	700	2·4			700	1·4			698	0·85		
6b			628	12							615	6			613	5
6a/S			535	20			474	20								
16b															451	1
16a															400	1
S/6a II											426	18			322	44
X ip be			341	5							293	6			248	5
X op be			220	18			169	30			199	18			185	25

Assignment	3-Methylpyridine hydrochloride				3-Cyanopyridine hydrochloride				3-Chloropyridine hydrochloride				3-Bromopyridine hydrochloride			
	Infrared		Raman		Infrared		Raman		Infrared		Raman		Infrared		Raman	
8a	1628	0·7	1632	41	1630	0·3	1634	100	1616	0·05	1622	22	1615	0·1	1619	22
8b	1610	0·6	1614	17	1598	0·5	1605	27	1597	0·5	1606	7	1591	0·3	1605	6
			1578	6							1551	5			1542	5
19a	1551	1·7			1548 1531	0·7 0·25	1555	18	1523	1·1			1518	0·8		
19b	1474	0·7	1472	4	1464	0·8			1455	0·7	1465	2	1459 1449	0·2 0·6	1463	2
	1352	0·3	1355	10	1349	0·2	1340	9	1355	0·05	1347	5	1342	0·05	1342	5
	1315	0·3	1327	8					1327	0·4	1315	6	1314	0·1	1317	5
N^+H ip be	1262	0·4	1267	15	1256	0·1	1260	18	1251	0·6	1257	13	1243	0·4	1256	11
S/9a I	1232	0·1	1234	43	1222	0·1	1216	86								
					1211	0·2										
3?	1182	0·1	1184	20	1190	0·2	1189	32	1183	0·2	1187	12	1175	0·03	1188	11
9a/S									1118	0·5	1124	23	1105	0·55	1104	23
9b?	1116	0·4	1119	8	1119	0·03	1116	12	1107	0·6	1113	8	1101	0·3		
1	1046	0·3	1049	100	1034	0·2	1035	96	1038	0·1	1043	100	1036	0·1	1041	100
12	1024	0·1	1033	87	1050	0·15	1050	23	1028	0·3	1029	33			1032	43
									1016	0·3			1012	0·4		
	996	0·2	987	12					993	0·3						
									869	0·5			880	0·4		
S/9a II			806	59	775	0·15	776	40								
10b	787	1·5	798	26	822	0·7	811	8	804	1·7			791	1·0	805	1
S/6a I									728	0·8	732	32	698	0·15	702	29
11	677	1·6			675	0·75			671	1·4			668	0·8		
6b			629	30			628	36			20	14			620	15
6a/S			534	36			472	22								
16b							548 541	14 14							460	2
S/6a II											431	16			325	35
16a							396	9			404	4			400	3
X ip be			343	8							297	9			253	8
X op be			226	30			171	32			205	22			194	30

‡ Owing to low solubility, weak Raman bands could not be detected.

TABLE 2. (*Continued.*)

