

Part XI. 2,2'-Iminodipyrindine

N. G. Keats and L. A. Summers

Department of Chemistry, University of Newcastle, 2308, New South Wales, Australia

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The base peak in the mass spectrum of 2,2'-iminodipyrindine is due to the M-1 ion. There are several minor fragmentation routes from the molecular ion but the principal pathway involves rupture of the central bonds.

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We have recently been interested in the mass spectral fragmentation pattern of relatives of 2,2'-bipyridyl containing an atom or group placed between the pyridine rings. So far we have studied the spectra of di-2-pyridyl ketone (1), 2,2'-oxydipyrindine (2), 2,2'-thiodipyrindine (3), 2,2'-dithiodipyrindine (4) and 1,2-di-(2-pyridyl)ethylene (5). We now report on the fragmentation pattern of 2,2'-iminodipyrindine (I).

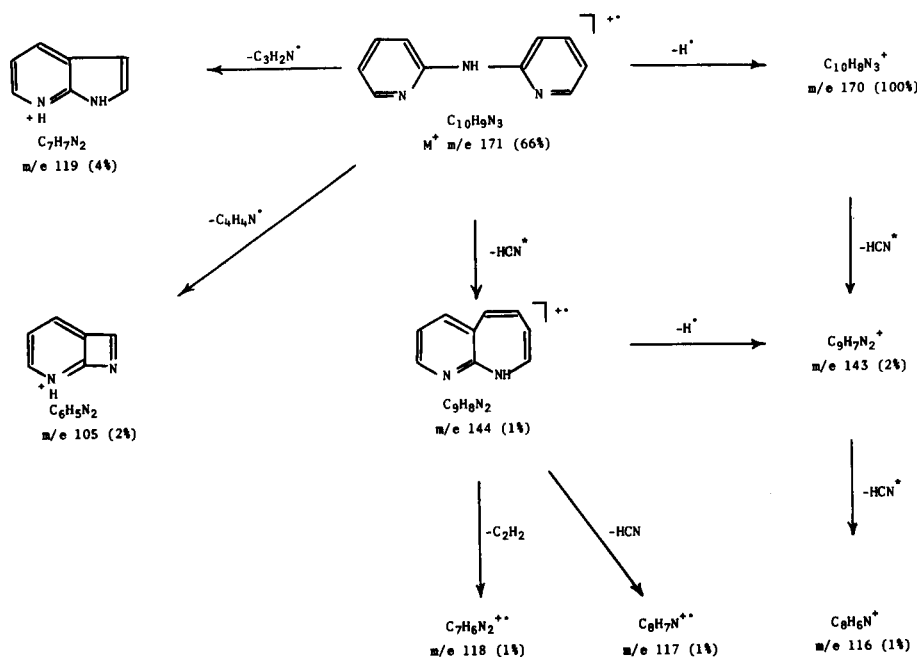
The mass spectrum of diphenylamine (II) obtained by electron impact has been reported (6-8). The spectrum (6,7) is dominated by the peak due to the molecular ion at mass 169 which is the base peak. The M-1 ion (~40%) at mass 168 and the M-2 ion (~20%) at mass 167 also give rise to prominent peaks in the spectrum. There is relatively little fragmentation of the molecule apart from rupture of the central bonds which produces peaks notably at mass 77, 66, 65 and 51 (~10%).

Unlike the spectrum of diphenylamine (6,7) the base peak in the spectrum of 2,2'-iminodipyrindine is due to the M-1 ion at mass 170. The molecular ion at mass 171 gives rise to a peak of 66% of the intensity of the base peak. This behaviour resembles that of 2,2'-thiodipyrindine (3)

and 1,2-di-(2-pyridyl)ethylene (5) where the base peaks are also due to the M-1 ions.

