Mass Spectral Fragmentation Pattern of 4,4'-Bipyridyls. Part I. 4,4'-Bipyridyl

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The mass spectral fragmentation pattern of 4,4'-bipyridyl is described. The fragmentation proposals which differ from those previously reported are supported by high resolution mass measurements and metastable transitions.

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The mass spectra of 2,2'-bipyridyl and 4,4'-bipyridyl have been reported (1) and fragmentation patterns suggested. We recently showed, however, on the basis of high resolution mass measurements and metastable transitions that the proposed fragmentation pattern for 2,2'-bipyridyl was incorrect (2). Because of this discrepancy we have carried out a careful analysis of the mass spectrum of 4,4'-bipyridyl as a preliminary to the study of a series of substituted 4,4'-bipyridyls (3).

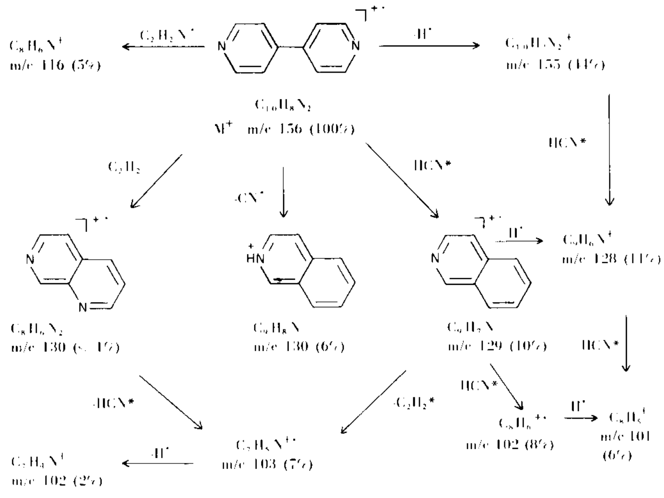
The most intense peak in the mass spectrum of 4,4'-bipyridyl is due to the molecular ion (Figure). The second most intense peak (44% of the molecular ion) at mass 155 results from loss of $H^{\bullet}$ to give the $C_{10}H_7N_2^+$ ion.

The peak at mass 130 was considered by the Russian group (1) to result from the loss of C_2H_2 from the molecular ion to give a $C_8H_6N_2$ species. Accurate mass measurements of this peak, however, show that it is made up of two components. The principal component (6% of the molecular ion) has the empirical formula of C_9H_8N due to the loss of $CN^{\bullet}$ from the molecular ion. It is depicted as being due to the isoquinolinium ion. This behaviour is analogous to that observed with 2,2'-bipyridyl (2). A small peak (less than 1% of the molecular ion) corresponds to the formula $C_8H_6N_2$ resulting from loss of C_2H_2 from the molecular ion, probably due to a naphthyridine molecular ion. No clear metastable transition for the fragmentation 156 → 130 was observed.

The peak at mass 129 (10% of the molecular ion) corresponds to loss of neutral HCN from the molecular ion to give the C_9H_7N species in agreement with the Russian group (1). It is considered to be due to the isoquinoline molecular ion. The peak at mass 128, C_9H_6N, (11% of the molecular ion) can result from loss of $H^{\bullet}$ from the isoquinoline molecular ion. As in the spectrum of 2,2'-bipyridyl (2), however, a strong metastable transition is present which is due to the loss of HCN from the M-1 ion ($C_{10}H_7N_2$) giving a C_9H_6N species. The $C_9H_6N^+$ ion thus arises from at least two sources.

