603. *The Vibration Spectra and Structures of the Hydrochlorides of Aminopyridines.*

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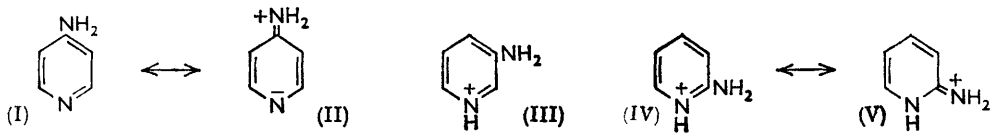
The infrared and Raman spectra of the hydrochlorides of 2-, 3-, and 4-aminopyridine, of 2-aminopyrimidine, and of the 3-, 4-, 5-, and 6-methyl derivatives of 2-aminopyridine, have been compared with those of the free amines. Whereas the vibration spectrum of 3-aminopyridine hardly changes on cation formation those of the α- and γ-amino-compounds change considerably, showing that there is a further structural change beyond mere proton addition. The spectral change being too drastic to be explained simply by cation structures in which the forms (IV) and (V), and (VIII) and (IX), contribute about equally, it is concluded that the cations are of the amidinium type and are represented essentially or largely by structures (V) and (IX). In agreement with this idea, the vibration spectrum of the 4-aminopyridine cation strongly resembles that of 4-pyridone (X) and differs considerably from that of the 4-methoxypyridine cation.

2- and 4-AMINOPYRIDINE, and aminopyridine monocations, are potentially tautomeric. However, it is firmly established that the former exist predominantly in the aminopyridine and not in the pyridone imine form,[1] and the predominant monocations are those in which the proton has added to the ring rather than to the exocyclic nitrogen atom, as is shown by the high base strengths of the aminopyridines relative to aniline,[2] and by the electronic spectra [3] and base strengths [4, 3c] of the monocations.



Resonance of the type (I) ⟷ (II) has been postulated for 2- and 4-aminopyridines,[1a] and resonance of the amidinium ion type, (IV) ⟷ (V) and (VIII) ⟷ (IX), for the monocations.[2, 4] Molecular-orbital treatments of aminopyridines and their cations have appeared,[5, 3b] but there is some disagreement concerning the relative importance of the contributing structures in the cations. It was of interest to see whether the vibration spectra shed light on this matter. The infrared spectra of 2-, 3-, and 4-aminopyridine have been examined thoroughly; [6] the other data in the annexed Tables are new.

Experimental.—Materials. The amino-compounds were commercial specimens recrystallized to constant purity. Monohydrochlorides were obtained from solutions in concentrated hydrochloric acid, and their purity and the absence of water of crystallization were checked by elemental analysis; being hygroscopic, they were sampled in a dry-box.

Infrared spectra. These were taken with a Perkin–Elmer 21 double-beam spectrophotometer, and, in the range 3800—2400 cm.$^{-1}$, with a Perkin–Elmer 12 single-beam instrument [7] fitted with

[1] (*a*) Angyal and Angyal, *J.*, 1952, 1461; (*b*) Angyal and Werner, *J.*, 1952, 2911.
[2] Albert, Goldacre, and Phillips, *J.*, 1948, 2240.
[3] (*a*) Steck and Ewing, *J. Amer. Chem. Soc.*, 1948, **70**, 3397; (*b*) Mason, *J.*, 1960, 219; (*c*) Albert, *J.*, 1960, 1020.
[4] Bender and Chow, *J. Amer. Chem. Soc.*, 1959, **81**, 3929.
[5] Murrell, *J.*, 1959, 296; Mason, *J.*, 1959, 1253; Mataga and Mataga, *Bull. Chem. Soc. Japan*, 1959, **32**, 600.
[6] (*a*) Katritzky and Hands, *J.*, 1958, 2202; Katritzky, Hands, and Jones, *J.*, 1958, 3165; Katritzky and Gardner, *J.*, 1958, 2198; (*b*) Goulden, *J.*, 1952, 2939; Mason, *J.*, 1958, 3619; Ramiah and Puranik, *J. Mol. Spectroscopy*, 1961, **7**, 89; *Proc. Indian Acad. Sci.*, 1961, **54**, *A*, 121.
[7] Albert and Spinner, *J.*, 1960, 1221.

a lithium fluoride prism. Except for 2-amino-3-methylpyridine, which was examined as the pure liquid, the spectra were obtained for the solids dispersed in potassium bromide discs.

Raman spectra. These were obtained as before,[8] 2-amino-3-methylpyridine being examined as the pure liquid and the other substances in solution in water [concentration, 50% by weight, except for 4-aminopyridine (25%), 2-amino-4-methylpyridine (15%), and 2-aminopyrimidine (33%)] and in concentrated hydrochloric acid (concentration of cation, ~42%).

