Mass Spectral Fragmentation Pattern of 2,2'-Bipyridyls. Part VIII. 2,2'-Bipyridyl-5-carboxylic Acid and 2,2'-Bipyridyl-5-sulphonic Acid

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The mass spectra of 2,2'-bipyridyl-5-carboxylic acid and 2,2'-bipyridyl-5-sulphonic acid obtained by electron impact are described. The principal initial fragmentation routes from the molecular ion of the carboxylic acid involve loss of CO, $CN^{\cdot}$, HCN, CO_2, $OH^{\cdot}$ and H_2O. From the molecular ion of the sulphonic acid the principal fragmentations are accompanied by loss of HCN, O_3, SO_2 and SO_3.

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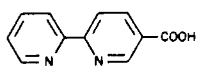
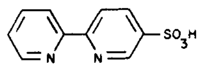
The mass spectral fragmentation patterns of 2,2'-bipyridyl (1) (2) and 5-hydroxy- and 5-alkoxy-2,2'-bipyridyls (3) have recently been reported. In continuation of our study of substituted 2,2'-bipyridyls we now report the mass spectra of 2,2'-bipyridyl-5-carboxylic acid (I) and 2,2'-bipyridyl-5-sulphonic acid (II) (4).

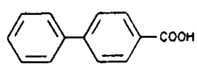
The mass spectra of benzoic acids have been the subject of considerable study (5-13). The spectrum of benzoic acid itself (5) is dominated by the M-OH peak at mass 105 which is the base peak. The molecular ion at mass 122 (~ 80% of base peak) and the peak at mass 77 (~ 60%) due to the M-COOH species are the only prominent peaks above a mass of 70 in the spectrum. In the spectrum of pyridine-3-carboxylic acid (nicotinic acid) (14) on the other hand the base peak is at mass 78 presumably due to the M-COOH species. The molecular ion at mass 123 gives a large peak about 90% of the intensity of the base peak. The M-OH species at mass 106 is less prominent (60% of base peak). Large peaks are also present at mass 105 due to M-H_2O species (~ 85%) and at mass 77 (~ 50%) due to M-H_2O-CO species. Some of the peaks in the mass spectrum of biphenyl-4-carboxylic acid (III) have also been recorded (15).



I



II

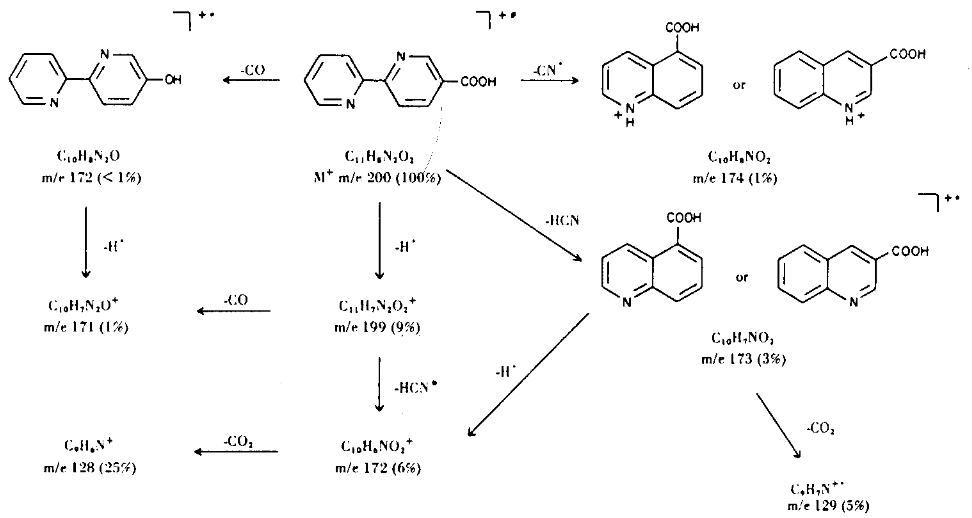


III

Unlike benzoic acid and nicotinic acid the base peak in the mass spectrum of 2,2'-bipyridyl-5-carboxylic acid (I) is due to the molecular ion at mass 200 (Figure 1). The M-1 ion at mass 199 gives rise to a peak of 9% of the intensity of the base peak.

