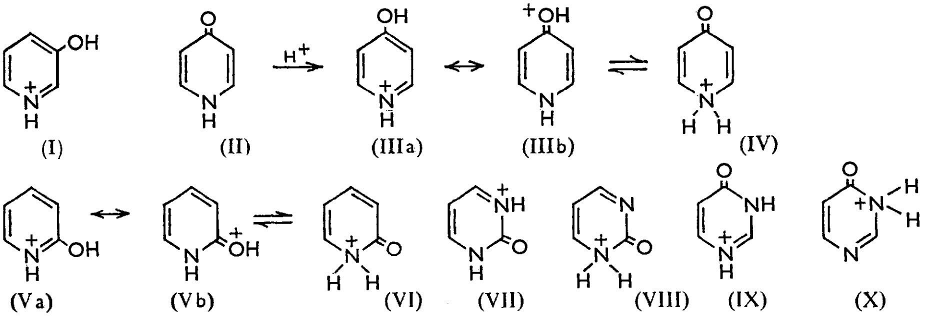
248. *The Vibration Spectra and Structures of the Hydrochlorides of Hydroxypyridines and Hydroxypyrimidines.*

By E. Spinner.

The infrared spectra of the hydrochlorides of the hydroxypyridines and hydroxypyrimidines in aqueous solution and in the solid state, and the Raman spectra of the aqueous solutions, have been determined. The spectrum of the cation of 3-hydroxypyridine is that of a truly aromatic compound. The cations preferentially formed by 2- and 4-hydroxypyrimidine are (VII) and (IX), those formed by 2- and 4-hydroxypyridine seem to be, not the ions of aromatic type (III) and (V), but the ions incapable of any major resonance, (IV) and (VI). The vibration spectra to be expected for truly intermediate mesomeric structures (III) and (V), in which the (*a*) and the (*b*) forms contribute equally, are discussed.

Addition of a proton to 3-hydroxypyridine can give only one cation (I), but addition to an α- or γ-hydroxyaza-aromatic compound, present mainly as a lactam or amide,[1] *e.g.*, (II), may occur at either the nitrogen or the oxygen atom. On the basis of the theory of π-electron delocalization one would expect the highly resonant cations (III) and (V) to be much more stable than (IV) and (VI), and up to the present the cations of 2- and 4-hydroxypyridine have generally [1,2,3] been taken to have the structures (III) and (V), respectively, ultraviolet spectral data [2] being interpreted as evidence therefor (but see p. 1237). Sensi and Gallo,[4] however, who previously examined the infrared spectra of the solid hydrochlorides of the hydroxypyridines, concluded that the cations formed were (VI), (I), and (IV); the present work fully confirms their findings.


(I) (II) (IIIa) (IIIb) (IV)

(Va) (Vb) (VI) (VII) (VIII) (IX) (X)

---

[1] Albert and Phillips, *J.*, 1956, 1294.

[2] Mason, *J.*, 1957, 5010.

[3] Mason, *J.*, 1958, 674.

[4] Sensi and Gallo, *Ann. Chim. Appl.* (*Italy*), 1954, **44**, 232.

If (like the author) one rejects the view that the π-electrons in conjugated systems are delocalized,* one would expect forms (IV) and (VI) to be more stable than (III) and (V), the equilibrium between, *e.g.*, (IIIa) and (IV) being exactly analogous to that between the two possible tautomers for the neutral molecule [(V) and (VI) on p. 1222]. Further, it has been found that proton addition to acetamide,[6] *N*-ethylacetamide,[7] and urea [8,6] gives, not the highly resonant cations $X{\cdot}C(={}^{+}OH){\cdot}NHR \longleftrightarrow X{\cdot}C(={}^{+}NHR){\cdot}OH$, but the (poorly resonant) ions $X{\cdot}CO{\cdot}{}^{+}NH_2R$, *i.e.*, there is proton addition to the nitrogen atom. The non-equivalence of different methyl-hydrogen atoms found in some protonated *N*-methylamides by proton magnetic resonance has been regarded [9] as evidence for *O*-protonation, but is also explicable for the *N*-protonated ions.[10]

Previous ultraviolet-spectral work [11] has shown that 2- and 4-hydroxypyrimidine are preferentially protonated at a nitrogen atom; the cation of the latter was proved to have structure (IX). This has been explained [1] by the resonance in (VII) and (IX) which spreads the positive charge between the two nitrogen atoms.

