

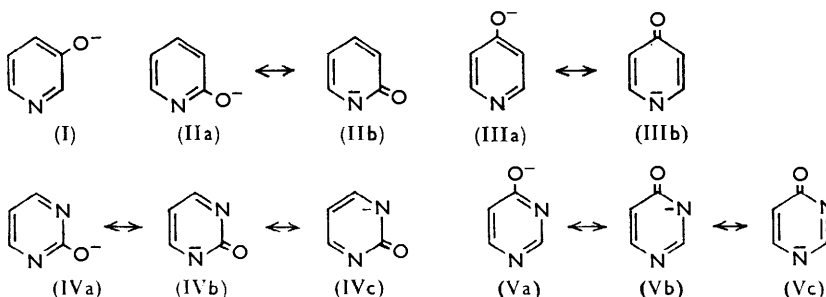
249. The Vibration Spectra and Structures of the Sodium Derivatives of Hydroxypyridines and Hydroxypyrimidines.

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Infrared and Raman spectra of the sodium salts of the hydroxypyridines and hydroxypyrimidines, in the solid state and in aqueous solution, respectively, have been determined. The anions of 3- and 4-hydroxypyridine possess the truly aromatic structures (I) and (IIIa); those of 2-hydroxypyridine and 4- and 2-hydroxypyrimidine are not truly aromatic, but seem to have structures (IIb), (Vb) and (IVb), which have the same arrangements of skeletal bonds as the neutral molecules. From the Raman spectrum it is, further, concluded that the last-named anion is not a resonance hybrid of the two equivalent canonical forms (IVb) and (IVc), but that its structure is correctly represented by one canonical form (IVb).

THE only possible structure for the anion of 3-hydroxypyridine is (I). The anions of the 2- and 4-hydroxyaza-compounds should, according to the theories generally accepted at present, be resonance hybrids (II), (III), (IV), and (V). The electron affinity of oxygen being higher than that of nitrogen,* the (two possible) (a) forms should make a greater contribution to the overall structures than forms (b) and (c), but more detailed predictions are hard to make.

If one rejects the idea that π -electrons and the unshared electrons on oxygen and nitrogen atoms are delocalised, these anions are not expected to be resonance hybrids, but should have structures (a) or (b) [or (c)].† Structures (b) contain the skeletal bond arrangements found to be energetically preferred in the neutral molecules² and the cations,³ but electron-affinity considerations, which, *a priori*, seem likely to be more important, favour structures (a).



Solubilities in water being far too low, infrared spectra were obtained for the solids only; these showed bands corresponding to most of the Raman bands observed, and there is no indication of the presence in aqueous solution of a major ionic species different from that present in the solid state (according to the theory of resonance only one ionic species is possible in all these cases).

The criteria used for structure diagnosis were the presence or absence of a strong Raman band attributable to aromatic ring-breathing; resemblance, or otherwise, to the vibration spectra of the neutral molecules,² or of comparable pyridine derivatives; resemblance, or

* The actual electron affinity of nitrogen is unknown, but should be at least 20 kcal./mole less than that of oxygen (cf. Johnson and Rohrlch¹ for atomic nitrogen and oxygen).

† To be more precise, in solution both (or all three) possible anions should always be present in equilibrium with one another, but normally one form would be expected to be much more stable than the others.

¹ Johnson and Rohrlch, *Nature*, 1959, **183**, 244.

² Albert and Spinner, *J.*, 1221.

³ Spinner, *J.*, preceding paper.

otherwise, to the vibration spectra expected of "modified aromatic" ions,³ where the truly aromatic (a) forms, and the non-aromatic forms (b) and (c), each contribute about 50% to overall structures. One cannot hope to identify carbonyl stretching bands unambiguously in these salts (see below).

TABLE I. *Band peaks* in the vibration spectra of the sodium salts (range 1800—680 cm.⁻¹).*