Apart from the loss of $H^{\cdot}$ there are several competing processes in the initial fragmentation of the molecular ion of I. At least six different routes of disintegration are present. One minor route (see Scheme I) involves the loss of CO from the molecular ion of (I) to give a species of mass 172 and empirical formula $C_{10}H_8N_2O$. This ion is present in small amounts (less than 1% of the base peak) and is presumably the 5-hydroxy-2,2'-bipyridyl molecular ion (3). It may lose $H^{\cdot}$ to give the $C_{10}H_7N_2O^+$

Scheme I

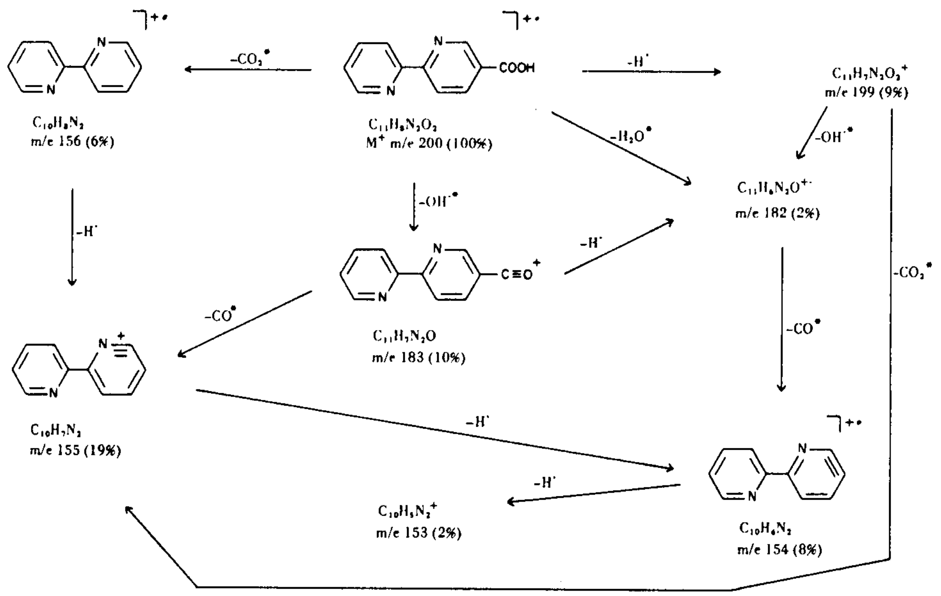


ion at mass 171 (1%) which can also be formed from the M-1 ion of 2,2'-bipyridyl-5-carboxylic acid at mass 199 by loss of CO. No clear metastable transitions were observed for these losses of CO.