The criteria used for structure diagnosis are essentially those used for the neutral molecules,[12] together with comparison with the spectrum of the corresponding neutral molecule. Infrared and Raman spectra were determined on concentrated solutions of hydroxypyridines and hydroxypyrimidines in concentrated hydrochloric acid. Detailed infrared spectra were obtained for the solid hydrochlorides. In no instance is there an indication of the presence in aqueous solution of a major molecular species different from that found in the solid state. The vibration spectra of the hydrochlorides of pyridine and pyrimidine were determined for reference.

EXPERIMENTAL

Materials.—The solid hydrochlorides (obtained by crystallization from concentrated hydrochloric acid) were dried and analysed to make certain of the absence of water of crystallization; where necessary the solids were ground and mixed with potassium bromide in a dry atmosphere (pyridine hydrochloride is very hygroscopic).

Raman Spectra.—These were recorded photoelectrically with a Hilger Raman spectrograph operated at effective slit widths of 4—6 $cm.^{-1}$. The wave-numbers obtained here are often less accurate than those obtained photographically for the neutral molecules,[12] because the dispersion of the double-pass system of two glass prisms used with photoelectric recording is quite sensitive to temperature; no constant-temperature room being available, rough empirical corrections for temperature changes had to be applied. On the other hand, the relative intensities of the various bands within a spectrum could be measured fairly accurately; the peak intensities read off the chart, and given in the Table, do not possess any absolute significance, *i.e.*, band intensities are not comparable between different substances.

There was no indication of photochemical decomposition of any of the substances, but fluorescence sometimes reduced the amount of detail obtainable in the Raman spectrum (especially for 2-hydroxypyrimidine hydrochloride). Concentrations used (weight of solute to weight of concentrated hydrochloric acid) were: pyridine, 1 : 3·5; pyrimidine, 1 : 6; 2-hydroxypyridine, 1 : 4·5; 3-hydroxypyridine, 1 : 5; 4-hydroxypyridine, 1 : 3·5; 2-hydroxypyrimidine, 1 : 8; 4-hydroxypyrimidine, 1 : 4.

Infrared Spectra.—These were determined as for the neutral molecules,[12] except that the backgrounds for the solution spectra were obtained with concentrated hydrochloric acid;

---

* For criticism of the concept of π-electron delocalization, see Burawoy [5] (further criticism will appear elsewhere).

[5] Burawoy, in " Contribution a l'Etude de la Structure Moleculaire (V. Henri Mem. Vol.)," Desoer, Liège, 1948, p. 73; *Trans. Faraday Soc.*, 1944, **40**, 537; *Chem. and Ind.*, 1944, 434.

[6] Spinner, *Spectrochim. Acta*, 1959, 95.

[7] Cannon, *Mikrochim. Acta*, 1955, 563.

[8] Davies and Hopkins, *Trans. Faraday Soc.*, 1957, **53**, 1563.

[9] Fraenkel and Niemann, *Proc. Nat. Acad. Sci., U.S.A.*, 1958, **44**, 688; Berger, Loewenstein, and Meiboom, *J. Amer. Chem. Soc.*, 1959, **81**, 62.

[10] Spinner, *J. Phys. Chem.*, 1960, **64**; in the press.

[11] Brown, Hoerger, and Mason, *J.*, 1955, 211.

[12] Albert and Spinner, preceding paper.

concentrations of solutions (weight of solute to weight of concentrated hydrochloric acid) were: pyridine, 1 : 1·5; pyrimidine, 1 : 1·5; 2-hydroxypyridine, 1 : 3·5; 3-hydroxypyridine, 1 : 2; 4-hydroxypyridine, 1 : 1·5; 2-hydroxypyrimidine, 1 : 2·5; 4-hydroxypyrimidine, 1 : 3·5. The concentrations of the potassium bromide discs were 1 in 200, except for the hydrochlorides of pyridine and pyrimidine (handled in a dry box) where they were unknown.

RESULTS AND DISCUSSION

The spectral results are collected in the Table.