Assignment	2-Methylpyridine				2-Cyanopyridine				2-Chloropyridine				2-Bromopyridine			
	Infrared		Raman		Infrared		Raman		Infrared		Raman		Infrared		Raman	
8b	1594	1·4	1592	32	1597	0·2	1598	4	1573	1·4	1576	21	1570	1·0	1571	18
8a	1570	0·5	1570	34	1580	1·0	1579	83			1566	25	1561	0·9	1561	40
					1573	0·2	1569	39	1546	0·3	1547	7				
19a	1480	1·5	1478	7	1462	0·8	1465	4	1453	1·1	1452	5	1448	1·0	1449	13
19b	1439	1·0	1429	11	1433	0·9	1430	13	1420	1·5	1418	3	1415	1·3	1415	4
3?	1297	0·6	1296	20	1287	0·3	1289	7	1286	0·4	1286	9	1288	0·2	1285	11
					1249	0·2	1252	12	1237	0·03	1237	6	1240	0·05	1238	6
S/18b I	1239	0·2	1238	50	1200	0·05	1202	61								
9b	1151	0·6	1152	13	1154	0·3	1153	11	1149	0·8	1148	12	1148	0·2	1147	10
15?	1102	0·2	1102	12	1089	0·2	1092	6	1117	1·6	1116	16	1106	1·2	1106	10
18b/S									1083	0·9	1082	16	1077	1·0	1077	13
12	1051	0·7	1050	100	1045	0·5	1044	35	1045	0·6	1043	71	1042	0·4	1042	70
1	998	0·5	999	93	992	0·9	991	100	991	0·7	989	100	988	0·6	987	100
	976	0·2	980	14					959	0·1	960	5				
S/18b II	798	0·2	812 800	33 63			779	30								
11	753	1·5	754	2	779	1·3			763	1·6	766	1	758	1·0		
	729	0·7	730	4	736	0·6	737	3								
S/6a I									721	1·4	726	32	699	1·0	699	28
6b			628	33			631	14			616	18			613	12
6a/S			546	42			477	14								
16b			472	5			550	17			482	2				
S/6a II											426	40			313	49
16a			406	2			396	3			371	3				
X ip be			360	5			262	3			313	9			261	5
X op be			208	46			176	24			188	35			174	36

Assignment	2-Methylpyridine hydrochloride				2-Cyanopyridine hydrochloride				2-Chloropyridine hydrochloride				2-Bromopyridine hydrochloride			
	Infrared		Raman		Infrared		Raman		Infrared		Raman		Infrared		Raman	
8a	1632	0·35	1633	43	1615	0·2	1623	98	1611	0·7	1605	24	1608	0·4	1596	36
8b	1620	0·75			1606	0·45	1610	100	1586	0·4	1588	20	1586	0·55		
19a	1538	0·25	1542	9	1533	0·4			1520	0·4			1519	0·3		
19b	1476	0·3			1459	0·25	1464	24	1449	0·6	1456	6	1445	0·4	1456	7
													1401	0·1	1400	6
14?	1396	0·2	1399	25	1392	0·15	1396	37	1371	0·4	1382	4	1370	0·5	1382	5
3?	1297	0·15	1295	21	1303	0·15	1307	68	1283	0·2	1289	18	1278 1266	0·2 0·15	1284	18
					1264	0·05	1264	23								
N+H ip be					1252	0·15			1233	0·2	1239	14	1242	0·02	1239	11
S/18b I	1257	0·04	1247	56	1220	0·15	1221	90								
9b	1164	0·15	1164	14	1164	0·15	1172 1165	20 17	1154	0·2			1155	0·1	1166	14
18b/S									1141	0·2	1147	57	1121	0·2	1126	71
15	1105	0·05	1105	9					1087	0·2	1089	20	1083	0·1	1087	18
12	1040	0·2	1074	65	1043	0·03	1042	60	1033	0·1	1043	100	1031	0·05	1042	100
1	1013	0·1	1015	100	1004	0·2	1009	80	996	0·3	1002	65	1015	0·2	1008	78
	992	0·2	993	20									994	0·15		
N+H op be	944	0·15														
S/18b II	802	0·05	806	93	776	0·1	777	45								
11	769	0·7	765	2	791	1·5			774	1·05	772	4	771	0·8		
									764	0·6			760	0·4		
S/6a I									725	0·2	734	65	694	0·1	702	67
6b			628	35			629	27			621	29			618	25
6a/S			542	12			477	33								
16b			473	5			535	23			481	6			466	4
S/6a II											441	51			329	95
16a			396	4							403 386	6 4			394	5
X ip be			358	7							316	12			265	14
X op be			218 210	20 10			168	30			197	47			185	56

TABLE 2. (*Continued.*)