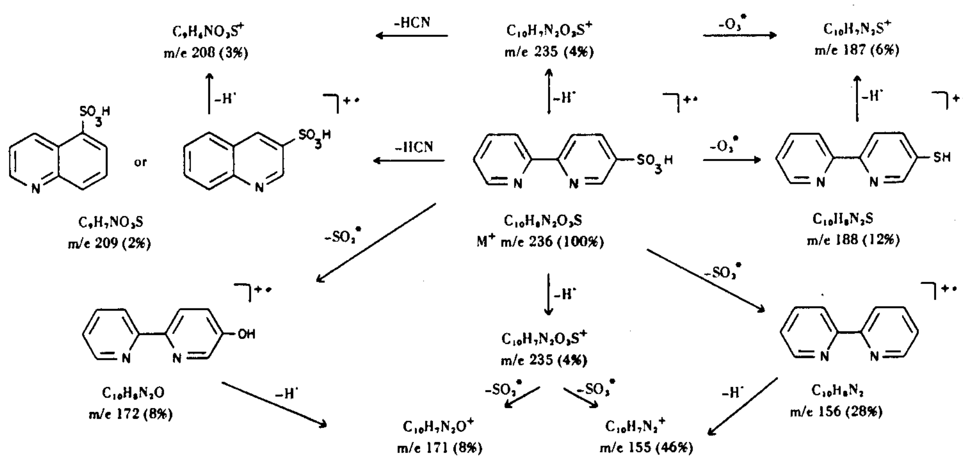
Two other routes of disintegration of the molecular ion of I involve loss of the elements CN$^{\cdot}$ and HCN (see Scheme 1) in a manner presumably akin to that already described for the loss of the same two groups of elements from the molecular ion of 2,2'-bipyridyl (1). The loss of CN$^{\cdot}$ gives rise to a species of formula $C_{10}H_8NO_2$ (1%) depicted as a carboxyquinolinium ion. The loss of HCN from the molecular ion of 2,2'-bipyridyl-5-carboxylic acid (I) gives a $C_{10}H_7NO_2$ species (3%) at mass 173 considered to be the corresponding carboxyquinoline molecular ion. This species may lose H$^{\cdot}$ to give the $C_{10}H_6NO_2{}^+$ ion at mass 172 (6%) which is also formed from the M-1 ion of 2,2'-bipyridyl-5-carboxylic acid at mass 199 by loss of HCN. A metastable peak for the transition 199 → 172 was observed.

The remaining three fragmentation pathways from the molecular ion of 2,2'-bipyridyl-5-carboxylic acid involve the initial loss of OH$^{\cdot}$, H_2O and CO_2 (see Scheme 2). The loss of OH$^{\cdot}$ produces a $C_{11}H_7N_2O^+$ ion of mass 183 (10%). The $C_{11}H_7N_2O^+$ ion disintegrates further by loss of CO to give a $C_{10}H_7N_2{}^+$ ion at mass 155 (19%) presumably the 2,2'-bipyridyl molecular ion less one hydrogen. The $C_{11}H_7N_2O^+$ ion may also lose a H$^{\cdot}$ to give a $C_{11}H_6N_2O^{+\cdot}$ species at mass 182 (2%). The $C_{11}H_6N_2O^{+\cdot}$ ion is also formed from the molecular ion of 2,2'-bipyridyl-5-carboxylic acid (I) by loss of H_2O and from the M-1 ion of I by loss of OH$^{\cdot}$. Metastable peaks for all these transitions were observed. The $C_{11}H_6N_2O^{+\cdot}$ species at

Scheme 2



Scheme 3



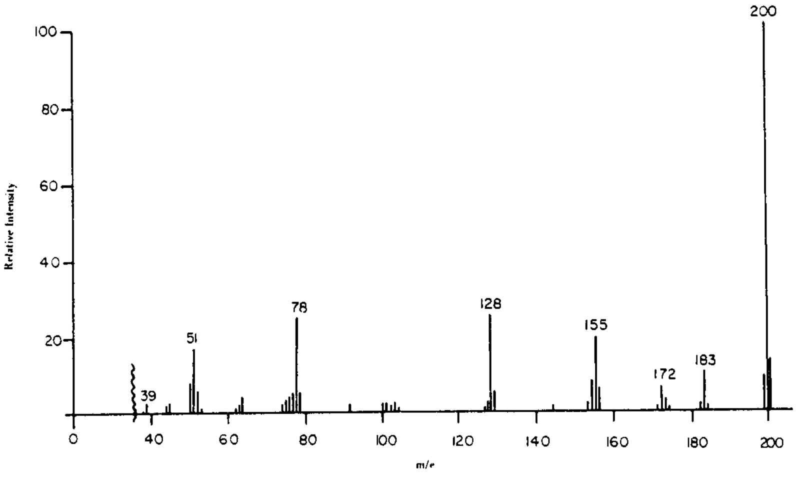


Figure 1. Mass Spectrum of 2,2'-Bipyridyl-5-carboxylic Acid.