Pyridine and Pyrimidine Hydrochloride.—The Raman spectra of the hydrochlorides bear a fair resemblance to those of the neutral molecules;[13] they show the very strong band expected near 1020 cm.$^{-1}$ and a fairly strong one above 1600 cm.$^{-1}$; the frequency of the skeletal stretching band at 1585 cm.$^{-1}$ in pyridine is shifted to 1635 cm.$^{-1}$ in the hydrochloride. In the infrared spectra of the hydrochlorides the band near 1630 cm.$^{-1}$, while quite prominent, is not the strongest one. Presumably the two very intense Raman bands of pyrimidine hydrochloride at 1001 and 1058 cm.$^{-1}$ are a resonance doublet. Their relative intensities are unaffected by dilution with water, and there is no evidence of the presence of the dication $C_4N_2H_6^{++}$ in ~8N-hydrochloric acid (of the three benzodiazines pyrimidine should form the dication most readily).

Hydrochlorides of "Hydroxy"-compounds.—The high-frequency region. This region does not yield any information about the structures of the compounds. Since no O–H stretching band can be identified in the infrared spectrum of 3-hydroxypyridine hydrochloride the absence in the spectra of the other four "hydroxy"-cations of a band clearly attributable to O–H stretching does not represent evidence for the absence of a hydroxyl group there. There is much overlap between the C–H and O–H or N–H stretching bands. The bands at 2680 and 2663 cm.$^{-1}$ for the pyrimidine and 4-hydroxypyrimidine cations, respectively, are assigned to $^+$N–H stretching, strong hydrogen bonding between the $^+$NH group and a nitrogen atom in a neighbouring molecule being postulated.

The region 1800—700 *cm.*$^{-1}$. The vibration spectrum of the cation of 3-hydroxypyridine shows all the features expected of a truly pyridinoid compound: a strong Raman band at 1042 cm.$^{-1}$, a reasonably strong one at 1625 cm.$^{-1}$, a prominent infrared band near 1490 cm.$^{-1}$, and one of only moderate intensity at 1625 cm.$^{-1}$.

The most intense bands in the Raman spectra of the cations of 2-hydroxypyridine and 4-hydroxypyrimidine are at 852 and 1552 cm.$^{-1}$, respectively; only much weaker bands occur near 1000 cm.$^{-1}$; it seems that the predominant cations are not truly pyridinoid here. The cation of 2-hydroxypyrimidine shows a strong Raman band at 1063 cm.$^{-1}$, but none near 1600 cm.$^{-1}$, and is thus unlikely to be pyridinoid. The Raman spectrum of the cation of 4-hydroxypyridine, like that of the neutral molecule, is compatible with a pyridinoid structure.

The strong infrared bands above 1700 cm.$^{-1}$ shown by the cations of 2- and 4-hydroxypyrimidine are undoubtedly C=O stretching bands, those near 1640 cm.$^{-1}$ shown by the cations of 2- and 4-hydroxypyridine are very likely to be due to C=O stretching in the ions (IV) and (VI),[4] though *a priori* they could also, conceivably, be skeletal stretching bands in (III) and (V) analogous to the band at 1630 cm.$^{-1}$ for the pyridinium cation. However, quite apart from the Raman spectral evidence to the contrary for the 2-isomer, these ions show fewer strong infrared bands in the range 1400—1600 cm.$^{-1}$ than does the pyridinium ion (the strong band near 1490 cm.$^{-1}$ seems to be missing), which would seem to show that they are not simply pyridinium ions with a 2- or 4-hydroxy-substituent. Moreover, the close resemblance between the vibration spectrum of the 4-hydroxypyridine cation and that of the neutral molecule, unless a coincidence, is evidence that proton addition produces

---

[13] Long, Murfin, Hales, and Kynaston, *Trans. Faraday Soc.*, 1957, **53**, 1171; Lord, Marston, and Miller, *Spectrochim. Acta*, 1957, **9**, 113.

no drastic change in the structure of the molecule, or in the orders of the bonds in it; this would agree with structure (IV) for the cation.

Band peaks * *in the vibration spectra of the hydrochlorides* (*range* 1800—680 cm.$^{-1}$).