Aromatic C–H stretching frequencies

	$X{\cdot}C_5H_4N$					$X{\cdot}C_5H_4N^+H\ Cl^-$				
2-Me	3050	0·2,	3050; §	3013	0·5	3045	0·25			
2-CN	3060	0·2				3024	0·2			
2-Cl	3060	0·2				3075	0·2			
2-Br	3053	0·1				3080	0·1			
3-Me	3025	0·35				3035	0·6			
3-CN	3060	0·35				3005	0·6			
3-Cl	3046	0·3,	3054 §			3015	0·5			
3-Br	3042	0·15	3055 §			3061	0·4			
4-Me	3035	0·4				3045	0·2			
4-CN	3095	0·15		3030	0·15	3060	0·2		3035	0·35
4-Cl			3057; §	3035	0·3	3040	0·5,	3048; §		
4-Br	3030	0·3				3040	0·4			
4-I	3025	0·1				3095	0·1		3040	0·15

Infrared N$^+$–H stretching (and overtone?) frequencies

	$X{\cdot}C_5H_4N^+H\ Cl^-$					
2-Me	2680 + 2635	1·1				
2-CN	2360	0·4	**2283**	1·3		
2-Cl	**2375**	0·8	1939	0·3		
2-Br	2415	0·6				
3-Me	**2675**	1·8	2050	0·3		
3-CN	**2500**	1·5	2100	0·4	1994	0·35
3-Cl	2670	0·4	**2530**	1·5		
3-Br	2775	0·4				
4-Me	**2580**	1·1	2035	0·2	1966	0·2
4-CN	**2490**	1·5	2083	0·4		
4-Cl	2578	1·6				
4-Br	2625 + 2570	1·9				
4-I	2635	0·8				

	Cyanopyridines				Cyanopyridine hydrochlorides			
	Infrared		Raman		Infrared		Raman	
	C≡N Stretching frequencies							
2-CN	2235	0·3	2237	230			2254	550
3-CN	2233	0·5	2241	250	2245	0·15	2251	450
4-CN	2240	0·25			2245	0·2	2250	230
	C–C≡N in-plane bending bands							
2-CN			362	6			359	10
3-CN							369	18

	Methylpyridines				Methylpyridine hydrochlorides			
	Infrared		Raman		Infrared		Raman	
	Antisymmetrical methyl CH bending bands							
2-Me	1459 1449	0·3 0·3	1461	8	1476	0·3		
3-Me	1459	0·25	1453	5	1445	0·1	1449	8
4-Me	1444	0·5	1467 1448	6 7	1441	0·2	1441	6
	Symmetrical methyl CH bending bands							
2-Me	1378	0·4	1377	28	1371	0·03	1385	30
3-Me	1384	0·2	1380	13	1385	0·2	1388	24
4-Me	1380	0·3	1378	18	1377 1366	0·2 0·2	1380	36

Infrared spectra of 4-iodopyridine and 4-iodopyridine hydrochloride

	Base		Salt	
8a	1563	1·2	1615	0·65
8b	1543	0·4	1601	0·4
19a	1467	0·2	1500	0·15
19b	1399	0·8	1471	0·45
14?			1352	0·25
3?	1308	0·1	1310	0·1

	Base		Salt	
N$^+$H ip be			1239	0·1
9a	1209	0·2	1200	0·15
18a	1057	0·4	1069	0·3
12?			1028	0·15
1	987	0·1	1004	0·4
11	803	1·0	788	1·0
	794	0·4		
	720	0·1		
S/6a I	658	0·8	662	0·03

§ Observed Raman band excited by Hg line at 4047 Å.

second band, at higher frequencies, here assigned to ν_{10b}. None of the cations shows the pattern observed [22] for monosubstituted benzenes; it is certain for 2- and 4- and probable for 3-substituted pyridinium ions that the N$^+$–H bond does not behave like another C–H bond so far as out-of-plane bending is concerned. ν_5 cannot be located.

CH *In-plane Bending Bands.*—Assignments to vibrations 3, 9, and 15 are very tentative; concerning vibration 18, see below. As these frequencies change little on cation formation, it now seems that in monosubstituted pyridinium ions the N$^+$–H bond does not perform in-plane bending in unison with the C–H bonds.

Substituent-sensitive Vibrations.—While the vibration spectra discussed here are, for the most part, affected only in minor ways by the substituent, some bands that are prominent in the Raman spectrum are strongly influenced by the substituent. In this respect each substituted pyridine and pyridinium ion strongly resembles the corresponding monosubstituted benzene.