Aminopyridine Spectra.—Previous band assignments for the infrared spectra of 2-, 3-, and 4-aminopyridine [6a] are slightly modified and extended, in the light of the Raman spectra now obtained and by correlation with the previous assignments [9] for pyridine [10] and its monodeutero-derivatives; [11] assignments for the other substances examined are given as far as possible (see Tables).

The ring-breathing vibration ν_1 *and the ring deformation* ν_{12}. These give rise to the two prominent Raman bands near 1000 cm.$^{-1}$, the aromatic ring-breathing band being the most intense one (below 2000 cm.$^{-1}$) for 3- and 4-aminopyridine; for 2-aminopyridine and even more so 2-aminopyrimidine, however, this band is surpassed in intensity by one near 850 cm.$^{-1}$. A very strong Raman band near 1000 cm.$^{-1}$ is observed for *meta*- but not for *ortho*- or *para*-disubstituted benzene derivatives; as expected, this band is observed for the 4- and 6-methyl derivatives of 2-aminopyridine (modified *m*-toluidines, one CH replaced by N) but not for the 3- and 5-methyl derivatives (modified *o*- and *p*-toluidine, respectively).

The strong Raman band near 850 cm.$^{-1}$. The intense band near 800 cm.$^{-1}$ in the Raman spectra of the picolines [12] and methoxypyridines [8] is near 850 cm.$^{-1}$ for both hydroxy- [7] and amino-pyridines. The position of this band is not determined by skeletal structure, being the same in 2-amino- and 2-hydroxy- and in 4-amino- and 4-hydroxy-pyridine, although the hydroxy-compounds are, in fact, 2- and 4-pyridone. However, the band is displaced to near 750 cm.$^{-1}$ in the 3- and 4-methyl derivatives of both 2-amino- and 2-hydroxy-pyridine.[13] This extreme sensitivity to methyl substitution at once suggests that the band is due to an out-of-plane CH bending vibration; the high Raman and low infrared intensity point to vibration ν_5.

The high-frequency skeletal stretching bands. Except in one or two cases the frequencies ν_{8a}, ν_{8b}, ν_{19a}, and ν_{19b} are readily placed, ν_{8a} being distinguished by its prominence in the Raman spectrum. The vibration spectrum of pyrimidine, however, is changed considerably on introduction of the 2-amino-group; the very intense infrared band near 1400 cm.$^{-1}$ in pyrimidine [9] and 2-methoxypyrimidine [14] (due to vibration ν_{19b}) is absent for 2-aminopyrimidine and must be displaced to either 1480 cm.$^{-1}$ or 1360 cm.$^{-1}$.

Any large contribution from zwitterion structures in 2- or 4-aminopyridine will reduce the average bond order in the rings [which, on the Pauling scale, is 1·5 for form (I) and 1·33 for form (II)], with a consequent lowering of the ring skeletal stretching frequencies [15] ν_1, ν_{14}, ν_{8a}, ν_{8b}, ν_{19a}, and ν_{19b}; of these only ν_{14} is unknown. Comparing each aminopyridine with the corresponding deuteropyridine,[9, 11] these frequencies are, on balance, unchanged for the 2- and somewhat raised for the 3- and 4-amino-compound; *i.e.*, the effect of mesomerism is not apparent here.

$^-NH_2$ *Frequencies.* The NH stretching [6b] and HNH scissoring bands, being prominent in the infrared spectra, are readily placed, but the other HNH bending frequencies are not. A localized $C-N_{amino}$ stretching motion, giving rise to a fairly intense Raman band, and of a frequency somewhat above 1100 cm.$^{-1}$ if the CN bond order is 1 (or close to it), is conceivable in these compounds but the spectra of 3- and 4-aminopyridine suggest mixing

[8] Spinner and White, preceding paper.
[9] Lord, Marston, and Miller, *Spectrochim. Acta*, 1957, **9**, 113.
[10] Corrsin, Fax, and Lord, *J. Chem. Phys.*, 1953, **21**, 1170.
[11] Andersen, Bak, Brodersen, and Rastrup-Andersen, *J. Chem. Phys.*, 1955, **23**, 1047.
[12] Long, Murfin, Hales, and Kynaston, *Trans. Faraday Soc.*, 1957, **53**, 1171.
[13] Spinner and White, unpublished work.
[14] Brown and Short, *J.*, 1953, 331.
[15] Spinner, *J.*, 1960, 1226.

TABLE 1.