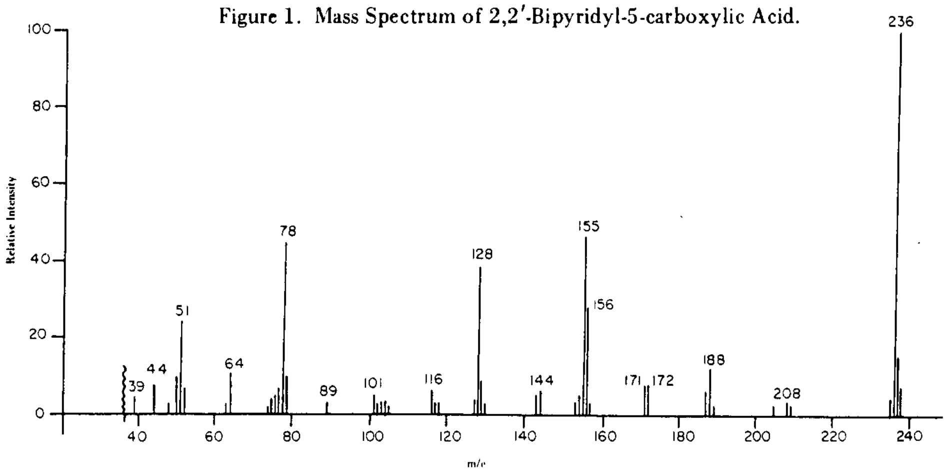


Figure 2. Mass Spectrum of 2,2'-Bipyridyl-5-sulphonic Acid.

mass 182 loses CO to give a $C_{10}H_6N_2^{+\cdot}$ species at mass 154 (8%) depicted as the 2,2'-bipyridyl molecular ion less two hydrogens. This species may lose another H$^\cdot$ to give the $C_{10}H_5N_2^+$ ion (2%) at mass 153.

The loss of CO_2 from the molecular ion of 2,2'-bipyridyl-5-carboxylic acid (I) affords the 2,2'-bipyridyl molecular ion ($C_{10}H_8N_2^{+\cdot}$) at mass 156 (6%). This may lose H$^\cdot$ to give the M-1 ion of 2,2'-bipyridyl ($C_{10}H_7N_2^+$) at mass 155 (19%). The M-1 ion of 2,2'-bipyridyl is also obtained by loss of CO_2 from the M-1 ion of 2,2'-bipyridyl-5-carboxylic acid. Metastable transitions for the loss of CO_2 were observed.

The peaks at mass 129 (5%; $C_9H_7N^{+\cdot}$), 128 (25%; $C_9H_6N^+$), 127 (3%; $C_9H_5N^{+\cdot}$) and 126 (1%; $C_9H_4N^+$) presumably result from the disintegration of the 2,2'-bipyridyl molecular ion at mass 156 or its dehydrogenated species in a manner similar to that already reported in the mass spectrum of 2,2'-bipyridyl (1). For instance, metastable peaks for the transitions 156 → 129 and 155 → 128 by loss of HCN were observed. Contributions to the $C_9H_7N^{+\cdot}$ species at mass 129 and the $C_9H_6N^+$ ion at mass 128 may also come from the fragmentation of the carboxyquinoline molecular ion at mass 173 ($C_{10}H_7NO_2^{+\cdot}$) and its dehydrogenated species at mass 172 ($C_{10}H_6NO_2^+$) (see Scheme 1) by loss of CO_2 but no metastable transitions for these fragmentations were observed. The cluster of small peaks (1-2%) in the mass range 101-105 in the spectrum of I are similar to those observed in the spectrum of 2,2'-bipyridyl (1) while the peaks below a mass of 80 are typical of those obtained from 2,2'-bipyridyl (1), pyridine and quinoline derivatives (16).

