Mass Spectral Fragmentation Pattern of 2,2′-Bipyridyls. Part III. 2-(2-Pyridyl)quinoline and 2,2′-Biquinoline

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The mass spectral fragmentation patterns of 2-(2-pyridyl)quinoline and 2,2′-biquinoline are reported. The former rearranges to acridine derivatives on electron impact while the latter shows very little fragmentation.

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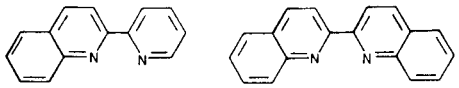
We recently reported (1) the mass spectrum of 2,2′-bipyridyl ($C_{10}H_8N_2$) obtained by electron impact. The principal initial fragmentation of the molecular ion of 2,2′-bipyridyl involved loss of H· to give the M-1 species (42% of the molecular ion), loss of CN· to give a $C_9H_8N^+$ ion (10% of molecular ion) and loss of neutral HCN to form a $C_9H_7N^{+\cdot}$ species (20% of molecular ion). In continuation of this study we now report on the mass spectral fragmentation patterns of two polycyclic derivatives of 2,2′-bipyridyl namely, 2-(2-pyridyl)quinoline (I) and 2,2′-biquinoline (II). The mass spectrum of 2,2′-



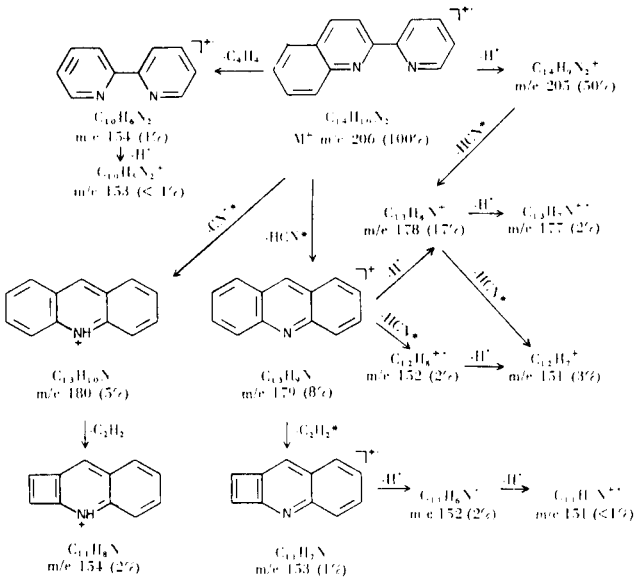
I II

biquinoline has been reported briefly previously but no high resolution mass measurements were recorded (2) (3).

As expected the most intense peak in the mass spectrum of 2-(2-pyridyl)quinoline (I) is due to the molecular ion (Figure 1). The second most intense peak (50% of molecular ion) at mass 205 results from loss of H· to give the $C_{14}H_9N_2^+$ ion.

Apart from the loss of H· the fragmentation of the molecular ion of (I) follows three pathways. The minor route leads to the $C_{10}H_6N_2^{+\cdot}$ species of mass 154 (1% of molecular ion), depicted as the 2,2′-bipyridyl molecular ion less two hydrogens, presumably formed by rupture of the benzene ring with loss of C_4H_4. No clear metastable transition was observed for this fragmentation however. Like 2,2′-bipyridyl (1) the two major fragmentation routes from the molecular ion of 2-(2-pyridyl)-quinoline involve loss of CN· and neutral HCN, respectively. Loss of CN· gives a $C_{13}H_{10}N^+$ ion of mass 180 (5% of molecular ion) considered to be the acridinium ion. The

Scheme



acridinium ion may then lose C_2H_2 to form the $C_{11}H_8N^+$ ion of mass 154 (2% of molecular ion) depicted as a fused cyclobutadiene type structure.

The other major fragmentation from the molecular ion of (I) involves loss of neutral HCN and leads to a species of mass 179 of formula $C_{13}H_9N$ (8% of molecular ion) which is considered to be the acridine molecular ion. The acridine molecular ion may lose H· to give a $C_{13}H_8N^+$ ion of mass 178 (17% of molecular ion) which is also formed from the M-1 species ($C_{14}H_9N_2^+$) by loss of neutral HCN. The $C_{13}H_8N^+$ ion may also lose H· to form a $C_{13}H_7N^{+\cdot}$ species of mass 177 (2% of molecular ion). In keeping with the formulation of the $C_{13}H_9N$ species as an acridine derivative the subsequent frag-