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

Assignment [b]	Infrared			Raman	
	2-Aminopyridine				
NH_2 sc	**1627**	0·55		1627	8
8b	1598	0·3		1607	28
8a	1560	0·3	A [c]	1571	52
19a	1490	0·45		1491	8
19b	1443	0·45		1445	12
3?	1339	0·15		1335	44
	1325	0·15			
	1277	0·15		1268	48
9a?	1156	0·1		1158	20
	1140	0·2		1128	20
12	1060	0·02		1050	40
1	984	0·10	A	997	68
5	855	0·02		**850**	100
				790	8
11	764	0·25			
	735	0·15			
				634	12
				562	16
16				412	8
	2-Aminopyridine hydrochloride				
$\overset{+}{N}H_2$ sc	**1664**	1·3			
$\overset{+}{C}$=N st [d]	1621	1·2		1627	4
	1550	0·3		1550	14
	1476	0·35		1481	14
	1408	0·1		1415	18
	1380	0·45	C [e]	1383	60
	1325	0·3		1328	72
	1244	0·2		1250	22
	1165	0·3		1169	10
				1132	16
	1113	0·1			
	1091	0·1			
	1055	0·1		1066	4
	1027	0·1		1035	4
	996	0·4		1001	12
	867	0·4			
5	845	0·15		**851**	100
11	754	0·45			
	712	0·15			
				628	12
				555	14

Assignment	Infrared			Raman	
	3-Aminopyridine				
NH_2 sc	1622	0·35		1623	11
8a	**1586**	0·7		1590	94
8b	1574	0·25		1534	4
19a	1489	0·6		1488	15
19b	**1440**	0·7		1443	22
	1347	0·1		1338	4
	1292	0·6		1292	18
	1260	0·5		1265	4
9a	1194	0·05		1197	27
15?	1129	0·15		1137	9
1	1046	0·3		**1047**	100
12	1014	0·25		1023	53
	908	0·15		897	6
5	841	0·1		842	53
	799	0·5		810	27
11	706	0·7			
4?				636	9
				548	14
16				385	9
	3-Aminopyridine hydrochloride				
NH_2 sc }	1637 [e]	0·65		1642	18
8a }				1625	42
	1604	0·05		1608	17
8b	**1550**	1·0		1565	11
19a	1482	0·5		1487	17
19b	1390	0·35		1394	24
3	1337	0·55		1344	29
	1323	0·25			
	1273	0·3		1285	11
	1253	0·5		1244	4
9a	1164	0·04		1182	21
15?	1138	0·2		1140	18
1	1044	0·25		**1048**	100
12	1009	0·2		1013	36
5	835	0·35		840	89
	792	0·3		809	7
11	782	0·8		784	7
	668	0·6			
4?				625	10
				544	12
16				397	12

Assignment	Infrared			Raman	
	4-Aminopyridine				
NH_2 sc	1645	1·0		1648	2
8a	**1596**	1·4	A	1609	7
8b	1555	0·15			
	1523	0·1			
19a	1508	0·8		1512	2
	1479	0·1			
19b	1435	0·6			
	1353	0·1		1353	2
	1334	0·75	A	1335	2
	1270	0·55		1276	4
9a?	1219	0·75		1217	6
12	1052	0·05		1058	3
1	990	0·95		**1002**	12
5	842	0·4		850	10
11	824	1·05			
4?	680	0·4		668	3
				536	2
	4-Aminopyridine hydrochloride				
$\overset{+}{N}H_2$ sc }	**1650** }	1·5		1644 [e]	22
d }	**1636** }				
d	1592	0·65			
d	1527	1·35	C	1537	72
				1482	5
	1402	0·1		1422	5
	1364	0·15		1378	7
	1262	0·2		1266	12
	1189	0·5		1201	7
				1120	5
d	1050	0·05		1046	62
	991	0·35		991	52
				942	5
5 [d]	846	0·05		**847**	100
				823	7
11	801	0·3		790	7
				744	5
				647	15
				526	22
				414	7

Assignment	Infrared			Raman	
	2-Aminopyrimidine				
NH_2 sc	1642	1·5		1629	12
8a	1576	1·4	A	1588	33
8b	1559	1·3			
				1518	7
19a (+ b?)	**1479**	1·7	A	1483	7
	1445	0·15		1452	2
19b?	1358	0·75		1360	20
3	1224	0·55			
15	1179	0·4			
9a?	1128	0·25		1132	17
1	1075	0·01		1090	52
	1038	0·2		1034	5
12	997	0·15		1005	25
" 5 " [f]	866	0·02		**876**	100
" 11 " [f]	803	0·85		818	10
	786	0·25			
	720	0·20			
6b?				594	15
	2-Aminopyrimidine hydrochloride				
$\overset{+}{N}H_2$ sc	**1665**	1·7			
	1637	1·1		} 1628 [e]	8
$\overset{+}{C}$=N st	1615	1·5			
	1591	0·1			
	1536	0·65	C	1544	19
	1508	0·1			
	1449	0·35		1465	8
	1407	0·35		1414	4
	1343	1·5		1359	8
	1287	0·4		1298	17
	1211	0·3		1223	19
	1073	0·2		1078	19
	992	0·55		997	8
" 5 "	872	0·35		**875**	100
	863	0·4			
" 11 "	792	1·05			
	776	0·15		778	2
				580	15

