Mass Spectral Fragmentation Pattern of N,N'-Diphenylformamidines

NEIL G. KEATS, JEAN E. ROCKLEY, and LINDSAY A. SUMMERS

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

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The base peaks in the mass spectra of N,N'-diphenylformamidines, N,N'-di-(4-chlorophenyl)formamidines and N,N'-di-(3-chlorophenyl)formamidines are due to the molecular ions of aniline, 4-chloroaniline and 3-chloroaniline respectively. The species responsible for the base peaks are thought to be formed by rupture of the CH-NH bond with concomitant hydrogen migration.

There has been very little investigation of the mass spectral fragmentation of formamidines on electron impact¹. The rearrangement processes involved in the fragmentation of N,N-dimethyl-N'-phenylformamidines have been the subject of some study²⁻⁶ but there has been no report of the fragmentation of simple formamidines. This paper is concerned with the mass spectral fragmentation of N,N'-diphenylformamidines (1) and two symmetrically substituted N,N'-di(chlorophenyl)formamidines (2) and (3).

The base peak in the spectrum of N,N'-diphenylformamidines (1) (Fig. 1) is not due to the molecular ion at mass 196. The base peak is at mass 93 due to a species of formula $C_6H_7N^+$. The molecular ion at mass 196 gives rise to a peak of 41% of the intensity of the base peak. Loss of H⁺ from the molecular ion gives the M-1 ion which is responsible for the peak at mass 195 (11%).

Fig. 1. Mass spectrum of N,N'-diphenylformamidines.

The fragmentation pattern of N,N'-diphenylformamidines (1) (Scheme) is an interesting one. The initial disintegration of the molecular ion of 1 at mass 196 involves rupture of the CH-NH bond to afford the two fragments at mass 104 (10%) and 92 (4%) due to $C_7H_6N^+$ and $C_6H_6N^+$ ions respectively. This bond rupture, however, may be accompanied by a hydrogen migration to afford the two species at mass 103 (2%) and 93 (100%) of empirical formula $C_7H_5N^+$ and $C_6H_7N^+$ depicted as the phenylisocyanide and aniline molecular ions respectively. A strong metastable peak in the

Requests for reprints should be sent to Prof. Dr. L. A. SUMMERS, Department of Chemistry, The University of Newcastle, 2308, New South Wales, Australia.

spectrum at mass 44.2 corresponds to the transition $196 \rightarrow 93$. The aniline molecular ion (at mass 93) which is known to be a very stable one⁷ is in fact the base peak in the spectrum of N,N'-diphenylformamidines.

The subsequent fragmentation of the $C_7H_6N^+$, $C_6H_6N^+$, $C_7H_5N^+$ and $C_6H_7N^+$ species involves the loss of HCN in each case. Metastable peaks are observed for these transitions. This results in the formation of the species giving rise to peaks at mass 77 (26%; $C_6H_5^+$), 65 (6%; $C_5H_5^+$), 76 (2%; $C_6H_4^+$) and 66 (7%; $C_5H_6^+$). The species considered to be the phenylisocyanide molecular ion at mass 103 ($C_7H_5N^+$) may also lose $CN^\bullet$ (*cf.* ⁸) and this fragmentation route provides another source of the $C_6H_5^+$ ion at mass 77. Successive losses of $H^\bullet$ from the $C_5H_5^+$ ion at mass 65 account for the small peaks (1–2%) at mass 64 ($C_5H_4^+$) and 63 ($C_5H_3^+$). The peaks below a mass of 60 in the spectrum are typical of those to be expected from further disintegration of the species shown in the Scheme and require no comment.

Table I. Empirical formula of fragment ions* in the mass spectrum of N,N'-diphenylformamidines (1).

m/e	Formula	Intensity [%]
196	$C_{13}H_{12}N_2$	41
195	$C_{13}H_{11}N_2$	11
194	$C_{13}H_{10}N_2$	2
104	C_7H_6N	10
103	C_7H_5N	2
93	C_6H_7N	100
92	C_6H_6N	4
91	C_6H_5N	1
77	C_6H_5	26
76	C_6H_4	2
66	C_5H_6	7
65	C_5H_5	6
64	C_5H_4	2
63	C_5H_3	1
51	C_4H_3	11
50	C_4H_2	3

* Only those ions of mass > 49 and of intensity $\geq 1\%$ of the base peak are recorded. Peaks due to ^{13}C species are omitted from the table.