It has long been established that in phenyl–X (other than deuteriobenzene) some of the vibrations performed do not correspond exactly to normal modes; instead,[11] one observes six frequencies recognised as " X-sensitive " by Whiffen.[15] The nature of the vibrations involved is to some extent reinterpreted here. The two of lowest frequency are readily assigned * to out-of-plane and in-plane bending by X, respectively, the latter vibration being mixed somewhat with 16b when an atom in the first row of the Periodic Table is attached to the benzene ring.

The three X-sensitive polarised Raman bands are due to mixed vibrations involving C–X stretching, a vibration in the A_1 class the unperturbed frequency of which is near 1080 cm.$^{-1}$, and 6a; when a first-row element is attached to the benzene ring, C–X stretching (unperturbed frequency near 1090 cm.$^{-1}$) mixes mainly with the aromatic vibration near 1080 cm.$^{-1}$; when a heavier element is attached it mixes mainly with 6a.

The aromatic A_1 vibration involved has often [12,15,16] been considered to be 12; Fuson and his collaborators,[14] on the other hand (and, apparently, also Stephenson *et al.*[23]), propose that it is 1. Though mixing between vibration 1 and C–X stretching undoubtedly occurs in 1,2- and 1,4-disubstituted benzenes in which two first-row elements are attached to the nucleus, and for which neither strong Raman band near 1000 cm.$^{-1}$ is observed, it is most unlikely to occur in monosubstituted benzenes, which show both bands.

For reasons given above, the strong Raman band near 1050 cm.$^{-1}$ is here assigned to vibration 12, and C–X stretching in monosubstituted benzenes is considered to mix with 18a (indeed, according to the vibration diagram by Lord *et al.*,[6] 18a in benzene, pyridine, and 4-substituted derivatives thereof automatically entails some C–X stretching and would naturally tend to mix with it).

In spectra of 2-substituted pyridines, and even more so of their cations, the X-sensitive frequency in the 1100—1250 cm.$^{-1}$ range is appreciably higher than it is in the substituted benzene, and interaction with a further vibration (presumably also CH in-plane bending) seems feasible.

Reassignment of Some Bands in the Amino- [2b] *and Methoxy-pyridine* [2a] *Spectra.*—In the light of the information now available several reassignments are necessary. Aminopyridines, 3-aminopyridinium ion, methoxypyridines and ions: prominent Raman band near 640 cm.$^{-1}$, previously 4?, now 6b; 2-substituted compounds, previously 9a, now 9b; 3-substituted compounds, previously 9a, now 3? Aminopyridines and 3-aminopyridinium ion: prominent Raman bands, near 550 cm.$^{-1}$, previously unassigned, now 6a/S; near 1270 cm.$^{-1}$, previously unassigned, now S/18 I; near 850 cm.$^{-1}$, previously 5, now S/18 II (N.B. This reassignment does not apply to the cations of 2- and 4-aminopyridine or to 2- and 4-pyridone). ν_{14} is probably 1400 cm.$^{-1}$ in the 4-mercapto- [2c] and 1383 cm.$^{-1}$ in the 4-methylthio-pyridinium ion.[2c] 4-Mercaptopyridinium ion, 715 cm.$^{-1}$ now C-S st/6a; 4-methylthiopyridinium ion, 731 cm.$^{-1}$ now C_{ar}–S st/C_{Me}–S st/6a.

Methoxypyridines and ions: prominent Raman band near 450 cm.$^{-1}$, previously 16, now 6a/S. 3-Methoxypyridinium ion, 1612 cm.$^{-1}$ now 8b, 1552 cm.$^{-1}$ now 19a. 4-Methoxypyridinium ion, 1530 cm.$^{-1}$ now 19a, 1512 cm.$^{-1}$ now 19b. The " S/18 " vibrations in the methoxy-compounds are more complicated; vibration 18a (18b in the 2-substituted compound) mixes with C_{ar}–O and C_{Me}–O stretching; this gives rise to three mixed vibrations, near 810, 1020, and 1290 cm.$^{-1}$ (previously assigned to ν_5, COC symmetric, and COC antisymmetric stretching, respectively). In spectra of 2-methoxypyridine and its ion the high-frequency band is split (conceivably by interaction with ν_3), the band near 1320 cm.$^{-1}$ (previously assigned to ν_3) being the major component. These reassignments become necessary in the light of recent data [16c,23] for anisole.