Hydroxypyridine							
2-		3-		4-			
I.R. Solid	Raman Aq. soln.	I.R. Solid	Raman Aq. soln.	I.R. Solid	Raman Aq. soln.	I.R. Solid	Raman Aq. soln.
1650 m		1684 mwvb		1675 mw			
1603 s	1592 (3)	1581 s	1570 (9)	1637 mw			
1548 ms	1543 (5)		1554 (4)	1601 s		1591 (5)	
1471 s		1479 s	1476 (2)	1534 mw			
1430 s		1408 s	1403 (4)	1502 ms			
	1374 (1)	1301 s	1294 (3)	1436 m			
1337ms } 1326 }	1336 (4)	1240 m	1233 (2)			1379 (3)	
1288 m	1280 (4)	1212 vw		1357 w			
1237 w	1235 (10)	1183 vw	1185 (2)	1324 ms		1324 (4)	
1194 w	1196 (2)	1126 w		1231 vw			
1147 m		1105 m	1101 (2)	1203 m		1214 (3)	
1100 w	1100 (2)	1045 w	1043 (13)	1185 w			
1075 vw		1009 m	1012 (10)			1114 (1)	
1037 w	1040 (5)	896 m }	948 (1)?	1082 vw		1075 (1)	
991 ms		881 w }	899 (1)	1043 vw		1043 (3)	
881 ms		852 m	850 (5)	997 ms		995 (7)	
861 ms	858 (9)		834 (3)	856 w }		853 (6)	
	839 (2)	800 s		844 ms }		814 (1)	
	823 (2)	706 m				800 (1)	
787 s	792 (2)						
740 s							

* For explanation of abbreviations, see p. 1223.

Peaks of Raman bands of sodium salts in aqueous solution in the range 680—200 cm.⁻¹:

- 2-Hydroxypyridine: 583 (1)?, 501 (1)?
- 3-Hydroxypyridine: 562 (1), 501 (1)
- 4-Hydroxypyridine: 660 (2), 503 (2), 464 (1)
- 2-Hydroxypyrimidine: 603 (2)
- 4-Hydroxypyrimidine: —

Hydroxypyrimidine							
2-		2-		4-		4-	
I.R. Solid	Raman Aq. soln.	I.R. Solid	Raman Aq. soln.	I.R. Solid	Raman Aq. soln.	I.R. Solid	Raman Aq. soln.
1758 w		1083 vw		1604 s	1595 (2)	1158 w	
1600 msb	1580 (5)	1070 vw	1087 (5)	1535 ms		1055 vw	1059 (1)
1535 s }		1004 w	1005 (1)		1515 (2)	1000 ms }	1002 (1)
1523 s }		959 w		1488 s		991 ms }	
1457 s		880 m	879 (7)	1432 ms		879 m }	880 (5)
1433 vw?		865 vw		1358 m	1361 (2)	875 vw }	
1368 m	1361 (3)	819 ms		1337 m }	1320 (3)	847 m }	
1261 ms	1259 (1)	789 mb		1326 w }		841 ms }	
1189 vw		747 ms		1206 vw			819 (1)
1134 w				1190 w	1198 (3)	796 w	
						782 w	

Infrared absorption peaks of the solid sodium salts in the range 3800—1800 cm.⁻¹:

- 2-Hydroxypyridine: 3404 msb, 3305 + 3258 mb, 3110 svb, 2523 vw?, 2478 w, 2316 mwb, 1897 vw
- 3-Hydroxypyridine: 3382 mvb, 3320 mb, 3256 mb, 3110 mvb, 2299 mwb, 1911 vw?, 1844 w,
- 4-Hydroxypyridine: 3280 svb, 3068 w, 2663 w, 2644 w, 2476 vw, 2223 vw, 1925 vw
- 2-Hydroxypyrimidine: 3478 w, 3264 mb, 3063 sb, 3006 w, 2972 w, 2870 vw, 2778 vw, 2615 vw, 2518 wb, 2240 vw, 2173 vw
- 4-Hydroxypyrimidine: 3372 msbv, 3258 sb, 3162 m, 3110 sb, 3042 + 3010 m, 2947 mvb, 1974 vw?

EXPERIMENTAL

Materials.—The solid sodium salts were crystallised from solutions of the hydroxy-compounds in aqueous sodium hydroxide, dried *in vacuo* at 80° or 110°, analysed to make certain of the absence of water of crystallisation, and ground with potassium bromide in a dry atmosphere.

Raman Spectra.—These were determined as before.³ There was no evidence of photochemical change with the hydroxypyridine and hydroxypyrimidine anions; there was a significant amount of fluorescence, especially with the two anions named. The solutions of sodium phenoxides examined became visibly brown as a result of irradiation, but this did not affect the reproducibility of the spectra; * for sodium *p*-chlorophenoxide, however, the effective slit width of the spectrograph had to be raised to 5 cm.⁻¹. Concentrations of solutions (g. of solute to ml. of solvent; the latter contained sufficient sodium hydroxide to leave the final solution at least *n*/4 with respect to excess of alkali) were: 2-hydroxypyridine 1 : 9; 3-hydroxypyridine 1 : 4.5; 4-hydroxypyridine 1 : 9; 2-hydroxypyrimidine 1 : 7; 4-hydroxypyrimidine 1 : 5; phenols 1 : 2.