[a] For units, and significance of figures for intensities, see footnote *a* to Table on p. 3116. However, for weak Raman spectra, instrumentally recorded intensities are given directly (*i.e.*, that of the strongest band has not been put equal to 100). [b] For diagrams, and the numbering, of aromatic vibrations, in benzene, see ref. 9; however, the precise form of some of these vibrations is not always the same in benzene and in a substituted pyridine. sc = scissoring. [c] Amine bands that seem to have no counterpart in the corresponding cation spectrum are marked A, and cation bands without a counterpart in the amine spectrum C. [d] See text for assignment. [e] Two bands merged into one. [f] Only three CH hydrogen atoms partake in this (out-of-plane bending) motion; in ν_{11} all three move in phase, in ν_5 adjacent H atoms move out of phase.

TABLE 2.

Vibration spectra [a] of methyl-substituted 2-aminopyridines in the range 1800—650 cm.$^{-1}$ (Raman spectra to 200 cm.$^{-1}$).

Assignment [b]	Infrared		Raman	
	3-Methyl			
NH_2 sc	1627, 1614	1·2	1633	11
8a	1595	0·4 A [c]	1599	57
8b	1579	0·5	1580	16
CH_3	1473	0·7		
19a	**1451**	1·7	1458	30
19b	1435	0·6		
CH_3?	1383	0·3	1385	14
	1325	0·15	1325	57
	1291	0·35		
	1274	0·30	1282	78
	1197	0·35	1199	3
9a?	1135	0·15	1142	24
	1035	0·2	1037	38
	992	0·3	997	15
" 11 " [f]	772	0·7	779	6
" 5 " [f]	743	0·1	**749**	100
			528	19

Assignment	Infrared		Raman	
	4-Methyl			
NH_2 sc	**1645**	0·85		
8a	1615	0·7 A	1625	4
			1601	1
8b	1556	0·7 A	1564	3
19a	1492	0·4	1497	2
CH_3	1469	0·35		
19b	1450	0·6	1431	2
CH_3	1372	0·2	1381	3
	1336	0·1	**1342**	5
	1310	0·4	1312	3
	1271	0·3	1267	2
	1180	0·2		
1	985	0·2	999	4
" 11 "	861	0·35		
" 11 "	792	0·8		
" 5 "	769	0·05	**769**	5
			570	2
			525	2

Assignment	Infrared		Raman	
	5-Methyl			
NH_2 sc	1628	0·45		
8a	1608	0·1 A	1618	28
8b	1563	0·25	1571	20
19a	**1503**	0·65		
19b	1392	0·35	1385	30
CH_3	1376	0·1		
	1316	0·2	1319	20
	1265	0·25	1269	45
	1221	0·05	1223	17
	1142	0·2	1156	2
	1067	0·1	1088	2
	1020	0·1		
" 5 "	855	0·03	**861**	100
" 11 "	825	0·3	830	5
	748	0·1	755	7
			487	17
			324	15

	6-Methyl			
NH_2 sc	1634	0·45		
8b	1598	0·45		
8a	1574	0·35 A	1585	1
19a + b	**1465**	0·7		
CH_3	1374	0·05		
	1345	0·15		
	1279	0·1		
	1161	0·1	1151	1
1	986	0·05 A	**996**	3
" 11 "	783	0·3		
" 5 "	726	0·05	**736**	3
			544	1

	3-Methyl hydrochloride			
$\overset{+}{N}H_2$ sc	1662	1·15		
$\overset{+}{C}$=N st	1633	0·45	1627	13
	1580	0·9	1574	14
CH_3	1475	0·35	1467	11
	1423	0·5	1415	16
	1399	0·35		
CH_3	1374	0·4	1384	18
	1355	0·02 C [e]	**1361**	100
	1327	0·25	1311	30
	1255	0·35	1253	27
	1210	0·25	1205	6
	1145	0·2	1147	8
	1083	0·2	1074	8
	1059	0·35	1042	13
	1018	0·3	1004	9
	837	0·25		
" 11 "	772	0·7	784	4
" 5 "	749	0·35	749	62