The mass spectra of arylsulphonic acids have not received much attention apart from a report on the spectra of some benzenesulphonic acids (17). In the spectrum of benzenesulphonic acid itself the base peak is due to the molecular ion at mass 158. The principal initial fragmentation routes from the molecular ion involve loss of SO_2 and OH$^\cdot$.

The mass spectrum of 2,2'-bipyridyl-5-sulphonic acid (II) is quite complex (Figure 2). The base peak in the spectrum is, as expected, at mass 236 due to the molecular ion. The M-1 ion at mass 235 gives rise to a peak only 4%

TABLE I

High Resolution Data

m/e	Elemental Composition	Observed Mass	Calculated Mass
	(a) 2,2′-Bipyridyl-5-carboxylic Acid		
183	$C_{11}H_7N_2O$	183.0559	183.0558
182	$C_{11}H_6N_2O$	182.0478	182.0480
174	$C_{10}H_8NO_2$	174.0550	174.0555
173	$C_{10}H_7NO_2$	173.0470	173.0476
172	$C_{10}H_8N_2O$ (6%)	172.0633	172.0637
172	$C_{10}H_6NO_2$ (<1%)	172.0398	172.0398
171	$C_{10}H_7N_2O$	171.0557	171.0558
156	$C_{10}H_8N_2$	156.0679	156.0687
155	$C_{10}H_7N_2$	155.0611	155.0609
154	$C_{10}H_6N_2$	154.0530	154.0531
153	$C_{10}H_5N_2$	153.0450	153.0453
129	C_9H_7N	129.0567	129.0578
128	C_9H_6N	128.0501	128.0500
127	C_9H_5N	127.0421	127.0422
126	C_9H_4N	126.0345	126.0344
	(b) 2,2′-Bipyridyl-5-sulphonic Acid		
209	$C_9H_7NO_3S$	209.0146	209.0146
208	$C_9H_6NO_3S$	208.0068	208.0068
188	$C_{10}H_8N_2S$	188.0405	188.0408
187	$C_{10}H_7N_2S$	187.0328	187.0330
172	$C_{10}H_8N_2O$	172.0635	172.0637
171	$C_{10}H_7N_2O$	171.0558	171.0558
156	$C_{10}H_8N_2$	156.0680	156.0687
155	$C_{10}H_7N_2$	155.0611	155.0609
154	$C_{10}H_6N_2$	154.0529	154.0531
153	$C_{10}H_5N_2$	153.0453	153.0453
144	$C_9H_8N_2$	144.0684	144.0687
143	$C_9H_7N_2$	143.0608	143.0609
130	C_9H_8N	130.0656	130.0657
129	C_9H_7N	129.0563	129.0578
128	C_9H_6N	128.0500	128.0500
127	C_9H_5N	127.0421	127.0422
118	$C_7H_6N_2$	118.0527	118.0531
117	C_8H_7N	117.0575	117.0578
116	C_8H_6N	116.0500	116.0500

of the intensity of the base peak. There are several initial fragmentation routes from the molecular ion of II (Scheme 3). One minor route involves the loss of HCN to give a small intensity peak at mass 209 (2%) due to a $C_9H_7NO_3S^{+\cdot}$ species depicted as a quinoline sulphonic acid molecular ion. The $C_9H_7NO_3S^{+\cdot}$ species may lose $H^\cdot$ to give a $C_9H_6NO_3S^+$ ion at mass 208 (3%). The $C_9H_6NO_3S^+$ ion can also be obtained from the M-1 ion of 2,2′-bipyridyl-5-sulphonic acid at mass 235 by loss of HCN. No clear metastable transitions for the loss of HCN were observed.