A minor fragmentation route from the molecular ion of 2,2'-iminodipyrindine at mass 171 involves loss of HCN to give a small peak at mass 144 (1%) due to a $C_9H_8N_2$ species (see Scheme 1). The loss of HCN presumably involves the bridging NH group since the similar small loss of HCN occurs on electron impact with the molecular ion of diphenylamine (9). The $C_9H_8N_2^{++}$ ion at mass 144 is depicted as a pyridoazepine molecular ion, the species previously considered to be formed by the loss of CO from the molecular ion of 2,2'-oxydipyrindine (2) and CS from the molecular ion of 2,2'-thiodipyrindine (3). The $C_9H_8N_2^{++}$ species may lose H^+ to form a $C_9H_7N_2^+$ ion at mass 143 (2%). The $C_9H_7N_2^+$ ion is also formed by loss of HCN from the M-1 ion of 2,2'-iminodipyrindine at mass 170. Metastable peaks for the loss of HCN were observed. The subsequent fragmentation of the pyridoazepine molecular ion at mass 144 and its dehydrogenated form at mass 143 accounts for the small peaks at mass 118 (1%; $C_7H_6N_2^{++}$), 117 (1%; $C_8H_7N^{++}$) and 116 (1%; $C_8H_6N^+$) by loss of C_2H_2 and HCN as described previously (2,3). A small metastable peak was observed for the transition $143 \rightarrow 116$.

Scheme 1



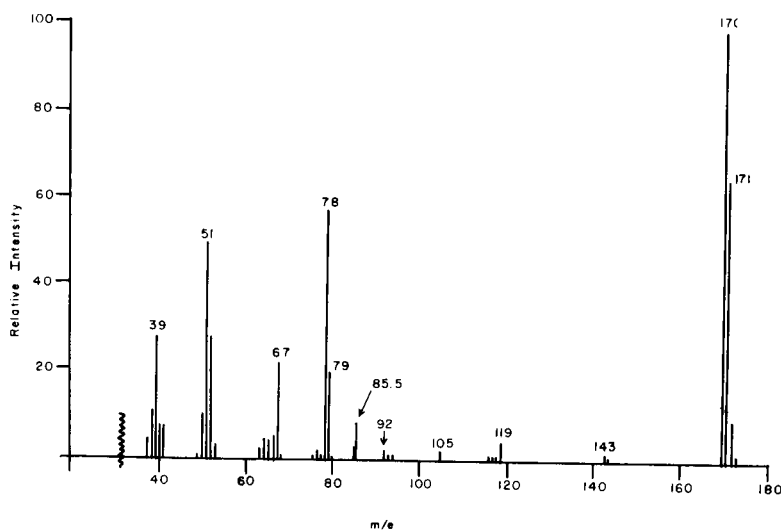
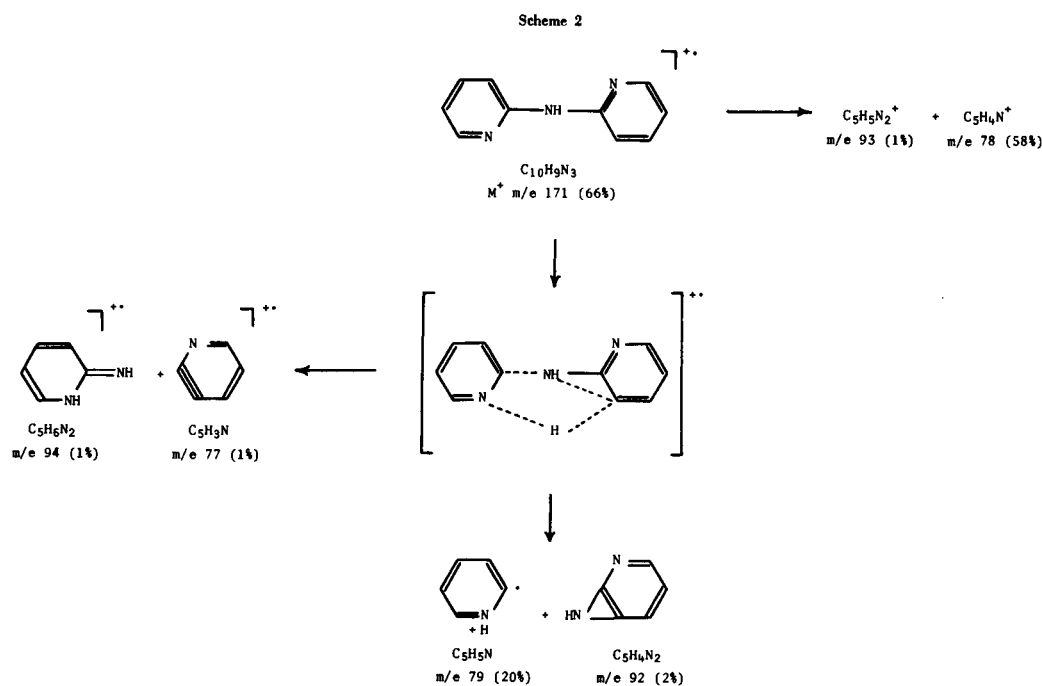
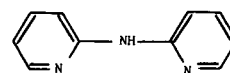