The relative peak intensities of the various bands within each spectrum (bracketed figures in Tables 1 and 2) are roughly intercomparable as between the phenoxide ion spectra, after allowance has been made for differences in molecular weight. This does, however, not apply to the spectra of the hydroxyaza-anions (even if allowance is made for differences in concentration): the background scatter (significantly increased by fluorescence) was high, and different for each solution. Low amplification of the signal had to be used, which is reflected in the low intensity values in Table 1; this did, however, ensure that the relative band intensities within each spectrum are correct to the nearest unit.

Infrared Spectra.—These † were determined as for the neutral molecules; the concentrations of the potassium bromide discs were not known.

RESULTS AND DISCUSSION

The results are given in Tables 1 and 2.

Infrared Spectra.—These are less informative than for the neutral molecules and cations. The carbonyl stretching frequency is, in general, raised by electron-withdrawing groups, and *vice versa*; a conjugated carbonyl group adjacent to a negatively charged nitrogen atom is expected to have a stretching frequency near 1600 cm.⁻¹, which makes it indistinguishable from an aromatic skeletal stretching frequency. (In conventional terms, a CO bond of bond order 1.8 would have a stretching frequency near 1600 cm.⁻¹.)

The resemblance between the infrared spectrum of the hydroxypyridine anion and that of the corresponding methoxy- or ethoxy-pyridine^{5,6,7} is quite close for the 3-substituted, and passably close for the 2- and 4-substituted derivatives, which would be in agreement with anion structures represented wholly or largely by (I), (IIa), and (IIIa), respectively. The 4-hydroxypyridine anion shows two more bands of fair intensity in the range 1400—1600 cm.⁻¹ than do the neutral molecule² and the cation,³ and is unlikely to have the same general structure as the neutral molecule and the cation [*i.e.*, (IIIb)]. However, the spectrum of the 2-hydroxypyridine anion does not differ sufficiently from that of the neutral molecule² to represent evidence against a structure represented wholly or largely by (IIb), *i.e.*, this infrared spectrum is inconclusive.

The spectra of the anions of 2- and 4-hydroxypyrimidine lack the band at 1400 cm.⁻¹ which is very strong in the infrared spectra of pyrimidine⁸ and 2-methoxypyrimidine,⁹

* All spectra were run at least in duplicate.

† The infrared spectrum of sodium 2-pyridyl oxide below 1700 cm.⁻¹ has been recorded by Gibson, Kynaston, and Lindsey.⁴

⁴ Gibson, Kynaston, and Lindsey, *J.*, 1955, 4340.

⁵ Katritzky and Hands, *J.*, 1958, 2202.

⁶ Katritzky, Jones, and Hands, *J.*, 1958, 3165.

⁷ Katritzky and Gardner, *J.*, 1958, 2198.

⁸ Lord, Marston, and Miller, *Spectrochim. Acta*, 1957, 9, 113.

⁹ Brown and Short, *J.*, 1953, 331.

and structures represented essentially by (IVa) and (Va) seem quite unlikely for these anions, especially for the former.

Raman Spectra.—These furnish more decisive evidence. As one expects for a truly aromatic substance, the strongest Raman band of the 3-hydroxypyridine anion is found near 1000 cm^{-1} (the bands at 1043 and 1012 cm^{-1} presumably being a resonance doublet), and there is quite an intense band near 1600 cm^{-1} . Similar features are shown by the Raman spectrum of the anion of 4-hydroxypyridine, which is compatible with, though not conclusive evidence for (cf. the neutral molecule ² and the cation ³), the truly aromatic structure (IIIa) for this anion.

However, structures represented essentially by (IIa), (IVa), and (Va), respectively, seem to be incompatible with the observed Raman spectra of the α -hydroxyaza-anions, the strongest bands in which are *not* found near 1000 cm^{-1} . In fact, the strongest band in each anion spectrum lies very close to the strongest Raman band observed for the corresponding neutral molecule, namely: 2-hydroxypyridine, anion 1235 (10) and 858 cm^{-1} (9), neutral 1260 (s) and 850 cm^{-1} (ms); 2-hydroxypyrimidine, anion 879 cm^{-1} , neutral 869 cm^{-1} ; 4-hydroxypyrimidine, anion 880 cm^{-1} , neutral 858 cm^{-1} . There is, thus, a strong *prima facie* case for assigning to these anions structures represented essentially by (IIb), (IVb), and (Vb), respectively, which would mean that each anion possesses the same bond skeleton as the corresponding neutral molecule.