	4-Methyl hydrochloride			
$\overset{+}{N}H_2$ sc	**1662**	1·3	1669	5
$\overset{+}{C}$=N st	1627	1·25	1634	17
	1541	0·02	1540	15
	1486	0·45	1490	40
	1435	0·1	1429	42
	1373	0·4	**1378**	100
	1298	0·15	1306	42
	1226	0·5	1245	40
	1182	0·2	1188	22
	1125	0·05	1136	17
	989	0·15	994	37
	950	0·15	944	37
	873	0·45		
	865	0·45		
" 11 "	783	1·2		
" 5 "	759	0·4	765	75
			568	50
			519	22

Assignment	5-Methyl hydrochloride Infrared		Raman	
$\overset{+}{N}H_2$ sc	**1665**	1·6	1670	3
$\overset{+}{C}$=N st	1627	1·5	1628	5
	1612	0·1		
	1549	0·15	1557	26
	1475	0·75	1472	10
CH_3	1459	0·15		
	1406	0·05	1412	45
CH_3?	1390	0·02	1389	19
	1351	0·55	1355	36
	1322	0·1	1326	51
	1249	0·25	1253	16
	1150	0·55	1156	16
	1052	0·25		
	864	0·3		
" 5 "	850	0·05	**857**	100
" 11 "	827	1·0		
	760	0·25	760	4
			479	13

Assignment	6-Methyl hydrochloride Infrared		Raman [g]	
	1745	0·2		
$\overset{+}{N}H_2$ sc	1660	1·45		
$\overset{+}{C}$=N st	1632	1·25		
	1615	0·45		
	1555	0·1		
	1471	0·25 C	1490	2
	1432	0·15		
	1402	0·6 C	1400	4
	1388	0·45		
	1308	0·3 C	**1315**	5
	1180	0·45		
	1072	0·25		
	1054	0·3		
	1005	0·25		
	880	0·35		
" 11 "	796	1·1		
" 5 "	735	0·1	**740**	5
	720	0·15	729	3

[a–f] See Table 1. Weak bands have been omitted. [g] Raman spectrum obtained was very weak because of fluorescence.

TABLE 3.

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

Assignment [b]	2-Aminopyridine		3-Aminopyridine		4-Aminopyridine		2-Aminopyrimidine	
				Amines				
							3350 }	1·0
HNH as st	3445	0·25	3376	0·6	3433	0·5	3335 }	
	3302	0·15	3308	0·5	3302	0·3	3247	0·1
HNH s at	3164	0·2	3159	0·55	3087	0·85	3169	1·2
Ar(CH) st	3073	0·05	3065	0·02				
	3026	0·02	3038	0·05	3038	0·05		
	2950	0·02			2995	0·1		
				Hydrochlorides				
HNH as st	3308 }	1·2	3332 }	0·9	3313	0·8	3339	0·8
	3238 }		3295 }		3195 }		3195	0·15
					3143 }	0·9		
HNH s st	3143	1·2	3183	0·9	3091 }		3143	0·85
Ar(CH) st	2965	0·15	3114 }	0·25	3042	0·4	3087	0·05
	2892	0·15	3094 }					
			2956	0·2				
+ NH st			3059 }	0·65	2968 }	0·7	2722 }	1·2
			3012 }		2936 }		2665 }	
			2898 }	0·15				
			2884 }					
			2840	0·2				
			2806	0·7				

Assignment	3-Methyl		4-Methyl		5-Methyl		6-Methyl	
				2-Aminopyridines				
HNH as st	3468	0·35	3428	0·6	3452	0·2	3458	0·2
	3317	0·6	3295	0·3	3308	0·15	3312	0·2
HNH s st	3180	0·65	3132	0·55	3164	0·25	3172	0·2
Ar(CH) st	3020	0·05	3054	0·1	3028 }		3070	0·02
	2968	0·01			3010 }	0·1		
					2983 }		2981	0·02
	2931 }							
Me(CH) st	2913 }	0·1	2914	0·15	2918	0·03	2918	0·02
	2850	0·1	2855	0·05	2864	0·03		
				2-Aminopyridine hydrochlorides				
HNH as st	3293	1·1	3338 }		3335 }		3395	0·35
			3290 }	0·6	3290 }	0·7		
	3247	0·15	3244 }		3250 }		3283	0·7
HNH s st	**3135**	1·3	3158	1·2	3155	0·9	3178	0·15
Ar(CH) st			3054	0·1			3068	0·2
	2960	0·15	2995	0·15	2976	0·05	2954	0·15
Me(CH) st	2939	0·15	2920	0·04	2939	0·1		
+ NH st	2850	0·05	2868	0·03	2831	0·1	2870	0·1
			2824 }					
			2781 }	1·3	2758	1·5	2816	1·2
			2730 }		2695	0·1	2756	0·25

[a] See Table 1. The wavenumbers in this Table were obtained with single-beam instrument with a lithium fluoride prism, but the intensities with a double-beam instrument with a sodium chloride prism. [b] as = antisymmetric, s = symmetric, st = stretching.

between C–N stretching and either NH_2 bending or an aromatic motion. The prominent Raman band(s) observed for 2-aminopyridine derivatives in the range 1270—1340 cm.$^{-1}$ may be due to the NH_2 group or to in-plane CH bending.