Pyridine		
I.R. Solid	I.R. Aq. soln.	Raman Aq. soln.
1630 s	1629 ms	1635 (12)
1604 s		1615 (4)
1527 vs	1538 m	
1479 s	**1489** s	
1428 w		
1369 mw		
1332 m	1339 w	1334 (2)
1245 ms	1251 w	1245 (3)
1238 ms		
1189 m	1200 w	1201 (10)
1155 m	1166 w	1162 (2)
1053 s	1057 w	1060 (5)
1027 w	1031 vw	1027 (22)
1012 w		
997 ms	1000 w	**1010** (75)
994 ms		
		952 (4)
910 mw	924 w	
880 w		866 (2)?
		812 (3)
749 sb	753 ms	
682 sb	684 m	

Pyrimidine		
I.R. Solid	I.R. Aq. soln.	Raman Aq. soln.
1792 vw		
1744 w		
		1677 (5)
1620 ms	1618 m	1617 (11)
1600 ms	1601 m	1597 (11)
		1549 (6b)
1530 m	1532 mw	
1453 ms	**1458** ms	
		1410 (2b)
1373 mw	1373 w	
1327 m		1345 (3b)
1296 m	1313 vw?	
1290 ms		
		1274 (1b)
1228 w	1232 vw	1236 (6)
1177 m	1182 mw	1179 (11)
1111 w		1111 (6b)
1082 vw		
1058 ms	1061 mw	**1058** (40)
1022 mw		
1000 ms	997 m	**1001** (37)
978 vw		
926 w	942 vw	
870 vw		
	843 w	
811 m	810 m	
693 ms	690 ms	
673 m		
663 m		667 (13)

2-Hydroxypyridine		
I.R. Solid	I.R. Aq. soln.	Raman Aq. soln.
1632 s	1635 ms	1638 (2)
1599 w		
1544 s	**1541** s	
1481 w	1500 vw?	1505 (2)
1426 w		
1398 m		
1369 m		
1344 s	1347 ms	1356 (3)
		1267 (2)
1242 m		1224 (1)?
1165 m	1161 w	
1125 vw		
1099 w		1099 (1)?
		1037 (2)
1004 w		1006 (4)
910 m		903 (1)?
869 w		
851 m	853 w	**852** (10)
780 s	778 ms	
731 w		

3-Hydroxypyridine		
I.R. Solid	I.R. Aq. soln.	Raman Aq. soln.
1627 m	1627 mw	1625 (8)
1554 s	**1564** ms	1553 (3)
1492 m	1487 mw	
1398 ms		1332 (4)
1315 m	1310 w	1305 (4b)
1268 ms	1279 vw	
1240 m	1240 w	1240 (2b)
1176 w		1174 (4)
1109 w	1111 w	1107 (4)
		1073 (2)
1042 w		**1042** (21)
1014 w		1014 (8)
988 w		
922 vw		
839 m	840 mw	838 (18)
805 ms	802 m	
767 vw		
759 vw		
690 w		
677 m		

4-Hydroxypyridine		
I.R. Solid	I.R. Aq. soln.	Raman Aq. soln.
1637 s	1641 s	1639 (6)
1611 m		1610 (1)
1551 m		
1510 s	**1516** s	
1466 vw?		
1388 m	1415 w	1393 (3)
1373 m		
1330 s	1343 ms	1336 (2)
1320 s		
1280 w	1279 w	
1228 mw	1227 w	
1218 ms		
1192 m	1196 m	1192 (2)
1130 vw	1150 vw	
1088 m	1090 mw	
		1046 (6)
1005 mw	1006 vw	**1006** (13)
1000 w		
977 vw		
912 vw		
848 m	*848* m	849 (10)
817 s	825 ms	
		793 (1)
760 w		
741 m		
		709 (1)

2-Hydroxypyrimidine		
I.R. Solid	I.R. Aq. soln.	Raman Aq. soln.
1731 s	1754 s	
1590 s	**1601** s	
1505 w		
1475 w		
1385 w		
1246 ms	1277 mw	
1194 ms	1215 mw	
1153 m		
1131 m	1140 w	
1093 w	1101 w	1103 (2)
		1084 (1)
1057 vw	1061 vw	**1063** (9)
1004 mw	1009 w	
990 vw		
864 mb		
849 m		855 (4)
783 ms	793 mw	
747 m	760 w	

---

* For explanation of abbreviations, see p. 1223.