Structure (Vc) possesses the same bond skeleton as occurs in neutral (and cationic) 4-hydroxypyridine; the vibration spectrum of this bears no resemblance to that of the 4-hydroxypyrimidine anion, which is thus very unlikely have a structure given essentially by (Vc). The absence of appreciably intense Raman bands near 1600 cm^{-1} is further evidence against truly aromatic structures for both 4-hydroxypyrimidine and 2-hydroxypyridine.

The conclusion that the α -hydroxyaza-anions possess structures (b), in which the negative charge resides largely or wholly on a nitrogen atom, is sufficiently unexpected to arouse doubts about the validity of the criteria used for structure diagnosis. The

TABLE 2. *Band peaks* in the Raman spectra of the sodium phenoxides in aqueous solution (range 1700—200 cm^{-1}).*

Unsubst.	2-Chloro-	4-Chloro-	Unsubst.	2-Chloro-	4-Chloro-
1667 (1)					
1624 (2)					
1586 (32)	1571 (29)	1579 (38)	965 (2)	973 (3)	
1528 (4)	1515 (3)	1525 (3)	936 (2)	931 (2)	
1479 (3)	1465 (5)	1477 (3)	891 (1)?		
1443 (3)	1433 (2)				847 (9)
		1382 (2)	824 (16)	849 (12)	830 (23)
1322 (2)	1304 (15)			825 (4)	
1276 (11)	1274 (5)	1288 (13)	770 (4)	761 (2)	776 (1)
	1237 (2)				709 (3)
1164 (6)				674 (13)	654 (7)
1150 (9)	1152 (9)	1164 (8)	615 (5b)		639 (8)
	1121 (9)		543 (2)	569 (5)	557 (2)
1068 (3)				528 (4)	
1023 (23)		1038 (2)	400 (1)?		
993 (48)	1031 (50)	1091 (36)	318 (1)	386 (10)	391 (4)
	991 (4)	999 (6)			

* Wave numbers in cm^{-1} , peak intensities (in parentheses) in arbitrary units (see exptl. section). Inflection in italics; b = broad.

Raman spectra of three phenoxide ions were therefore examined. The replacement of a ring CH group by a nitrogen atom has no major mechanical effect on the skeletal vibrations, *i.e.*, the skeletal motions of the phenoxide ion and of a truly aromatic hydroxypyridine anion are practically identical. However, the electron-withdrawing effect of ring-nitrogen

produces an electric distortion which could conceivably upset the expected intensity relations.

ortho- and *para*-Chlorophenol (pK_a 10.0 and 9.9, respectively) are stronger acids than phenol (pK_a 10.5);¹⁰ in the chlorophenoxide ions the chlorine atom is unquestionably electron-withdrawing, and the electric distortions obtaining in truly aromatic 2- and 4-hydroxyaza-aromatic anions are simulated there.* The results in Table 2 show clearly that in these compounds the ring-breathing vibration (located in the range 990—1090 cm^{-1}) and the skeletal stretching vibration near 1580 cm^{-1} give rise to by far the strongest Raman bands; the criteria used for diagnosing true aromaticity are thus valid for substances of this type, and the above conclusions are firmly based.

"*Modified Aromatic*" Structures.—The possibility that these anions have structures to which the forms (b) [and (c)] contribute as much, or nearly as much, as the forms (a), has yet to be considered. The ring-breathing and skeletal stretching frequencies in such ions are lower than those in comparable truly aromatic compounds, by amounts previously estimated.³ The observed frequency shifts for the strongest Raman band (expected, ~ -70 cm^{-1}), and for the four infrared bands in the region 1400—1600 cm^{-1} (average value; expected ~ -40 cm^{-1}) obtained by such comparisons are: anion of 2-hydroxypyridine, compared to 2-methylpyridine,^{5,11} +255 and -5 ; anion of 3-hydroxypyridine, compared to 3-methylpyridine,^{6,11} +2 and -6 ; anion of 4-hydroxypyridine, compared to 4-methylpyridine,^{7,11} +1 and -1 ; anion of 2-hydroxypyrimidine, compared to pyrimidine,⁸ -112 and +3 (or, conceivably, -14); anion of 4-hydroxypyrimidine, compared to pyrimidine,⁸ -111 and +12 cm^{-1} .