Cation Spectra.—*3-Aminopyridine hydrochloride.* The vibration spectrum of this substance (Table 1) strongly resembles those of 3-hydroxy-[15] and 3-methoxy-pyridine.[8] Like proton addition to pyridine,[15] pyrimidine,[15] and 3-hydroxy- and 3-methoxy-pyridine, proton addition to 3-aminopyridine produces only minor changes in the spectrum (and no unexpected frequency changes).

2-Aminopyridine hydrochloride. Cation formation by 2-aminopyridine, by contrast, results in a profound change in the vibration spectrum, especially the Raman spectrum (see Table 1). The difference between the spectra of the cations of 2-methoxy-[8] and 2-amino-pyridine is equally striking. The latter shows no intense Raman bands near 1000 cm.$^{-1}$ attributable to ring-breathing ν_1 or ring deformation ν_{12}, and none near 1630 cm.$^{-1}$ attributable to skeletal stretching ν_{8a}; instead, it shows an intense Raman band at

1380 cm.$^{-1}$, for which there is no counterpart in either the 2-aminopyridine or the 2-methoxypyridinium ion spectrum.

In the infrared spectrum, the lowering of the mean H–N–H stretching frequency due to cation formation is about 70 cm.$^{-1}$ and the raising of the H–N–H scissoring frequency 40 cm.$^{-1}$, as compared with 10 cm.$^{-1}$ and 20 cm.$^{-1}$ in the case of 3-aminopyridine. There are no really intense bands below 1600 cm.$^{-1}$, which is surprising for an ion (IV), and the moderately intense band at 1380 cm.$^{-1}$ is not readily assigned.

These spectral changes point to a structural change on cation formation that is far more drastic than the mere addition of a proton to give an ion represented mainly by form (IV). The observed spectrum does not even agree with a "modified aromatic" structure, in which forms (IV) and (V) contribute about equally. In such an ion the exocyclic C–N bond (bond order ~1·42 on the Pauling scale) would vibrate in unison with the ring bonds, in motions bearing a simple relation [15] to ordinary aromatic modes, and bands due to "modified" ring-breathing ν_1 and "modified" skeletal stretching ν_{8a} should still be strong in the Raman spectrum; the modified frequencies ν_1 and ν_{8a}, and to a lesser extent ν_{8a} and ν_{19b}, would be lower * than for the pyridinium ion.

The observed spectrum is, however, readily interpreted on the basis of a cation structure represented essentially (or largely) by the amidinium form (V) [contribution from form (IV), <25%]. The bands at 1625 and 1665 cm.$^{-1}$ are assigned to exocyclic C=N$^+$ stretching and H–$\overset{+}{\text{N}}$–H scissoring (with some mixing between the two motions,[16] and perhaps also with C=C stretching), which, for an amidinium ion, should give the most intense infrared bands below 2000 cm.$^{-1}$. It is also noteworthy (though perhaps coincidental) that the bands in the N–H stretching region are in almost the same position for the cations of 2-aminopyridine (see Table 3) and formamidine [17] (3338, 3220, and 3138 cm.$^{-1}$, for the solid in potassium bromide). The location of the strongest Raman band of the 2-aminopyridine cation at 851 cm.$^{-1}$ (out-of-plane CH bending, like ν_5) is readily reconciled with structure (V); 2-pyridone [*i.e.*, (V); =O in place of =NH$_2^+$] also shows a strong Raman band there. (However, there is no very marked resemblance between these two spectra in general.)

Hydrochlorides of methyl derivatives of 2-aminopyridine. Like the parent compound, these (see Tables 2 and 3) show hardly any very intense bands except near 1630 and 1662 cm.$^{-1}$, and in the N–H stretching region. The cations of the 4-, 5-, and 6-methyl derivative (but not those of the 3-methyl derivative or of the parent compound) show a strong band near 2790 cm.$^{-1}$ which is undoubtedly associated with strongly hydrogen-bonding $^+$NH protons, but which one cannot rationalize further. The lowering of the H–N–H stretching frequencies in aminopyridines on cation formation is also due mostly to ($^+$N–H···N) hydrogen bonding. The (for a cation) unusually high values of these frequencies in the 2-amino-6-methylpyridine ion probably reflect steric hindrance by the methyl group to the approach of an $^+$NH$_2$ group towards the ring-nitrogen atom that, on the basis of ion structure (V), would have to be the hydrogen-bond acceptor.

