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JMS Letters

Dear Sir,

Mass Spectral Fragmentation of N^1,N^1-Dimethyl-N^2-azinylformamidines

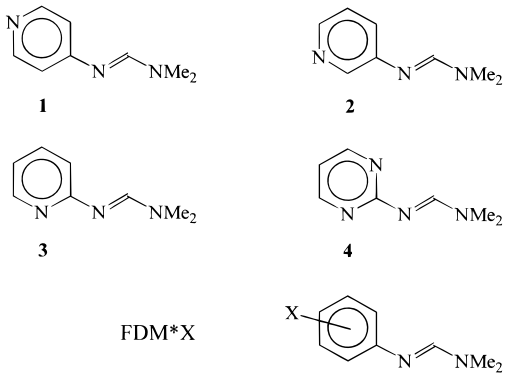
Polyfunctional nitrogen ligands present very interesting properties. In particular, they exhibit exceptionally high basicity. In many cases chelation of the proton by two basic nitrogen atoms is possible. This effect strongly increases the gas-phase basicity. The chelation effect of protons in the proton-transfer reaction in the gas phase and of hydrogen in the hydrogen bonding reaction in non-polar solvent has recently been studied for amidinazines.[1–3] For our experimental studies in the gas phase we used Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry. We report here the standard 70 eV mass spectra of N^1,N^1-dimethyl-N^2-azinylformamidines **1**–**4** (FDM*Aza). As model compounds we used a series of N^1,N^1-dimethyl-N^2-phenylformamidines (FDM*X) for which mass spectral fragmentation has been already reported.[4–9]

Amidinazines **1**–**4** were synthesized by the same procedure as for the series of model formamidines FDM*X studied previously.[10] Compounds **1** and **4** were recrystallized from MeOH, then sublimed *in vacuo*. Compounds **2** and **3** were purified by distillation under reduced pressure. The structures of FDM*Aza were confirmed by their IR and ^{1}H NMR spectra.

Mass spectra (electron ionization (EI), 70 eV) were recorded using the FT-ICR mass spectrometer constructed at the University of Nice–Sophia Antipolis.[11] The conditions of measurements were the same as described previously.[12] Except for time-consuming signal accumulations, ion abundances of less than about 3–5% were not significant. The usual mass range was 17–400 u. The spectral resolution was close to 1000 at m/z 100 with a digital resolution of ~23 Hz (10^{-2} u at 100 u).

For isomeric amidinazines **1**–**3** (formula $C_8H_{11}N_3$, M_r = 149), only the position of the aza group varies. Therefore, almost the same fragment ions (with different abundances) were observed in the mass spectra (Table 1). For compound **4** (formula $C_7H_{10}N_4$, M_r = 150), containing two aza groups, fragments slightly different from those given in Table 1 are obtained (Fig. 1).

FDM*Aza



FDM*X

Table 1. Selected mass spectral data for amidinazines 1–3

Ion	*m/z*	Intensity of peak (%) 1	2	3
$M^{+\cdot}$	149	87	81	69
$[M-H]^+$	148	**100**	**100**	18
$[M-CH_3]^+$	134	27	22	85
$[(M-H)-HCN]^+$	121	19	21	2
$[(M-H)-C_2H_3N]^+$ and/or $[(M-CH_3)-HCN]^+$	107	55	53	10
$[C_6H_5N_2]^+$	105	35	35	26
$[C_5H_5N_2]^+$	93	10	10	**100**
$[C_5H_5N]^+$	79	18	15	78
$[C_5H_4N]^+$	78	62	67	91
$[C_3H_7N]^+$	57	8	5	4
$[C_4H_3]^+$	51	36	27	22
$[C_2H_6N]^+$	44	80	66	36
$[C_2H_4N]^+$	42	25	31	24

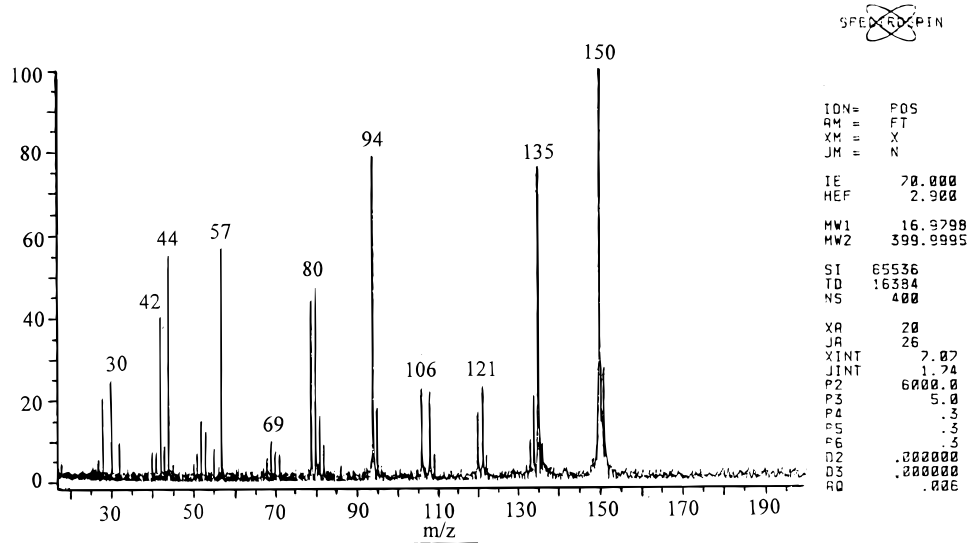


Figure 1. Mass spectrum (EI, 70 eV) of **4**.