TABLE. (*Continued.*)

4-Hydroxypyrimidine		
I.R. Solid	I.R. Aq. soln.	Raman Aq. soln.
1704 vs	**1726** s	1722 (16)
1656 ms	1663 w	1660 (7)
1564 s	1584 w	1585 (3)
		1552 (20)
		1501 (1)?
1448 ms		1468 (2)
1381 m		1398 (3)
1328 w		
1304 w		1310 (1)
1261 s	1243 m	
1246 w		
1216 w		1209 (9)
1181 m		
1147 vw		
1127 mw	1140 w	1138 (3)
1105 vw	1101 w	
1025 w		
1016 m		1019 (4)
1003 m		
994 ms	1000 vw	
880 m		
860 vw		
852 m		
829 ms	837 m	831 (6)
757 vw		
746 vw		
738 w		

Infrared absorption peaks in the range 3800—1800 cm.$^{-1}$ (solid states)						
		2-	3-	2-	2-	4-
Pyridine	Pyrimidine	Hydroxypyridine			Hydroxypyrimidine	
3418 svb	3407 mwvb	3253 mb	3241 mw		*3322* m	3272 w
3222 mb	3195 w	3169 mb	3180 m	3210 m	*3156* w	3212 m
3095 w	3130 w	3103 w	3114 m	3159 w	3105 ms	3153 s
3065 m	3105 mw	3082 m	3089 m	3108 w	3012 ms	3100 }
3022 w	3057 m	3014 m	3071 w	3077 m	2918 ms	3075 } s
2956 w	3033 m	2997 vw	**3008** s	3017 m	**2835** s	3049 }
2925 w	3010 w	2960 vw	2846 m	2954 w	2727 m	3020 }
2852 w	2976 w	2935 vw	2807 ms	**2876** s	2444 vw	2952w
2807 mb	2902 m	**2827** sb	2725 m	2807 vw	2172 vw?	2898 } m
2262 vw	2835 ms	2702 vw	2657 w	2722 m		2878 }
2189 vw	**2679** svb	2682 vw	1995 w	2695 w		2835 m
2128 vw	2583 wb	2633 w	1904 w	2638 w		*2758* w
2045 mwb	2403 w	2561 w	1834 vw	2609 vw		2725 s
1946 wb	2277 vw	2529 w		2577 m		**2663** s
	2214 vw	2492 w		2490 wb		2623 s
	2068 w	2459 w		2435 w		2558 m
	2009 w	1872 vw		2004 vw		2128 vw
	1953 mw	1813 vw		1887 vw		2023 vw
	1858 w			1818 vw		1970 vw

Band peaks * in the Raman spectra of the hydrochlorides in the range 680—200 cm.$^{-1}$.

Pyridine: 639 (11), 611 (7), 393 (2)
Pyrimidine: 623 (5), 401 (3), 345 (2)
2-Hydroxypyridine: 627 (1), 555 (2)
3-Hydroxypyridine: 624 (4), 543 (4), 435 (2), 236 (4)
4-Hydroxypyridine: 646 (4), 615 (1), 529 (3), 223 (1)?
2-Hydroxypyrimidine: 573 (3), 472 (1)
4-Hydroxypyrimidine: 637 (4), 548 (4), 490 (1b), 389 (1)?

" *Modified aromatic structures.*" The presence of a carbonyl group in the cations of 2- and 4-hydroxypyridine has not been proved beyond doubt; they could possess structures truly intermediate between (Va) and (Vb), and (IIIa) and (IIIb), respectively.

Any removal of π-electron density from the ring to the nitrogen atom reduces the bond orders in the ring, relatively to those obtaining in the truly aromatic ions, and so lowers the skeletal stretching frequencies: *e.g.*, a reduction in the CC bond order from 1·5 to 1·42 should lower the CC stretching frequency by ~50 cm.$^{-1}$ (from ~1350 to ~1300 cm.$^{-1}$, according to a logarithmic plot). Conversely, the raising of the CO bond order (from 1 to, say, 1·42) correspondingly raises the CO stretching frequency. By reference to the pyridinium ion spectrum one can roughly predict the vibration spectra of the " modified aromatic " ions, in which the CO bond has roughly the same bond order as the average bond in the ring (~1·42), and in which all these bonds vibrate in unison.

