MASS-SPECTROMETRIC STUDY OF METHYL-SUBSTITUTED AZOMETHINES OF THE 4-AZAFLUORENE SERIES

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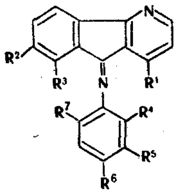
The M^+ and $[M-H]^+$ ion peaks are the peaks of maximum intensity in the mass spectra of Schiff bases belonging to the 4-aza-9-fluorenylidenearylamine series. The dependence of the relative intensity of the $[M-H]^+$ fragment on the structures of the I-XI molecules provides evidence for the possibility of the occurrence of rearrangement processes involving the formation of this ion. The formation of $[M-CH_3]^+$, $[M-HCN]^+$, $[M-Ar]^+$, and $[M-CNAr]^+$ ions is also characteristic for the fragmentation of the investigated compounds. It was found that, in contrast to other types of Schiff bases, the ejection of an HCN molecule during the mass-spectrometric fragmentation of the investigated compounds occurs without participation of the nitrogen atom of the azomethine group. The elimination of a CNAr particle by the molecular ions is a distinctive feature of the investigated series of Schiff bases.

The dissociative ionization of Schiff bases has been studied in greatest detail in the case of relatively simple anils [1-4]. The data on the fragmentation of azomethines of the heterocyclic type are extremely limited [5, 6], and there are no available data on the mass-spectral behavior of polynuclear azomethines in which the carbon atom of the azomethine bond is included in the composition of the polycondensed heteroaromatic ring. In the present research we investigated the fragmentation, under the influence of electron impact, of a new group of Schiff bases – methyl-containing N-(4-aza-9-fluorenylidene)arylamines (II-XI), which differ with respect to the number and position of the methyl groups. The hydrocarbon analog of these compounds – N-(9-fluorenylidene)aniline (I) – was selected as the model compound.



II-XI

II $R^{1-7}=H$; III $R^1=CH_3$, $R^{2-7}=H$; IV $R^2=CH_3$, $R^{1,3-7}=H$; V $R^3=CH_3$, $R^{1,2,4-7}=H$; VI $R^4=CH_3$, $R=^{1-3,5-7}=H$; VII $R^5=CH_3$, $R^{1-4,6,7}=H$; VIII $R^6=CH_3$, $R^{1-5,7}=H$; IX $R^{1,4}=CH_3$, $R^{2,3,5-7}=H$; X $R^{4,6,7}=CH_3$, $R^{1-3,5}=H$; XI $R^{2,4,6,7}=CH_3$, $R^{1,3,5}=H$

The most intense peaks in the mass spectra of bases I-XI (Figs. 1-3) are the M^+ and $[M-H]^+$ ions (Table 1). The stability of the molecular ions (W_M) of monomethyl-substituted azomethines III-VIII depends on the orientation of the methyl group relative to the exocyclic $>C=N-$ bond. The W_M values decrease appreciably for compounds that contain a methyl group in the peri or ortho position relative to this bond (III, V, and VI) and become close to the W_M values for polymethyl-substituted IX-XI.

Intense peaks of a doubly charged M^{2+} ion are observed in the mass spectra of all of the investigated compounds. On passing from the fluorene (I) to the azafluorene (II) system the relative intensity of the M^{2+} ion peak increases only slightly. The introduction of a methyl substituent in the azafluorene ring (III-V) lowers the relative size of the M^{2+} ion peak, whereas this value is determined by their position for azomethines VI-VIII, which contain methyl groups attached to the N-phenyl group.

The high relative intensity of the $[M-H]^+$ ion peak in the mass spectra of azomethines I-XI as compared with the mass spectra of the previously investigated azafluorenes [7] and azafluorenones [8] can be explained

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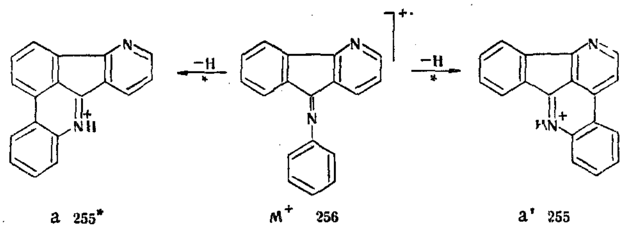
TABLE 1. Stabilities of the Molecular Ions (W_M) and Relative Intensities of the Peaks of the Characteristic Fragments (in Percent Relative to the Maximum Peak) in the Mass Spectra of N-(4-Aza-9-fluorenylidene)arylamines