Another fragmentation route from the molecular ion of 2,2′-bipyridyl-5-sulphonic acid involves loss of O_3 to give a peak at mass 188 (12%) due to a $C_{10}H_8N_2S^{+\cdot}$ species, presumably the 2,2′-bipyridyl-5-thiol molecular ion. A small metastable for the transition 236 → 188 was observed. The $C_{10}H_8N_2S^{+\cdot}$ species may lose $H^\cdot$ to afford a $C_{10}H_7N_2S^+$ ion at mass 187 (6%). The $C_{10}H_7N_2S^+$ ion is also formed from the M-1 ion of II at mass 235 by loss of O_3. Because of the absence of appropriate metastable transitions it was not possible to be certain of the subsequent disintegration pattern of the 2,2′-bipyridyl-5-thiol molecular ion or its M-1 species but it seems reasonable to assume that contributions to peaks in the spectrum of 2,2′-bipyridyl-5-sulphonic acid at mass 156 ($C_{10}H_8N_2$), 155 ($C_{10}H_7N_2$), 144 ($C_9H_8N_2$) and 143 ($C_9H_7N_2$) arise by the loss of S, $SH^\cdot$, CS and $CSH^\cdot$ respectively from the molecular ion of 2,2′-bipyridyl-5-thiol at mass 188 in a manner akin to the fragmentation of thiophenol (18).

One of the major fragmentation routes from the molecular ion of 2,2′-bipyridyl-5-sulphonic acid (II) involves loss of SO_2 to give a $C_{10}H_8N_2O^{+\cdot}$ species at mass 172 (8%) almost certainly due to the 5-hydroxy-2,2′-bipyridyl molecular ion. A strong metastable peak was present corresponding to this transition. The 5-hydroxy-2,2′-bipyridyl molecular ion may lose $H^\cdot$ to afford the $C_{10}H_7N_2O^+$ ion at mass 171 (8%). The $C_{10}H_7N_2O^+$ ion is also formed from the M-1 ion of II at mass 235 by a similar loss of SO_2. A very strong metastable peak corresponding to the transition 235 → 171 was observed. Peaks are present in the spectrum of 2,2′-bipyridyl-5-sulphonic acid corresponding to most of the peaks which would be expected from the subsequent fragmentation of the molecular ion of 5-hydroxy-2,2′-bipyridyl and its M-1 ion, the disintegration patterns of which have already been reported (3). In particular, the peaks in the spectrum of 2,2′-bipyridyl-5-sulphonic acid at mass 144 (6%; $C_9H_8N_2^{+\cdot}$), 143 (5%; $C_9H_7N_2^+$), 117 (3%; $C_8H_7N^{+\cdot}$) and 116 (6%; $C_8H_6N^+$) can be attributed largely to the disintegration of the 5-hydroxy-2,2′-bipyridyl molecular ion or its M-1 species.

Another major fragmentation route from the molecular ion of 2,2′-bipyridyl-5-sulphonic acid (II) involves loss of SO_3 to give a $C_{10}H_8N_2^{+\cdot}$ species at mass 156 (28%) almost certainly due to the 2,2′-bipyridyl molecular ion. The $C_{10}H_8N_2^{+\cdot}$ species may lose $H^\cdot$ to form a $C_{10}H_7N_2^+$ ion, the M-1 ion of 2,2′-bipyridyl, at mass 155 (46%). The $C_{10}H_7N_2^+$ ion is also formed from the M-1 ion of II at mass 235 by loss of SO_3. Metastable transitions for the loss of SO_3 were observed. Peaks which would be expected (1) from the subsequent disintegration of the 2,2′-bipyridyl molecular ion or its M-1 species are present in the spectrum of 2,2′-bipyridyl-5-sulphonic acid. In particular the peaks at mass 130 (3%; $C_9H_8N^+$), 129 (9%; $C_9H_7N^{+\cdot}$), 128 (38%; $C_9H_6N^+$), 127 (4%; $C_9H_5N^{+\cdot}$) and the cluster of small peaks (2-5%) at mass 101-105 are typical of those observed in the spectrum of 2,2′-bipyridyl (1).