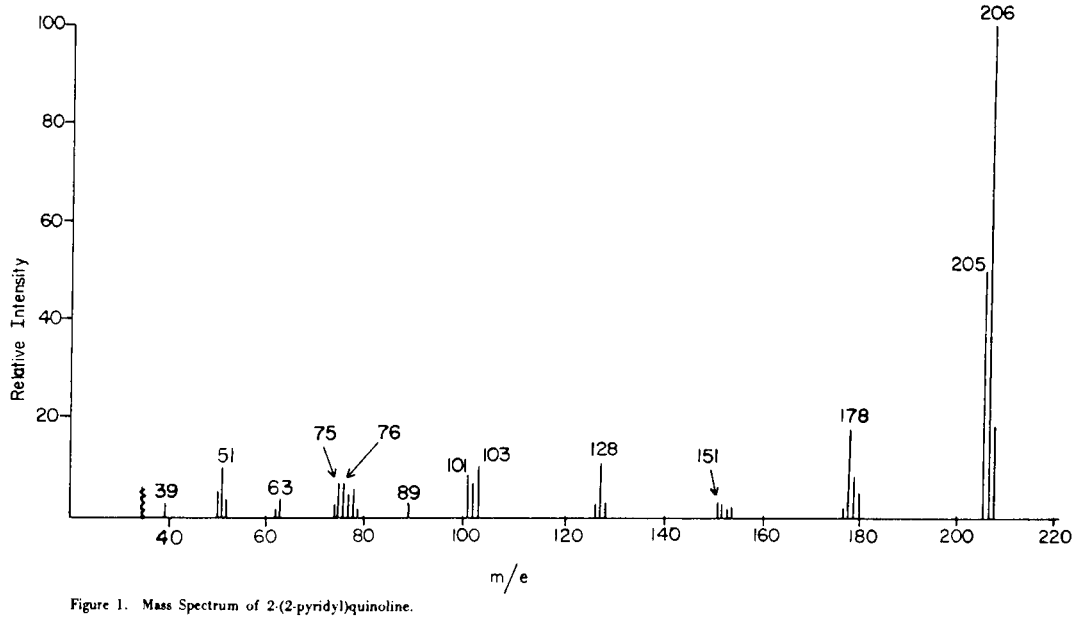


Figure 1. Mass Spectrum of 2-(2-pyridyl)quinoline.

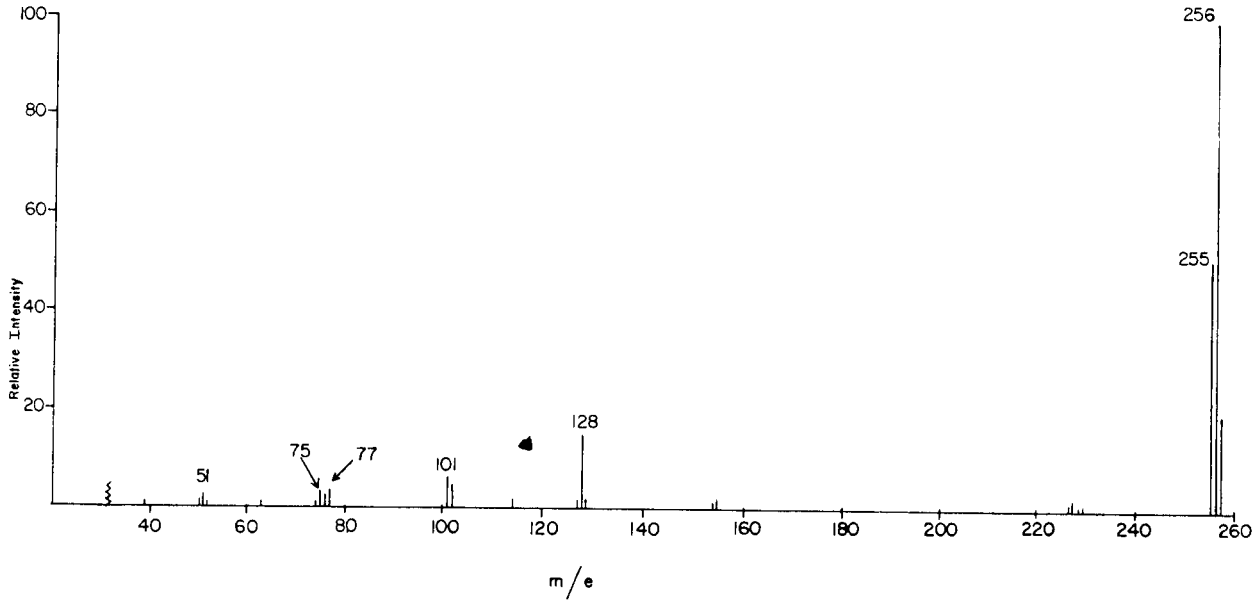


Figure 2. Mass Spectrum of 2,2'-biquinoline.

mentation of the $C_{13}H_9N^{+\cdot}$ and $C_{13}H_8N^{+}$ species is substantially the same as that already reported for the acridine molecular ion and the corresponding dehydrogenated species (4). This fragmentation gives rise to a cluster of small peaks (1-3% of molecular ion) of mass 153 ($C_{11}H_7N^{+\cdot}$), 152 ($C_{12}H_8^{+\cdot}$ and $C_{11}H_6N^{+}$) and 151 ($C_{12}H_7^{+}$ and $C_{11}H_5N^{+\cdot}$) by loss of HCN, C_2H_2 and H$^{\cdot}$ as shown in the Scheme. Fragmentations where metastable transitions were observed are denoted by an asterisk in the Scheme.