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* Benzene ring-vibration frequencies lower than 340 cm.$^{-1}$ do not seem credible (though they have been proposed occasionally [16]).

[23] Stephenson, Coburn, and Wilcox, *Spectrochim. Acta*, 1961, **17**, 933.

SUBSTITUENT AND RELATED EFFECTS

The Effect of Cation Formation on the Vibration Spectra.—As observed previously for pyridine,[1] the methoxypyridines, 3-hydroxy-[1] and 3-amino-pyridine (but not 2- and 4-aminopyridine, the anomalous behaviour [2b] of which is thereby strikingly demonstrated), cation formation produces only minor changes in the vibration frequencies, and, in the Raman spectrum, relative band intensities also undergo comparatively little change. The high-frequency skeletal stretching frequencies are, in general, appreciably raised in the cations; ν_1 is raised to a much smaller extent, as are the X-sensitive 18/S/6a bands. Cation formation of 2-substituted pyridines considerably reduces the intensity of the Raman band due to ν_1; for the 3-substituted pyridines it reduces the frequency ν_{11} by 25—30 cm.$^{-1}$.

Substituent Effects on Vibration Frequencies in Pyridinium Ions.—Aromatic frequencies may be affected by the mass of the substituent, strongly (Whiffen's "X-sensitive" group), appreciably (*e.g.*, ν_{8a} and ν_{19a} in 4-substituted pyridines are lowered by 30 cm.$^{-1}$ for the 4-iodo-compound), or hardly (if at all). In neutral pyridines the frequencies [8] (unlike some infrared band intensities [8,24]) are usually unaffected by the electronic effect of the substituent. In the ions, however, polar and conjugation effects might be expected to be more prominent, and a knowledge of these effects may be helpful in structural elucidation where the exact structure of an ion is uncertain. The results for the more prominent bands are summarised below (previous [2] results being taken into account).

Few frequencies are appreciably influenced by the polar effect of the substituent; those that are so influenced are normally raised by electron-donating groups, and *vice versa*. The reason for such shifts is not known; some frequencies in spectra of neutral pyridines,[8] however, are also affected in this manner. Substituents which conjugate strongly with the aromatic nucleus with consequent electron-delocalisation would be expected: (1) to reduce the average mobile bond order in the ring and thereby lower [1,2b] the skeletal frequencies ν_8, ν_{19}, ν_{14}, and ν_1; and (2) to raise the C_{ar}–X bond order and thereby raise the intrinsic C–X stretching frequency and, hence, the S/6a and S/18 frequencies. In the comparisons between the vibration spectra of phenol [25] and the phenoxide ion [18] both these expectations are realised, but the frequency shifts are small (average for ν_8 and ν_{19}, -19 cm.$^{-1}$, for "S" frequencies, $+15$ cm.$^{-1}$). Comparing monosubstituted benzenes with the corresponding monosubstituted pyridinium ions, for the substituents Me, Cl, Br, OMe, and CN, one finds (*a*) that the skeletal stretching frequencies in the ions are always raised and not lowered, and (*b*) that the frequencies of the "S" vibrations are always raised in the ions, but that this rise is not related to the conjugating ability of the substituent. Thus the effects of electron delocalisation do not manifest themselves in these spectra.

Substituent Effects on the Relative Intensities of the Major Bands in Pyridinium Ion Spectra.—In general these effects are not very pronounced. Where there is an appreciable substituent effect, as in the relative intensities of the Raman bands of 2-substituted pyridinium ions, it is not very regular. Electron-withdrawing substituents in the latter ions cause some mixing between vibrations 8a and 8b, which confers appreciable Raman intensity on 8b; for the 2-chloro-derivative it has the unusual result of making 8a more intense than 8b in the infrared spectrum. In the 2- and 3-cyano-derivatives there is a specific substituent effect which greatly intensifies ν_{8a} in the Raman spectrum.