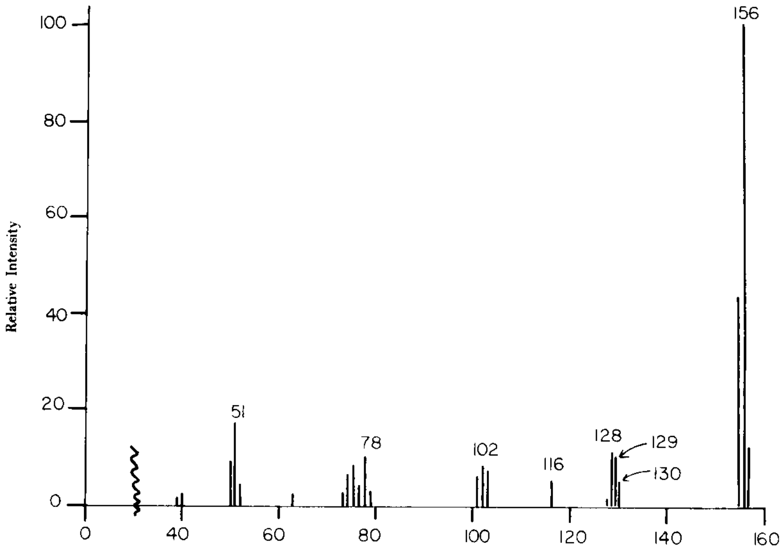
There is an interesting peak at mass 116 (5% of the molecular ion) corresponding to the $C_8H_6N^+$ ion. It is presumably formed by the loss of $C_2H_2N^{\bullet}$ from the molecular ion by a process analogous to the loss of the same elements from the pyridine molecular ion (4).

Scheme



The peak at mass 103 (7% of molecular ion) corresponds to the C_7H_5N species. There are small metastable transitions corresponding to the loss of HCN from the $C_8H_6N_2$ species and the loss of C_2H_2 from the isoquinoline molecular ion which account for the formation of the C_7H_5N species.

The peak at mass 102 is made up of two components. The principal component (8% of molecular ion) corresponds to the C_8H_6 species formed from the isoquinoline molecular ion by loss of HCN. The minor component (2% of molecular ion) comprises the $C_7H_4N^+$ ion formed



Mass Spectrum of 4,4′-Bipyridyl

Table 1

High Resolution Data for 4,4′-Bipyridyl

m/e	Elemental Composition	Observed Mass	Calculated Mass
130	C_9H_8N	130.0659	130.0657
130	$C_8H_6N_2$	130.0532	130.0531
129	C_9H_7N	129.0578	129.0578
128	C_9H_6N	128.0496	128.0500
116	C_8H_6N	116.0501	116.0500
103	C_7H_5N	103.0421	103.0422
102	C_8H_6	102.0463	102.0469
102	C_7H_4N	102.0346	102.0344
101	C_8H_5	101.0385	101.0391

by loss of $H^{\cdot}$ from the C_7H_5N species.

The peak at mass 101 (6% of molecular ion) is due to the $C_8H_5^+$ ion formed by loss of hydrogen from the C_8H_6 species or by loss of HCN from the $C_9H_6N^+$ ion.

The peaks of mass lower than 80 are typical of those obtained from pyridine and isoquinoline and require no comment. The fairly intense peak at mass 78 (10% of molecular ion) is made up of contributions from the M^{++} species and the $C_5H_4N^+$ ion presumably formed by rupture of the central bond of 4,4′-bipyridyl.

The elemental composition of all the ions depicted in the Scheme was in accord with high resolution data (Table 1). The loss of the components, depicted in the Scheme by an asterisk, was supported by the observation of the appropriate metastable transitions.

EXPERIMENTAL

The mass spectra were determined with an A.E.I. MS-30 mass spectrometer. The sample was analysed by a direct insertion probe at an ionising current by 70eV. Elemental compositions were obtained by the peak matching method.

4,4′-Bipyridyl was analytically pure.

Table 2

Metastable Ions Present in the Mass Spectrum of 4,4′-Bipyridyl

Initial Ion	Resultant Ion	Transition	Calculated m*	Found m*	Fragment Expelled
$C_{10}H_8N_2$	C_9H_7N	156 → 129	106.7	106.8	HCN
$C_{10}H_7N_2$	C_9H_6N	155 → 128	105.7	105.8	HCN
$C_8H_6N_2$	C_7H_5N	130 → 103	81.6	81.5	HCN
C_9H_7N	C_7H_5N	129 → 103	82.2	82.2	C_2H_2
C_9H_7N	C_8H_6	129 → 102	80.7	80.7	HCN
C_9H_6N	C_8H_5	128 → 101	79.7	79.7	HCN

REFERENCES AND NOTES

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