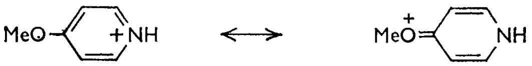
602. *The Vibration Spectra of the Cations of Methoxypyridines.*

By E. Spinner and J. C. B. White.

The infrared and Raman spectra of the hydrochlorides of 2-, 3-, and 4-methoxypyridine have been compared with those of the free bases and assignments have been made for the principal bands. Cation formation does not change the spectra profoundly.

THE structures of methoxypyridine cations are known in essentials. It is true that, for the 2- and the 4-isomer, the extent to which the form bearing the positive charge on the oxygen atom [*e.g.*, (II)] contributes is uncertain; however, the major contribution must be presumed to come from the form in which the nitrogen atom is positively charged [*e.g.*, (I)]. The methoxypyridine cations are therefore useful reference compounds for vibration spectral studies of ions such as hydroxy-[1-4] and amino-pyridine[5] cations, the structures of which are not known *a priori.*

(I)



(II)

A contrary view concerning the structure of the 4-methoxypyridinium ion, to the effect that form (II), and not (I), makes the major contribution, was expressed by Tsubomura[6] on the basis of a (very limited) ultraviolet- and infrared-spectral study of the 4-methoxy-2,6-dimethylpyridinium ion. However, contrary to what Tsubomura implies, the ultraviolet spectrum of the 4-methoxypyridinium ion[7] ($\lambda_{\text{max.}}$ 235 mμ, ε 9500) is neither strikingly different from that of 4-methoxypyridine[7] (222 mμ, ε 9300; 235 mμ, ε 2000, infl.) nor strikingly similar to that of 4-pyridone[7] (253 mμ, ε 14,800). The assignment of

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[1] Sensi and Gallo, *Ann. Chim. Appl.*, 1954, **44**, 232.

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

[3] Spinner and White, unpublished work.

[4] R. A. Y. Jones, Katritzky, and Lagowski, *Chem. and Ind.*, 1960, 870; Katritzky and R. A. Y. Jones, *Proc. Chem. Soc.*, 1960, 313.

[5] Following paper.

[6] Tsubomura, *J. Chem. Phys.*, 1958, **28**, 355.

[7] Mason, *J.*, 1959, 1253.

Vibration spectra[a] in the range 1800—650 cm.$^{-1}$ (Raman spectra to 200 cm.$^{-1}$).

2-Methoxypyridine

Assignment[b]	Infrared		Raman	
	Neutral species			
8b	1606	0·75	1601	13
	1589	0·1		
8a	1575	0·7	1570	50
19a	**1484**	1·0		
CH_3 be	1447	0·6	1443	19
19b	1422	0·8	1417	5
3?	1314	0·4	1308	56
COC a-st	1292	0·85	1286	27
	1257	0·55	1256	5
	1180	0·02	1177	9
9a?	1144	0·35	1140	7
	1119	0·1		
	1099	0·05	1095	19
12	1046	0·6	1043	33
COC s-st	1022	0·65	1021	11
1	988	0·35	**988**	100
	956	0·05	930	5
	828	0·03	826	5
5	812	0·4	810	56
11	781	0·7	781	7
	736	0·25		
			622	14
			602	12
16			456	25
			231	11

3-Methoxypyridine

Assignment	Infrared		Raman	
	Neutral species			
8a	1588	0·2	1588	50
8b	1578	0·45	1579	20
19a	1482	0·55		
CH_3 be	1465	0·1	1460	15
19b	1427	0·55	1426	10
COC a-st	**1284**	0·7	1282	35
	1269	0·65	1271	30
	1234	0·55	1233	10
9a	1193	0·3	1191	25
	1179	0·05	1179	20
	1130	0·1		
15?	1111	0·25	1111	15
1	1052	0·4	**1051**	100
12	1018	0·45	1014	70
	923	0·1		
5	799	0·5	798	90
11	706	0·5		
4?			620	16
			570	8
			515	10
16			443	25
			256	15
			209	15