The peak at mass 128 (11% of molecular ion) corresponds to the formula C_9H_6N and is presumably due to the quinoline molecular ion less one hydrogen formed by rupture of the central bond of (I). This species may lose H$^{\cdot}$ to form the $C_9H_5N^{+\cdot}$ species of mass 127 (3% of molecular ion).

The peaks at mass 103 (10% of molecular ion) and 89 (4%) are due to doubly charged ions from 2-(2-pyridyl)-quinoline, M^{++}, and acridine, $(M\text{-}1)^{++}$ (4) respectively, while those at mass 102 (6% of molecular ion) due to a

Table 1

High Resolution Data

m/e	Elemental Composition	Observed Mass	Calculated Mass
	(a) 2-(2-Pyridyl)quinoline		
180	$C_{13}H_{10}N$	180.0812	180.0813
179	$C_{13}H_9N$	179.0729	179.0735
178	$C_{13}H_8N$	178.0658	178.0657
177	$C_{13}H_7N$	177.0579	177.0578
154	$C_{11}H_8N$ (2%)	154.0650	154.0657
154	$C_{10}H_6N_2$ (1%)	154.0531	154.0531
153	$C_{11}H_7N$ (1%)	153.0579	153.0578
153	$C_{10}H_5N_2$ (<1%)	153.0457	153.0453
152	$C_{12}H_8$ (2%)	152.0615	152.0626
152	$C_{11}H_6N$ (2%)	152.0502	152.0500
151	$C_{12}H_7$ (3%)	151.0551	151.0548
151	$C_{11}H_5N$ (<1%)	151.0421	151.0422
129	C_9H_7N	129.0574	129.0578
128	C_9H_6N	128.0500	128.0500
127	C_9H_5N	127.0422	127.0422
102	C_8H_6	102.0463	102.0469
101	C_8H_5	101.0390	101.0391
	(b) 2,2'-Biquinoline		
128	C_9H_6N	128.0497	128.0500
102	C_8H_6	102.0470	102.0469
101	C_8H_5	101.0390	101.0391

$C_8H_6^{+\cdot}$ species and at mass 101 (8% of molecular ion) due to the $C_8H_5^+$ ion are presumably formed from the $C_9H_6N^+$ ion (mass 128) by loss of $CN^\cdot$ and HCN respectively. A metastable ion for the transition 128 → 101 was observed. The peaks below a mass of 80 in the spectrum of (I) are typical of those obtained from pyridine (5), quinoline (5) and acridine (4).

The elemental compositions of those ions of importance in elucidating the fragmentation pattern are recorded in Table 1 and the metastable transitions in Table 2.

In contrast to the spectra of 2,2'-bipyridyl (1) and 2-(2-pyridyl)quinoline (I), the mass spectrum of 2,2'-biquinoline (II) shows that there is very little fragmentation of the molecule (Figure 2). The only large peaks in the spectrum are those due to the molecular ion $C_{18}H_{12}N_2^{+\cdot}$ of mass 256, which is, as expected, the base peak, the M-1 ion, $C_{18}H_{11}N_2^+$ (52% of molecular ion) of mass 255, and the peak at mass 128 (15% of molecular ion) of formula C_9H_6N made up of contributions from the M^{++} species and the quinoline molecular ion less one hydrogen formed by rupture of the central bond of 2,2'-biquinoline. The small peak at mass 102 (5% of molecular ion) is due principally to the $C_8H_6^{+\cdot}$ species formed from the $C_9H_6N^+$ ion by loss of $CN^\cdot$ while the peak at mass 101 (7% of molecular ion) of formula $C_8H_5^+$ is likewise formed from the $C_9H_6N^+$ ion by loss of HCN. The peaks below a mass of 80 in the spectrum are typical of those observed from quinoline (5).

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 of 70 eV. Elemental compositions were obtained by the peak matching method.

2-(2-Pyridyl)quinoline and 2,2'-biquinoline were analytically pure.

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Table 2

Metastable Ions

Initial Ion	Resultant Ion	Transition	Calculated m*	Found m*	Fragment Expelled
		(a) 2-(2-Pyridyl)quinoline			
$C_{14}H_{10}N_2$	$C_{13}H_{10}N$	206 → 180	157.3	157.2	CN
$C_{14}H_{10}N_2$	$C_{13}H_9N$	206 → 179	155.6	155.8	HCN
$C_{14}H_9N_2$	$C_{13}H_8N$	205 → 178	154.5	154.6	HCN
$C_{13}H_9N$	$C_{11}H_7N$	179 → 153	130.8	130.7	C_2H_2
$C_{13}H_9N$	$C_{12}H_8$	179 → 152	129.0	128.9	HCN
$C_{13}H_8N$	$C_{12}H_7$	178 → 151	128.1	128.2	HCN
C_9H_6N	C_8H_5	128 → 101	79.7	79.7	HCN
		(b) 2,2'-Biquinoline			
C_9H_6N	C_8H_5	128 → 101	79.7	79.7	HCN