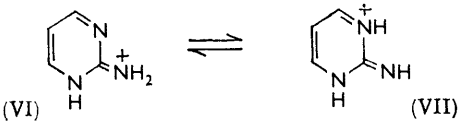
The Raman spectra of these substances change strikingly on cation formation, particularly for the 6-methyl derivative. In the region 1250—1420 cm.$^{-1}$ cation bands do not at all match the amine bands; the strongest Raman band for the cations of the 3- and the 4-methyl derivative near 1370 cm.$^{-1}$ seem to have no counterpart in the amine spectra. The band near 1630 cm.$^{-1}$ in the cation spectra is far less intense than that near 1610 cm.$^{-1}$ in the amine spectra, and the two are presumably not counterparts of each other.

* Contrary to a previous statement,[15] the frequency ν_{19a} may not be significantly lowered (the direction of movement of the exocyclic atom in modes 19a and 19b [there [15] (XIIIA) and (XIIIB)] is the opposite from that shown).

[16] Davies and Parsons, *Z. phys. Chem.* (*Frankfurt*), 1959, **20**, 34.
[17] Spinner, unpublished work.

Though these spectra are somewhat complex, everything indicates a profound structural change on cation formation, all the ions being essentially of structure (V), including the 2-amino-3-methylpyridine ion, even though there might have been steric opposition here to the planar structure required for an ion (V).

2-Aminopyrimidine hydrochloride. The vibration-spectral changes resulting from cation formation by 2-aminopyrimidine (see Tables 1 and 3), though less drastic, resemble those observed for 2-aminopyridine. At least one, and probably both, of the prominent Raman bands for 2-aminopyrimidine in the range 1000—1100 cm.$^{-1}$, and the Raman band at 1588 cm.$^{-1}$ disappear; cation Raman bands, not very intense, but without counterparts in the amine spectrum, appear at 1544, 1298, and 1223 cm.$^{-1}$. The infrared spectrum of the 2-aminopyrimidine cation above 1600 cm.$^{-1}$ resembles that of the 2-aminopyridine cation (except for an intense doublet near 2700 cm.$^{-1}$ due to strongly hydrogen-bonding $^{+}$NH).

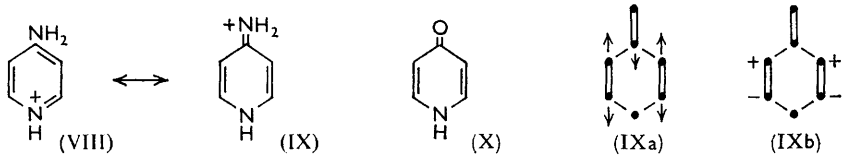


(VI) (VII)

The spectrum of the 2-aminopyrimidine ion is consistent with structure (VI). The potentially mesomeric tautomeride of this ion (VII) is not considered to predominate, for two reasons: (*a*) the very strong infrared band at 1665 cm.$^{-1}$, which lacks a counterpart in the Raman spectrum, is almost certainly due to H–$\overset{+}{\text{N}}$–H scissoring (rather than to C=N or skeletal stretching, which should be Raman-active), and the ion (VII) contains no NH_2 group; (*b*) the Raman spectrum of the 2-aminopyrimidine cation is quite different from that of the 2-hydroxypyrimidine cation, which is ion (VII; =O in place of =NH).

4-Aminopyridine hydrochloride. Cation formation by 4-aminopyridine results in a very striking simplification of the infrared spectrum: below 1500 cm.$^{-1}$ the ion shows no intense bands, and, indeed, very few bands of any measurable intensity. This points to a very simple skeletal structure for the ion, or to a high degree of symmetry. The Raman spectrum, too, is simplified, though not to the same extent; the cation shows 8 bands of an intensity in excess of 10% of that of the strongest Raman band, the amine (at least) * 13.

In these respects the vibration spectrum of the 4-aminopyridine cation is quite different from that of the 4-methoxypyridine cation, and there are formidable obstacles to a structure represented mainly by form (VIII) for the former ion. Though the Raman bands at 1046 and 991 cm.$^{-1}$ could (a little implausibly) be assigned to aromatic ring-breathing ν_1 and ring-deformation ν_{12}, it would be difficult to assign the four skeletal stretching frequencies ν_{8a}, ν_{8b}, ν_{19a}, and ν_{19b}. The band at 1530 cm.$^{-1}$, strong in both the infrared and the Raman spectrum, has to be assigned to a vibration for which there is no parallel in either 4-aminopyridine or the 4-methoxypyridinium ion.