The spectra of N,N'-di-(4-chlorophenyl)-formamidines (2) (Fig. 2) and N,N'-di-(3-chlorophenyl)-formamidines (3) (Fig. 3) are very similar and their fragmentation pathways follow much the same route as that observed with N,N'-diphenylformamidines (1). In both cases the base peak is at mass

Fig. 2. Mass spectrum of N,N'-di-(4-chlorophenyl)-formamidine.

Fig. 3. Mass spectrum of N,N'-di-(3-chlorophenyl)-formamidine.

127 due to the molecular ion of the corresponding chloroaniline of formula C_6H_6NCl . The molecular ion of the di-(chlorophenyl)-formamidines at mass 264 gives rise to a peak of 18% of the intensity of the base peak with the 4-chloro derivative (2) and 14% of the intensity of the base peak with the 3-chloro analogue (3). The peaks at mass 138 (13%; $C_7H_5NCl^+$) and mass 126 (2–6%; $C_6H_5NCl^+$) are likewise considered to arise largely by rupture of the CH–NH bond while those at mass 137 (1%; $C_7H_4NCl^+$) and 127 (100%; $C_6H_6NCl^+$) are formed by hydrogen migration accompanying the rupture of this bond. The peaks at mass 111 (15–26%; $C_6H_4Cl^+$), 99 (3%; $C_5H_4Cl^+$), 110 (1%; $C_6H_3Cl^+$), and 100 (3%; $C_5H_5Cl^+$) may be formed by subsequent loss of HCN but metastable peaks were observed only for the transitions $138 \rightarrow 111$ and $127 \rightarrow 100$. It is interesting to note that the central bond rupture occurs before loss of Cl $\cdot$ from the molecular ions of 2 and 3. The peaks below a mass of 99 in the spectra of 2 and 3 require little comment (see Table II). They are typical of those to be expected from benzene, chlorobenzene and chloroaniline derivatives.

Table II. Empirical formula of fragment ions* in the mass spectra of N,N'-di-(chlorophenyl)-formamidines.

<i>m/e</i>	Formula	Intensity [%]	
		2	3
266	$C_{13}H_{10}^{37}Cl_2N_2$	12	10
264	$C_{13}H_{10}^{35}Cl_2N_2$	18	14
140	$C_7H_5^{37}ClN$	5	5
138	$C_7H_5^{35}ClN$	13	13
137	$C_7H_4^{35}ClN$	1	1
129	$C_6H_6^{37}ClN$	31	26
127	$C_6H_6^{35}ClN$	100	100
126	$C_6H_5^{35}ClN$	6	2
113	$C_6H_4^{37}Cl$	5	8
111	$C_6H_4^{35}Cl$	15	28
110	$C_6H_3^{35}Cl$	1	1
100	$C_5H_5^{35}Cl$	3	3
99	$C_5H_4^{35}Cl$	3	3
92	C_6H_6N	4	6
91	C_6H_5N	2	3
90	C_6H_4N	1	1
85	$C_4H_2^{35}Cl$	1	1
77	C_6H_5	1	2
76	C_6H_4	2	4
75	C_6H_3	11	19
74	C_6H_2	2	3
73	C_6H	1	2
65	C_5H_5	4	6
64	C_5H_4	1	3
63	C_5H_3	3	5
62	C_5H_2	1	1

* Only those ions of mass > 60 and of intensity $\geq 1\%$ of the base peak are recorded. Peaks due to ^{13}C species are omitted from the table.

Experimental

The mass spectra were determined with an A.E.I. MS-30 mass spectrometer. The samples were analysed by a direct insertion probe at an ionizing current of 70 eV. The ion source temperature was

140 °C. Elemental compositions were obtained by the peak matching method.

N,N'-Diphenylformamidines, N,N'-di-(4-chlorophenyl)-formamidines and N,N'-di-(3-chlorophenyl)-formamidines were analytically pure.

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