4-Methoxypyridine

Assignment	Infrared		Raman	
	Neutral species			
8a	**1597**	1·6	1590	23
8b	1574	0·8	1569	4
19a	1507	1·1	1501	4
CH_3 be	1465	0·4	1460	8
	1445	0·3	1441	1
19b	1423	0·5	1419	1
	1333	0·05	1332	5
COC a-st	**1289**	1·6	1284	20
	1244	0·2	1240	8
9a?	1215	1·1	1208	15
	1183	0·05	1180	6
	1089	0·1	1073	2
12?			1051	4
COC s-st	1029	1·5	1025	3
1	990	0·4	**987**	100
11	818	1·1		
5	802	0·6	801	33
	707	0·1		
4?			661	19
			537	2
16			442	15
			261	1

2-Methoxypyridine hydrochloride

Assignment	Infrared		Raman	
8a	1631	0·8	1630	23
8b	**1613**	1·5		
19a	1540	0·8	1545	4
	1520	0·1		
19b + CH_3 be	1462	0·6	1461	21
CH_3 be	1384	0·55		
3?	1321	0·8	1326	80
COC a-st	1297	1·4	1295	36
	1235	0·5	1240	16
9a?	1175	0·5	1186	6
			1167	11
	1102	0·25	1105	11
12	1037	0·25	1046	56
COC s-st	1012	0·7		
1	981	0·8	986	86
$\overset{+}{\mathrm{N}}$H be	939	0·3		
5	810	0·1	**809**	100
	799	0·1		
11	774	1·2		
	723	0·2		
			621	29
			560	20
16			465	47
			242	6

3-Methoxypyridine hydrochloride

Assignment	Infrared		Raman	
8a	1620	0·3	1628	38
	1612			
8b + 19a?	**1552**	1·5	1561	8
			1508	18
CH_3 be	1461	0·5	1464	15
19b	1444			
CH_3 be	1356	1·2	1362	23
3	1323	0·35	1324	5
COC a-st	1279	1·6	1282	33
9a	1191	0·2	1185	23
	1148	0·02	1147	9
15?	1109	0·1	1116	13
1	1050	0·5	**1051**	100
COC s-st?	1023	0·2		
12	1012	0·6	1006	57
COC s-st?	998	0·8	998	5
	874	0·3		
11	807	1·4		
5	796	1·1	800	70
	673	0·75		
4?			620	20
			563	13
16			446	20
			407	7
			253	7

4-Methoxypyridine hydrochloride

Assignment	Infrared		Raman	
8a	1635	1·0	1640	78
8b	1600	0·4		
19b	1529	0·25	1536	11
19a	**1512**	1·3		
CH_3 be	1459	0·1	1466	20
	1433	0·2	1442	20
	1398	0·5	1403	28
COC a-st	1322	1·0	1318	33
	1304	0·8		
	1259	0·1	1265	33
9a?	1192	0·6	1200	33
	1099	0·1	1102	8
12	1044	0·05	1049	48
COC s-st	1012	0·8	1015	40
1	991	0·4	**994**	100
	856	0·1		
11	826	1·1	828	5
5	803	0·2	803	89
4?			642	43
			522	8
16			449	40
			259	15

[a] Wavenumbers are in cm.$^{-1}$; estimated band peak intensities (over and above background absorption or scatter) are in absorbance units in the infrared region, and in arbitrary units, making the strongest band equal 100, in the Raman spectra; most intense band in bold type; very weak bands omitted.

[b] For the numbering of aromatic vibrations, see ref. 12, and for diagrams thereof, Lord *et al.*, *Spectrochim. Acta*, 1957, **9**, 113. s-st = symmetric stretching; a-st = antisymmetric stretching; be = bending.

Infrared spectra in the range 3800—1800 cm.$^{-1}$.