The most intense vibrational bands, in general summary, are as follows. 4-Substituted pyridinium ions: Raman, ν_1 (most intense), ν_{8a}, one of the "S" bands; infrared, ν_{8a} or ν_{19b}, ν_{11} $\nu_{S/18a\,II}$ sometimes. 3-Substituted pyridinium ions: Raman, ν_1 (most intense), ν_{12}, an "S" band; infrared, ν_{11}, ν_{10b}, ν_{19a} (ν_{19b} for cyano derivative). 2-Substituted

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[24] Katritzky, *J.*, 1958, 4162.

[25] J. C. Evans, *Spectrochim. Acta*, 1960, **16**, 1382.

4-Substituted pyridinium ions.

ν_{8a}: slightly mass-sensitive.
ν_{8b}: no substituent effect.
ν_{19a} (1535—1507 cm.$^{-1}$): no regular substituent effect.
ν_{19b}: somewhat mass-sensitive; raised somewhat by electron-donating groups (and *vice versa*).
$\nu_{14?}$: raised somewhat by electron-donating groups.
ν_{12}: no substituent effect.
ν_{1}: no substituent effect.

Frequencies of X-sensitive vibrations in $X{\cdot}C_5H_5N^+$ relative to those in $X{\cdot}C_6H_5$.

$\nu_{X\ op\ be}$ and $\nu_{X\ ip\ be}$: very slightly raised; no regular substituent effect.
$\nu_{S/6a\ II}$ or $\nu_{6a/S}$: appreciably raised only if substituent is heavy.
$\nu_{S/6\ I}$ or $\nu_{S/18a\ II}$: raised; rise is not correlated with the polar or conjugating effect of X.
$\nu_{S/18a\ I}$ or $\nu_{18/S}$: raised by about 20 cm.$^{-1}$.

3-Substituted pyridinium ions.

ν_{8a} and ν_{8b}: slightly mass-sensitive.
ν_{19a} (1555—1518 cm.$^{-1}$): mass-sensitive.
ν_{19b} (1490—1455 cm.$^{-1}$): raised by electron-donating substituents.
ν_{14} raised by electron-donating substituents.
ν_{1}: slightly raised by electron-donating substituents.
ν_{12}: slightly lowered by electron-donating substituents.

Frequencies of X-sensitive vibrations in $X{\cdot}C_5H_5N^+$ relative to those in $X{\cdot}C_6H_5$.

$\nu_{X\ op\ be}$: slightly raised; no regular substituent effect.
$\nu_{X\ ip\ be}$: unchanged.
$\nu_{S/6a\ II}$ or $\nu_{6a/S}$: raised; rise not determined by polar or conjugating effect of X.
$\nu_{S/6a\ I}$ or $\nu_{S/9a\ II}$: raised by 20—30 cm.$^{-1}$; no regular substituent effect.
$\nu_{S/9a\ I}$ or $\nu_{9a/S}$: raised by 10—70 cm.$^{-1}$; no regular substituent effect.

2-Substituted pyridinium ions.

ν_{8a}, ν_{8b}, ν_{19a}, ν_{19b}: slightly mass-sensitive; tend to be raised by electron-donating substituents, but the correlation is not good.
$\nu_{14?}$: mass-sensitive.
ν_{12} and ν_{1}: no regular substituent effects.

Frequencies of X-sensitive vibrations in $X{\cdot}C_5H_5N^+$ relative to those in $X{\cdot}C_6H_5$.