Compound	W_M	M^{2+}	$[M-H]^+$	$[M-2H]^+$	$[M-CH_3]^+$	$[M-HCN]^+$	$[M-H, -HCN]^+$	$[M-Ar]^+$	$[M-NAr]^+$	$[M-NAr, -H]^+$	$[M-CNAr]^+$	$[M-CNArH]^+$
I	0,34	11,5	80,0	12,0	—	—	—	0,6	5,2	7,2	1,2	2,3
II	0,30	13,2	62,2	8,3	—	3,8	5,5	1,8	1,2	3,0	1,9	4,9
III	0,28	8,1	79,9	18,3	12,0	0,9	2,8	0,6	0,4	1,0	0,9	1,6
IV	0,34	7,5	35,2	8,3	18,5	1,0	1,9	1,5	1,1	1,7	1,2	1,9
V	0,26	9,0	72,1	15,2	14,1	3,8	4,1	1,6	1,2	3,0	8,2	8,0
VI	0,23	13,1	100,0	19,2	4,0	1,9	4,2	1,8	3,0	4,8	2,4	3,0
VII	0,30	6,8	50,8	10,8	17,2	1,6	2,2	1,5	1,9	5,5	1,8	3,6
VIII	0,36	6,2	37,2	9,3	9,3	1,1	2,1	0,9	1,0	3,1	0,6	1,5
IX	0,22	9,3	50,3	83,7	83,7	1,1	3,1	0,9	1,4	1,3	1,2	2,4
X	0,21	11,5	63,9	15,6	12,1	—	0,9	1,7	2,1	3,7	1,4	2,3
XI	0,25	7,4	47,5	8,8	29,6	—	1,1	1,1	1,6	1,5	1,2	1,0

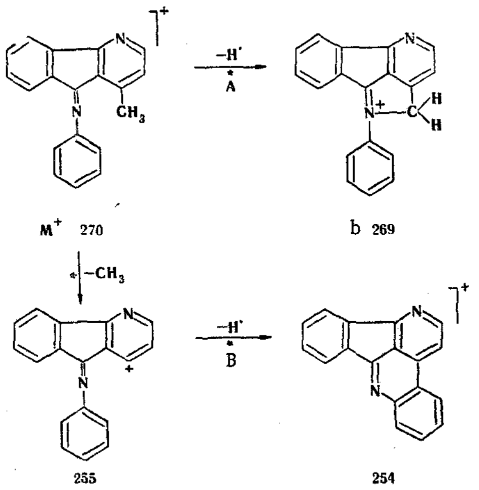
by cyclization processes that take place in the molecular ions. In the case of the fragmentation of unsubstituted azomethines I and II this process evidently occurs as a result of the formation of a bond between the ortho carbon atom of the N-phenyl group and the C_1 or C_8 atom; this presupposes migration of hydrogen from these atoms to the nitrogen atom of the azomethine group (Scheme 1).

Scheme 1



The higher intensity of the $[M-H]^+$ fragment peak in the mass spectrum of I as compared with II is evidently due to the preferred participation of the benzene ring rather than the pyridine ring of the azafluorenylidene fragment in the cyclization process. When there is a methyl substituent in the ortho or peri position relative to the azomethine bond in the 4-aza-9-fluorenylidenearlylamine molecules, the formation of an $[M-H]^+$ fragment may occur through the detachment of a hydrogen atom from the methyl group, which should be accompanied by cyclization at the exocyclic nitrogen atom. This process can be represented by Scheme 2 (pathway A) in the case of III. However, the presence in the mass spectra of III-VIII of metastable ions, which indicate subsequent splitting out of a methyl group by the $[M-H]^+$ ions, constitutes evidence that the elimination of a hydrogen atom by the molecular ions of III-VIII is realized not only via pathway A. One must also note that

Scheme 2



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*The numbers that characterize the ion are the mass-to-charge ratios.