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A quick perusal at the mass spectral data obtained for **1**–**4** confirms the general routes of fragmentation proposed by Grützmacher and Kuschel[5,6] for series of model formamidines FDM*X. For **1** and **2** containing the aza group in the *para*- and *meta*-position, respectively, two fragmentation routes (A and B in Scheme 1) predominate, one with formation of the corresponding azabenzimidazolium $[M - H]^+$ (*m/z* 148) ion and the other with formation of the $[C_2H_6N]^+$ (*m/z* 44) ion. The azabenzimidazolium $[M - H]^+$ ion is the base peak and the $[C_2H_6N]^+$ ion is a very significant peak.

Cyclization reactions and formation of benzimidazolium ions have been observed for FDM*X, but the $[M - H]^+$ ion was not the base peak.[5,6] Its intensity varies with the nature of X. An increase in peak intensity is observed for electron-withdrawing substituents. This was explained on the grounds of easier abstraction of the hydrogen atom in the *ortho*-position to the amidine group by the electron-withdrawing group during cyclization. Our results confirmed this observation. The aza group in a *para*- ($\sigma_p = 0.76$[13]) or *meta*-position ($\sigma_m = 0.45$[13]) is a stronger electron-withdrawing group than those studied previously: Cl ($\sigma_m = 0.37$[14]), COOMe ($\sigma_m = 0.35$[14]) and COMe ($\sigma_m = 0.36$[14]) in a *meta*-position. Therefore, a high abundance (100%) of the azabenzimidazolium $[M - H]^+$ ion is observed for the aza derivatives **1** and **2**.

The contribution of route A is not significant in the fragmentation of the derivative **3** (*m/z* 148, 18%), containing one aza group in the *ortho*-position. In the mass spectrum of derivative **4**, containing two aza groups (both groups in *ortho*-positions), the azabenzimidazolium $[M - H]^+$ (*m/z* 149) ion is not present. This confirms that the absence of the hydrogen atom in the *ortho*-position eliminates the formation of the corresponding imidazolium ion. For this reason, the other fragmentation routes (C and D in Scheme 2) predominate for derivatives **3** and **4**.

The $[M - CH_3]^+$ ion formed by route C is a prominent peak for **3** (85%) and **4** (76%). The $[C_5H_5N_2]^+$ (*m/z* 93) ion formed by route D is the base peak for **3** whereas for **4** the corresponding $[C_4H_4N_3]^+$ (*m/z* 94) ion is very significant (79%). The molecular ion $M^{+\cdot}$ (*m/z* 150) is the base peak for **4**.

In conclusion, the behaviour of FDM*Aza containing aza group(s) in different position(s) on the phenyl ring confirms the general route of fragmentation proposed by Grützmacher and Kuschel[5,6] for FDM*X, for which the benzimidazolium $[M - H]^+$ ion can be formed.

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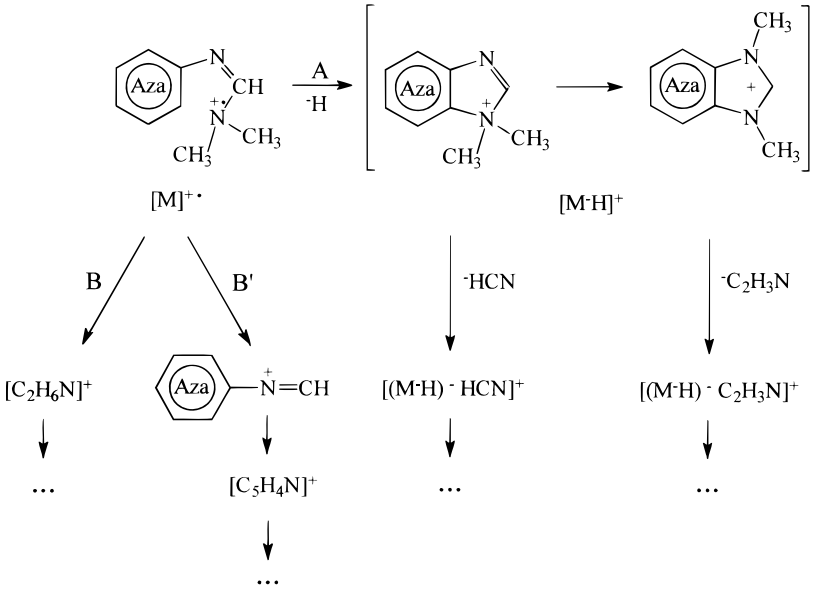
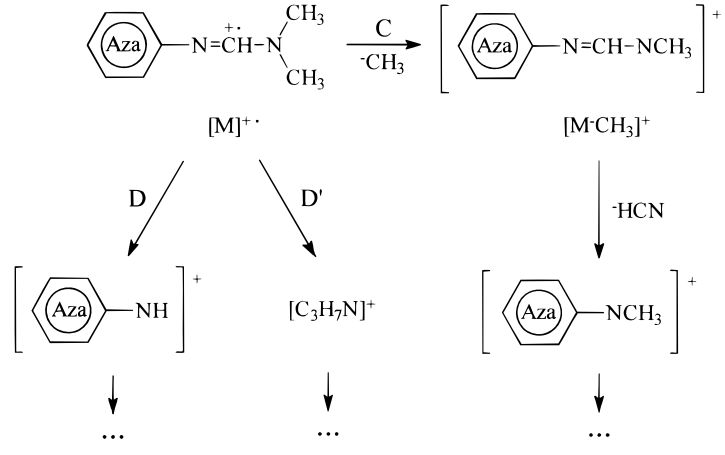


Scheme 1. Favoured general routes of fragmentation for **1** and **2**.



Scheme 2. Favoured general routes of fragmentation for **3** and **4**.

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Yours,

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