2-		3-		4-		2-		3-		4-	
Methoxypyridine						Methoxypyridine hydrochloride					
3045	0·05	3015	0·15	3040	0·1	3105	0·1	3055	0·55	3070	0·3
3000	0·1					3040	0·2	2900	0·1	3015	0·15
2942	0·2	2950	0·15	2970	0·3	3010		2660	1·6	2925	0·1
2860	0·5	2835	0·1	2840	0·05	2750	0·1	2040	0·2	2795	0·2
						2510	1·2	1939	0·1	2700	0·1
						2000	0·15	1896	0·1	2635	0·9
						1926	0·25			2025	0·1
						1867	0·2			1931	0·2
						1784	0·5			1833	0·1
						Chloromercuriates (strong bands)					
						3085	0·8	3240	0·3	3250	0·5
								3075	0·5	3155	0·2
										3095	0·3

a band of medium intensity at 1654 cm.$^{-1}$ in the infrared spectrum of 4-methoxy-2,6-dimethylpyridinium picrate to carbonyl stretching seems very dubious (in the present work on 4-methoxypyridinium chloride no infrared band was found at 1654 cm.$^{-1}$). Thus, neither of Tsubomura's two lines of evidence shows the cation structure to be represented better by form (II) than by form (I).

The infrared spectra of 2-methoxy-,[8, 9] 4-methoxy-,[9, 10] and 3-ethoxy-pyridine [11] are known to be typical of 2-, 4-, and 3-substituted pyridines, respectively. The band assignments made previously [8–11] are only slightly modified, and extended, in the light of the Raman spectra, which have now been measured. For the hydrochlorides both the infrared and the Raman spectra are new. All these results appear in the annexed Table; the numbering of the vibrations is that used by Corrsin, Fax, and Lord.[12] The infrared spectra of the trichloromercuriates in general closely resemble those of the hydrochlorides and are not given here.

Experimental.—The neutral methoxypyridines were examined as pure liquids. The infrared spectra of the hydrochlorides and the trichloromercuriates were obtained for potassium bromide discs, and the Raman spectra of the cations for solutions of the methoxypyridines in concentrated hydrochloric acid (cation concentration, 40—45%). (No hydrolysis or other chemical change was experienced under these conditions.) The solid hydrochlorides were precipitated by means of hydrogen chloride in anhydrous ether, and the trichloromercuriates by the action of concentrated aqueous trichloromercuric acid on the pure methoxy-compound (1 mol.).

Infrared spectra were taken with a Perkin–Elmer 21 double-beam spectrophotometer fitted with a sodium chloride prism, Raman spectra (from 200—1800 cm.$^{-1}$) with a Hilger Raman spectrograph with photoelectric recording, operated at effective slit widths of 4—6 cm.$^{-1}$, mercury light at 4358 Å being used as the incident radiation; the range covered was unobscured by source emission except for a weak barium line at 986 cm.$^{-1}$.

Discussion.—The ring-breathing vibration ν_1 *and the ring deformation* ν_{12}. The "ring-breathing" motion gives rise to the most intense Raman band below 2000 cm.$^{-1}$ in all the spectra except that of the 2-methoxypyridinium ion, where it is somewhat surpassed in intensity by the band near 800 cm.$^{-1}$. The second very strong Raman band in this region in the pyridine spectrum (at 1030 cm.$^{-1}$) is due [11] to the deformation ν_{12}; this frequency is readily placed in all the spectra except that of neutral 4-methoxypyridine, which only shows one strong Raman band near 1000 cm.$^{-1}$.

The strong Raman band near 800 *cm.*$^{-1}$ This is also observed for the picolines,[13] though

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[8] Katritzky and Hands, *J.*, 1958, 2202.

[9] Katritzky and Coats, *J.*, 1959, 2062.

[10] Katritzky and Gardener, *J.*, 1958, 2198.

[11] Katritzky, Hands, and R. A. Jones, *J.*, 1958, 3165.

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

[13] Long, Murfin, Hales, and Kynaston, *Trans. Faraday Soc.*, 1957, **53**, 1171.

not for pyridine. For reasons to be discussed [5] it is assigned to a hydrogen out-of-plane bending vibration, presumably ν_5.