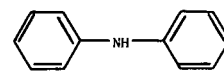
Figure: Mass Spectrum of 2,2'-Iminodipyridine.

Other minor fragmentation routes probably arising directly from the molecular ion of 2,2'-iminodipyridine at mass 171 involve loss of $CH=CH-CN^+$ to give a peak at mass 119 due to a $C_7H_7N_2^+$ ion (4%) depicted as a pyrrolopyridinium ion and loss of $C_4H_4N^+$ to give a peak at mass 105 due to a $C_6H_5N_2^+$ ion (2%) depicted as an azetopyridinium ion but no clear metastable peaks for these transitions were observed.

The major fragmentation route (Scheme 2) from the molecular ion of 2,2'-iminodipyridine involves rupture of the central bonds. Like the similar fragmentation observed with 2,2'-oxydipyridine (2) and 2,2'-thiodipyridine (3)



I



II

Table I
High Resolution Data

m/e	Elemental Composition	Observed Mass	Calculated Mass
144	C ₉ H ₈ N ₂	144.0686	144.0687
143	C ₉ H ₇ N ₂	143.0607	143.0609
119	C ₇ H ₇ N ₂	119.0607	119.0609
118	C ₇ H ₆ N ₂	118.0531	118.0531
117	C ₈ H ₇ N	117.0576	117.0578
116	C ₈ H ₆ N	116.0500	116.0500
105	C ₆ H ₅ N ₂	105.0453	105.0453
94	C ₅ H ₆ N ₂	94.0531	94.0531
93	C ₅ H ₅ N ₂	93.0450	93.0453
92	C ₅ H ₄ N ₂	92.0374	92.0374
79	C ₅ H ₅ N	79.0420	79.0422
78	C ₅ H ₄ N	78.0344	78.0344
77	C ₅ H ₃ N	77.0264	77.0265
76	C ₅ H ₂ N	76.0187	76.0187
75	C ₅ HN	75.0107	75.0107

hydrogen migrations sometimes accompany the central bond rupture perhaps by way of the route depicted in Scheme 2. The probable structures of the ions so formed are given in Scheme 2 and the high resolution data in Table I.

The peaks below a mass of 75 in the spectrum are typical of these to be expected from pyridine derivatives. The peaks at mass 85.5 (8%) and 85 (3%) are due to M⁺⁺ and (M-1)⁺⁺ ions respectively.

EXPERIMENTAL

The mass spectrum was determined with an A.E.I. MS-30 mass spectrometer. The sample was analysed by a direct insertion probe at an ionizing current of 70 eV. The ion source temperature was 60°. Elemental compositions were obtained by the peak matching method.

2,2'-Iminodipyridine was analytically pure.

Table II

Metastable Ions Present in the Mass Spectrum of 2,2'-Iminodipyridine

Initial Ion	Resultant Ion	Transition	Calculated m*	Found m*	Fragment Expelled
C ₁₀ H ₉ N ₃	C ₉ H ₈ N ₂	171 → 144	121.3	121.3	HCN
C ₁₀ H ₈ N ₃	C ₉ H ₇ N ₂	170 → 143	120.3	120.3	HCN
C ₉ H ₇ N ₂	C ₈ H ₆ N	143 → 116	94.1	94.2	HCN

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