$\nu_{X\ op\ be}$: hardly raised.
$\nu_{X\ ip\ be}$: tends to be raised; no regular substituent effect.
$\nu_{S/6a\ II}$ or $\nu_{6a/S}$: raised by 15—25 cm.$^{-1}$; no regular substituent effect.
$\nu_{S/6a\ I}$ or $\nu_{S/18b\ II}$: raised by 12—30 cm.$^{-1}$; rise increases with mass and perhaps with electron-donating effect of X.
$\nu_{S/18b\ I}$ or $\nu_{18b/S}$: raised by 35—60 cm.$^{-1}$; no regular substituent effect.

pyridinium ions: Raman, ν_{12}, ν_1, one or more of the "S" bands, order of intensities variable, but all within a factor of about 1·5; infrared, ν_{11} and ν_{8b}.

C≡N *Stretching Bands of Cyano-derivatives.*—These are quite weak in the infrared but very intense indeed in the Raman spectra. The frequencies are in the region expected [26] for cyano-groups attached to very strongly electron-withdrawing aromatic rings and are raised on cation formation.

N^+–H *Bands in Pyridinium Chlorides.*—Since the N^+–H vibrations appear to be independent of the CH vibrations, N^+–H out-of-plane and N^+–H in-plane bending bands, near 910 cm.$^{-1}$ and 1250 cm.$^{-1}$, respectively,[27] are to be expected. 3- and 4-Substituted pyridinium ions show the band near 1250 cm.$^{-1}$, but only the 2-methyl- and 2-methoxypyridinium ions [2a] show the out-of-plane bending band. The N^+–H stretching bands, by contrast, are very intense in the infrared spectra; their low frequencies show that there is strong hydrogen-bonding in the solids.

Some evidence concerning the type of hydrogen-bonding involved is obtained from the substituent effect on the N^+–H stretching frequency. Amongst the methylpyridinium

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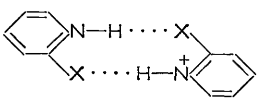
[26] Kiston and Griffith, *Analyt. Chem.*, 1952, **24**, 334; Thompson and Steel, *Trans. Faraday Soc.*, 1956, **52**, 1451; El-Sayed, *J. Inorg. Nucl. Chem.*, 1959, **10**, 168.
[27] Spinner, *J.*, 1963, 3870.

chlorides the frequency is lowest (hydrogen-bonding strongest) for the 4-isomer; for all the other substituted pyridinium ions examined it is lowest for the 2-isomer. The principal difference between methyl on the one hand, and cyano, chloro, bromo, and methoxyl on the other, is that methyl cannot act as a hydrogen-bond acceptor whereas the others can. In the methylpyridinium chlorides the hydrogen-bonding must be cation-to-anion; in the others cation-to-cation bonding is possible. The latter has previously been proposed[28] for 2-bromopyridinium chloromercuriate, in which there is appreciable hydrogen bonding, although cation-to-anion bonding must be quite weak. To account for the low N^+–H stretching frequencies in 2-substituted pyridinium chlorides (other than 2-picolinium), hydrogen-bonded cation pairs (*e.g.*, as shown), are suggested. For this explanation to be acceptable, chlorine should be a stronger hydrogen-bond acceptor than bromine; it is noteworthy therefore that West and his collaborators[29] have now concluded that this is so.



The strength of the NH^+ group as a hydrogen-bond donor will increase with the electron-withdrawing effect of the substituent. This might be considered to provide an adequate explanation for the low N^+–H stretching frequencies in 2-substituted pyridinium ions, amongst which, indeed, the lowering of the frequency parallels the decrease in base strength of the pyridine. However, this correlation with ionisation constants[17,30] is less good for 3- and quite poor for 4-substituted pyridinium ions; it breaks down when 4- and 3-substituted ions are compared with 2-substituted ones. For the last-mentioned a special effect, such as cation-to-cation bonding, is therefore indicated; weaker cation-to-cation bonding in some of the other chlorides is not ruled out, but there is no positive indication of it.

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[28] R. F. Evans and Kynaston, *J.*, 1962, 1005.

[29] West, Powell, Whatley, Lee, and Schleyer, *J. Amer. Chem. Soc.*, 1962, **84**, 3221.

[30] Albert, " Heterocyclic Chemistry," Athlone Press, London, 1959, pp. 343—344; Mason, *J.*, 1959, 1247.