The high-frequency skeletal stretching bands. Unlike the bands discussed above, which are almost unchanged in frequency on cation formation, the frequencies ν_{8a}, ν_{8b}, ν_{19a}, and ν_{19b} tend to be raised in the cations. ν_{8a}, which is characterized by its prominence in the Raman spectrum, is located near 1630 cm.$^{-1}$ in the ions; in the infrared spectrum this band is very strong for the 4-methoxypyridinium ion, but a good deal weaker for the 2-isomer and quite weak for the 3-isomer. The very strong infrared band at 1613 cm.$^{-1}$ for the 2-isomer must be due to vibration ν_{8b}, that at 1552 cm.$^{-1}$ for the 3-isomer to ν_{8b} or ν_{19a}, or, more probably, a super-position of both. The infrared band due to vibration ν_{19b} is weaker, probably overlaps with the methyl–CH antisymmetric bending band, and cannot always be placed reliably in the ion spectra.

C–O–C *Stretching bands.* These [9] were identified unambiguously for the neutral methoxypyridines, and for the 4-methoxypyridinium ion, as the only appreciably strong infrared bands without counterparts in the corresponding methylthiopyridine spectrum [14, 15] above 800 cm.$^{-1}$. The symmetrical C–O–C stretching band of 3-methoxypyridine cannot be identified and is presumably submerged. As expected on the basis of previous experience,[16] the antisymmetric stretching frequency is raised on cation formation; the symmetric stretching frequency seems to be lowered. The band due to the antisymmetric stretching vibration is surprisingly intense in the Raman spectra, especially those of the ions (and very intense in the infrared spectra).

NH^+ *Vibrations.* All three hydrochlorides show very intense ^+N-H stretching bands, in the range 2500—2700 cm.$^{-1}$. The frequency is so low because the ^+NH group is a very powerful hydrogen-bond donor; the acceptor may be either a chloride ion or a methoxyl-oxygen atom in a neighbouring ion.

The trichloromercuriate anion $HgCl_3^-$ is known to be a much weaker hydrogen-bond acceptor [17] than chloride, and, by virtue of its large size, it also keeps the cations far apart. Accordingly, the ^+N-H stretching bands in the methoxypyridinium trichloromercuriates are located in the range 3000—3200 cm.$^{-1}$, corresponding to only weak hydrogen-bonding.

In the range 2000—650 cm.$^{-1}$ the band frequencies observed for the trichloromercuriates normally agree closely ($\pm$20 cm.$^{-1}$) with those found for the chlorides. However, a band at 939 cm.$^{-1}$ in the spectrum of the 2-methoxypyridinium chloride is strongly displaced (to 884 cm.$^{-1}$) in the trichloromercuriate, and is attributed to ^+N-H out-of-plane bending. No other ^+N-H bands have been identified. The in-plane ^+N-H bending motion in a pyridinium ion is presumably strongly coupled with the $C_{ar}-H$ in-plane bending motions. Thus the vibration ν_3, placed at 1335 cm.$^{-1}$ for the pyridinium ion, is regarded as an in-phase bending motion of all these hydrogen atoms.

General. Cation formation in methoxypyridines changes some of the characteristic frequencies somewhat (a little more so than it does in the case of pyridine). The relative band intensities in the infrared spectrum change considerably, but those of the main bands in the Raman spectrum far less. All three cations unmistakably exhibit the vibration spectral features expected for pyridinium ions. The comparison between the spectra of the cations of hydroxy- and methoxy-pyridines, and of substituted derivatives thereof, will be dealt with elsewhere.[3]

We thank Dr. R. F. Evans for bringing to our attention the usefulness of trichloromercuriates in infrared spectral studies.

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[14] Spinner, *J.*, 1960, 1237.
[15] Spinner, *J.*, 1962, 3127.
[16] Goldman, Lehman, and Rao, *Canad. J. Chem.*, 1960, **38**, 171.
[17] Evans and Kynaston, *J.*, 1962, 1005.