TABLE II

Metastable Ions

Initial Ion	Resultant Ion	Transition	Found m*	Calculated m*	Fragment Expelled
		(a) 2,2'-Bipyridyl-5-carboxylic Acid			
$C_{11}H_7N_2O_2$	$C_{10}H_6NO_2$	199 → 172	148.6	148.6	HCN
$C_{11}H_8N_2O_2$	$C_{11}H_7N_2O$	200 → 183	167.5	167.5	OH
$C_{11}H_7N_2O$	$C_{10}H_7N_2$	183 → 155	131.2	131.2	CO
$C_{11}H_8N_2O_2$	$C_{11}H_6N_2O$	200 → 182	165.6	165.6	H_2O
$C_{11}H_7N_2O_2$	$C_{11}H_6N_2O$	199 → 182	166.3	166.4	OH
$C_{11}H_6N_2O$	$C_{10}H_6N_2$	182 → 155	130.2	130.3	CO
$C_{11}H_8N_2O_2$	$C_{10}H_8N_2$	200 → 156	121.7	121.7	CO_2
$C_{11}H_7N_2O_2$	$C_{10}H_7N_2$	199 → 155	120.7	120.7	CO_2
$C_{10}H_8N_2$	C_9H_7N	156 → 129	106.5	106.7	HCN
$C_{10}H_7N_2$	C_9H_6N	155 → 128	105.8	105.7	HCN
		(b) 2,2'-Bipyridyl-5-sulphonic Acid			
$C_{10}H_8N_2O_3S$	$C_{10}H_8N_2S$	236 → 188	149.6	149.8	O_3
$C_{10}H_7N_2O_3S$	$C_{10}H_7N_2S$	235 → 187	148.6	148.7	O_3
$C_{10}H_8N_2O_3S$	$C_{10}H_8N_2O$	236 → 172	125.4	125.3	SO_2
$C_{10}H_8N_2O_3S$	$C_{10}H_8N_2O$	235 → 171	124.4	124.4	SO_2
$C_{10}H_8N_2O_3S$	$C_{10}H_8N_2$	236 → 156	103.1	103.1	SO_3
$C_{10}H_7N_2O_3S$	$C_{10}H_7N_2$	235 → 155	101.9	102.2	SO_3

The peaks below a mass of 100 in the spectrum of 2,2'-bipyridyl-5-sulphonic acid are similar to those in the spectra of 2,2'-bipyridyl (1) and 5-hydroxy-2,2'-bipyridyl (3) and require no comment apart from the peak at mass 64 (10%) which is largely due to the SO_2 molecular ion.

The origin of the small intensity (3%) peak at mass 118 in the spectrum of 2,2'-bipyridyl-5-sulphonic acid is not clear. It corresponds to a species of formula $C_7H_6N_2^{+\bullet}$. It may arise from the $C_9H_8N_2^{+\bullet}$ species at mass 144 by loss of C_2H_2 but no metastable corresponding to the transition 144 → 118 was observed.

The elemental composition of the ions of importance in elucidating the fragmentation patterns are recorded in Table I and the important metastable transitions in Table II.

EXPERIMENTAL

The mass spectra were determined with an A.E.I. MS-30 mass spectrometer. The samples were analyzed by a direct insertion probe at an ionising current of 70 eV. The ion source temperature was at 200° for 2,2'-bipyridyl-5-carboxylic acid and at 250° for 2,2'-bipyridyl-5-sulphonic acid. Elemental compositions were obtained by the peak matching method.

2,2'-Bipyridyl-5-carboxylic acid (4) and 2,2'-bipyridyl-5-sulphonic acid (4) were analytically pure.

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