(VIII) (IX) (X) (IXa) (IXb)

One could assign this band to the " modified " vibration [15] ν_{8a} in a mesomeric cation in which the canonical forms (VIII) and (IX) make roughly equal contributions, but it would now be impossible to assign the modified vibrations ν_{19a} and ν_{19a} to any observed band (also, 1046 cm.$^{-1}$, or even 991 cm.$^{-1}$, would be too high a frequency for ν_1 in such

* Mainly owing to the low solubility of 4-aminopyridine in water, very weak bands could not be detected (see Table 1).

an ion). In any case, such a structure would be no simpler or more symmetrical than that of 4-aminopyridine itself.

On the other hand, the vibration spectrum is very readily interpreted on the basis of a cation structure represented essentially or largely by the form (IX), by comparison with the vibration spectrum [7] of 4-pyridone (X), which it strongly resembles. This leads to the following assignments: * 1636 cm.$^{-1}$ to vibration (IXa) (all three double bonds stretch in unison), possibly mixed with $H\overset{+}{N}H$ scissoring; 1530 cm.$^{-1}$ to another composite vibration in which the C=C bonds stretch while the C=N$^+$ bond contracts (and *vice versa*); 1592 cm.$^{-1}$ to N_{ring}–H in-plane bending, 1650 cm.$^{-1}$ to H–$\overset{+}{N}$–H scissoring; 1046 cm.$^{-1}$ to "*pseudo*-ring-breathing," in which the four single bonds in the ring stretch in unison; 847 cm.$^{-1}$ to the C–H out-of-plane bending vibration (IXb) (equivalent to ν_5). The only prominent (Raman) band left unassigned is that at 991 cm.$^{-1}$, for which there is no counterpart in the 4-pyridone spectrum, and which may be associated with the NH_2^+ group.

Amidinium structures for 2- and 4-aminopyridine cations. The result that these ions are essentially (or largely) of the amindinium type, rather than ordinary aromatic ions, is not altogether expected, although it does not contradict any of their known properties. Thus, the ultraviolet spectrum of the 2-aminopyridine cation [3b] does not differ from that of $N_{(1)}$-methyl-2-pyridone imine [3b] (V; NMe in place of NH, and NH in place of $\overset{+}{N}H_2$) by more than the expected amount, while that of the 4-aminopyridine cation shows a (remarkably) close resemblance to that of $N_{(1)}$-methyl-4-pyridone imine [3b] (IX; NMe in place of NH, and NH in place of NH_2^+).

The reason for the amidinium character of these ions, presumably, is that, in a 2- or 4-aminopyridine ion protonated at the ring-nitrogen atom, the exocyclic nitrogen atom accepts the positive charge much more readily than does the the ring-nitrogen because no unsaturated grouping is attached to it. For comparison, the basic ionization constants, in pK_a units, are 12·5 for acetamidine,[19] 11·6 for benzamidine,[2] and 11·5 ± 0·2 for formamidine (new determination). However, in *NN*-diphenylformamidine (unsaturated grouping attached to =N) it has dropped to [20] 7·85, and in imidazole, in which the formamidine residue forms part of a cyclic unsaturated system, to [21] 7·2. This factor seems to outweigh the lack, in ions (V) and (IX), of the aromatic stabilization present in ions (IV) and (VIII). Of course, ions (V) and (IX), though not aromatic, are still extensively stabilized by conjugation (irrespective of whether this is attributed to π-electron delocalization or to other effects [22, 23]) and by the electron-donating effect of the NH grouping (attributable either to the mesomeric effect of NH or to an inductive polarization of the N–C bond(s) by the highly polar C=N$^+$ bond).

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* Coupling between the C=C and C=O stretching motions in 4-pyridone (tentatively proposed before [7]) is considered to be extensive. Alternatively, the band near 1530 cm.$^{-1}$ in the spectrum of 4-pyridone and the 4-aminopyridine cation may be assigned to C=C stretching and that near 1640 cm.$^{-1}$ to C=O or C=N$^+$ stretching, respectively; or, in accordance with Bellamy and Rogasch's interpretation of the 4-pyridone spectrum,[18] one may reverse the latter assignments.

[18] Bellamy and Rogasch, *Spectrochim. Acta*, 1960, **16**, 30.
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[20] De Wolfe, *J. Amer. Chem. Soc.*, 1960, **82**, 1585.
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[23] Dewar and Schmeising, *Tetrahedron*, 1959, **5**, 166.