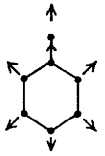
The modes of skeletal vibration of interest here are depicted in (XI) to (XIII). Beneath each diagram is the frequency of the corresponding vibration in (*a*) benzene,[14] (*b*) the pyridinium ion; (*c*) gives the lowering of the frequency due to the removal of π-electrons from the ring, (*d*) the (very roughly) estimated effect of the vibration of the CO side chain in assisting or hindering the ring vibration concerned, (*e*) the estimated vibration frequency in the " modified aromatic " cation.

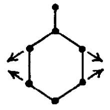
In (V) the spreading of the positive charge is limited, and band intensities not very different from those observed for the pyridinium ion and for (I) are to be expected. In (III), however, charge spreading increases the electrical symmetry; this will reduce the intensities of the infrared bands due to vibrations (XI) and (XII) (but not those of the Raman bands).

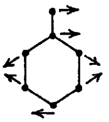
---

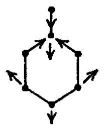
[14] Broderson and Langseth, *Mat. fys. Skrifter, Kgl. danske Videnskab. Selskab.*, 1956, **1**, 1.

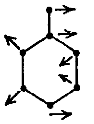
Most of the above predictions are not realized (or approached) in the observed vibration spectra of the cations of 2- and 4-hydroxypyridine. Thus (VI) and (IV) appear to be the only satisfactory structures for these ions.











	(XI)	(XIIA)	(XIIB)	(XIIIA)	(XIIIB)
(*a*)	992 cm.$^{-1}$	1585 cm.$^{-1}$ 1606 ,,	1585 cm.$^{-1}$ 1606 ,,	1485 cm.$^{-1}$	1485 cm.$^{-1}$
(*b*)	1010 ,,	1630 ,,	1530 ,,	1485* ,,	1428* ,,
(*c*)	−50 ,,	−50 ,,	−35† ,,	−35† ,,	−50 ,,
(*d*)	−20 ,,	0 ,,	0 ,,	0 ,, ?	0 ,, ?
(*e*)	940 ,,	1580 ,,	1495 ,,	1450 ,,	1380 ,,

* It is possible that these two assignments should be reversed.
† Only four of six ring bonds change in length here.

Cations of 2- *and* 4-*Hydroxypyrimidine*.—While protonation has little effect on the vibration spectra of 2- and 4-hydroxypyridine, it changes both the Raman and the infrared spectra of 2- and 4-hydroxypyrimidine quite markedly (*e.g.*, it raises the respective C=O stretching frequencies by 100 and 40 cm.$^{-1}$). Clearly, proton addition follows a different course in the two series; the cations formed preferentially here must be (VII) and (IX), not (VIII) and (X).

According to the theory of π-electron delocalization, (VII) is actually a resonance hybrid of the two equivalent canonical forms. In the " partial breathing " vibration of such an ion the four bonds of bond order 1·5 stretch and contract in unison, with a frequency roughly given by formula (XIV):[15]

$$\nu = \nu_0\sqrt{1 - A\cos\pi/(n+1)} \quad . \; . \; . \; . \; . \; . \quad \text{(XIV)}$$

where ν_0 is here the average intrinsic stretching frequency of the CC and CN bonds of bond order 1·5, taken as 1380 cm.$^{-1}$, and A is a constant for a given system (here a planar six-membered ring with bond angles of 120°) containing n bonds stretching in unison with a frequency ν. If $\nu = 1010$ cm.$^{-1}$ when $n = 6$ (pyridinium ion), (XIV) yields $\nu = 1055$ cm.$^{-1}$ for $n = 4$. The frequency of the strongest Raman band of the 2-hydroxypyrimidine cation, 1063 cm.$^{-1}$, agrees well with this calculated value. (This does, however, not *prove* that the cation is such a resonance hybrid.)

The author thanks Professor A. Albert for helpful discussion, Dr. D. J. Brown for samples of 2- and 4-hydroxpyrimidine, Mr. D. T. Light for technical assistance, and Dr. J. E. Fildes for microanalyses.

DEPARTMENT OF MEDICAL CHEMISTRY, THE AUSTRALIAN NATIONAL UNIVERSITY,
CANBERRA, AUSTRALIA. [*Received, June* 15*th*, 1959.]

---

[15] Bartholome and Teller, *Z. phys. Chem.*, 1932, *B*, **19**, 366.