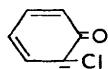
None of the observed anion spectra fits a "modified aromatic" structure even remotely. There is no evidence of a contribution from form (IIIb) to the structure of the 4-hydroxypyridine anion; though too much quantitative significance must not be attached to the above negligible frequency shifts, this contribution must be less than 15% at the very most.

The 2-hydroxypyrimidine anion could simply be a resonance hybrid of (IVb) and (IVc). The strongest Raman band of such an ion would be given by the "partial ring-breathing" motion of the four bonds of bond order 1.5; its frequency should be somewhat higher than 990 cm^{-1} (the ring-breathing frequency in pyridine), about 1040 cm^{-1} according to a rough calculation analogous to that performed for the corresponding cation (see p. 1231). Actually the strongest Raman band is found at 879 cm^{-1} .

It is concluded that the only satisfactory structures for the α -hydroxyaza-anions are, in essence, (IIb), (IVb) (one canonical form), and (Vb); the contributions from the forms (IIa), (IVa), and (Va) could, however, conceivably be as high as 25% (a CO stretching frequency of 1590 cm^{-1} corresponds to a CO bond order of ~ 1.75).

Evidence from Electronic Spectra.—The electronic spectra of 2-hydroxypyridine¹² and 2- and 4-hydroxypyrimidine¹³ are not drastically changed on either cation- or anion-formation; they are certainly compatible with the above conclusion that in each case the same skeleton of bonds is present in all three ionic species. The spectral sequences are usually continuous: cation, neutral molecule, anion.

For 4-hydroxypyridine,¹² on the other hand, the sequence is discontinuous, the λ_{max} values being: cation, 2340 Å; anion, 2390 Å; neutral molecule, 2530 Å. This rules out structure (IIIb) for the anion. The electronic spectrum of the cation closely resembles



(A)

* The form (A) for the *o*-chlorophenoxide ion is exactly analogous to (IIb) for the 2-hydroxypyridine anion.

¹⁰ Bennett, Brooks, and Glasstone, *J.*, 1935, 1821.

¹¹ Long, Murfin, Hales, and Kynaston, *Trans. Faraday Soc.*, 1957, **53**, 1171.

¹² Mason, *J.*, 1959, 1253.

¹³ Brown, Hoerger, and Mason, *J.*, 1955, 211.

that of hexa-1,4-dien-3-one* (2280 Å + 2360 Å),¹⁴ as required for structure (IV) on p. 1226, since the effect of the $^+\text{NH}_2$ group should be very small. The spectrum of the anion (which also shows a second band, of lower intensity) resembles that of the phenoxide ion (2345 Å), as expected for structure (IIIa). The replacement of the 4-CH group in the phenoxide ion by a nitrogen atom displaces the high-intensity band to longer wavelengths, as expected [the same change in the 3-position produces a smaller effect (+15 Å) in the same direction]. By contrast, it should be noted that the replacement of 4-CH in the 2-hydroxypyridine anion by nitrogen displaces the band to *shorter* wavelengths (from 2300 to 2270 Å), which confirms the view that the α -hydroxyaza-anions are different.

Relative Stabilities of the Possible Ionic Species.—For neutral α - and γ -hydroxyaza-compounds and their cations the tautomers containing carbonyl groups are always more stable than the (truly aromatic) hydroxy-tautomers; the higher aggregate bond energies in the former outweigh the stabilisation associated with the aromatic ring \dagger in the latter. For the anions, however, this seems to be true only if there is a nitrogen atom α to the CO bond, *i.e.*, if the effective electron affinity of the nitrogen atom is raised sufficiently by the electron-withdrawing inductive effect of an adjacent carbonyl group. It is hoped that work on substituted compounds will shed further light on this matter.

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* The cation of 4-methoxypyridine also has a similar spectrum,¹² but this does not prove that all three substances (or any two of them) possess identical chromophoric groupings.

\dagger Such a stabilisation must be present even if the π -electrons are localised.¹⁵

¹⁴ Bowden, Heilbron, Jones, and Weedon, *J.*, 1946, 39.

¹⁵ Spinner, *J. Amer. Chem. Soc.*, 1957, **79**, 504.