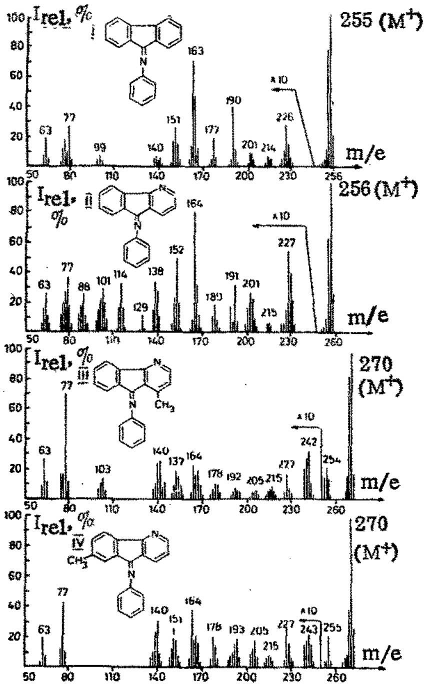

Fig. 1

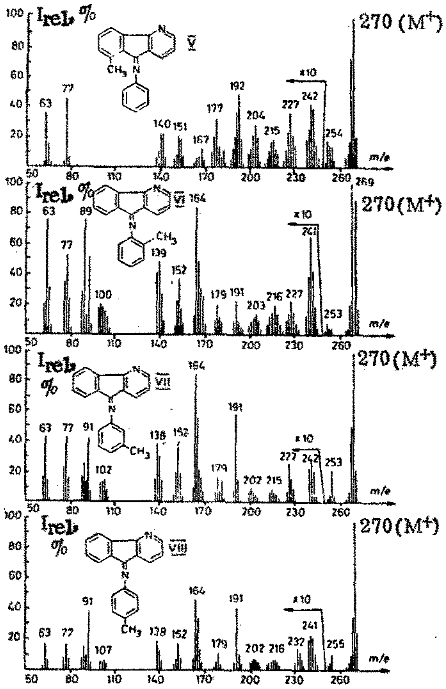

Fig. 2

Fig. 1. Mass spectra of N-(9-fluorenylidene)aniline (1), N-(4-aza-9-fluorenylidene)aniline (II), N-(1-methyl-4-aza-9-fluorenylidene)aniline (III), and N-(7-methyl-4-aza-9-fluorenylidene)aniline (IV).

Fig. 2. Mass spectra of N-(8-methyl-4-aza-9-fluorenylidene)aniline (V), N-(4-aza-9-fluorenylidene)-o-toluidine (VI), N-(4-aza-9-fluorenylidene)-m-toluidine (VII), and N-(4-aza-9-fluorenylidene)-p-toluidine (VIII).

the presence of a methyl group in the 7 position of the investigated compounds lowers the relative intensity of the $[M-H]^+$ fragment peak to a considerable extent.

The formation of a rather intense $[M-2H]^+$ ion peak in the spectra of the investigated compounds is probably due in the case of the a and a' ions to splitting out of the hydrogen atom attached to the exocyclic nitrogen atom (Scheme 1) and in the case of the b ion is probably due to splitting out of a hydrogen atom from the methylene group (Scheme 2). The dissociative ionization of monomethyl-substituted azomethines III-VIII gives $[M-CH_3]^+$ ions, the relative intensity of the peaks of which depend only slightly on the position of the methyl group in the azafluorene ring but is determined to a significant degree by its position on the phenyl ring (the following dependence obtains for VI-VII: $J^*_{m\text{-}CH_3} > J_{p\text{-}CH_3} > J_{o\text{-}CH_3}$). Anomalously high intensity of the $[M-CH_3]^+$ ion peak is observed in the mass spectrum of IX; this is probably associated with steric interaction of the two methyl groups in the molecular ion of IX, which hinders rotation of the aryl substituent about the Ph−N bond and promotes detachment of the methyl group. A comparison of the relative intensities of the peaks of the $[M-CH_3, -H]^+$ and $[M-CH_3]^+$ fragments in the mass spectra of III-VII makes it possible to assume that in the case of fragmentation of azomethines III, V, and VI, which contain a methyl group in the ortho or peri position, the appearance of an $[M-CH_3, -H]^+$ ion is accompanied by recyclization of the phenyl ring to give an azofluorene ring (Scheme 2, pathway B). In the case of the dissociative ionization of IV, VII, and VIII the indicated process is impossible, and the intensity of the peak of the $[M-CH_3, -H]^+$ fragments becomes considerably lower than the intensity of the peak of the parent ion. Peaks of $[M-CH_3, -CH_3]^+$ ions of appreciable intensity are observed in the mass spectra of polymethyl-substituted azomethines IX-XI; the intensity is independent of the number of methyl groups in the molecule. In the case of the fragmentation of azomethines of the azafluorene series (II-XI) the formation of $[M-HCN]^+$ and $[M-H, -HCN]^+$ fragments occurs through elimination of an HCN particle by the M^+ and $[M-H]^+$ ions from the pyridine ring rather than from the azomethine group. This conclusion follows from the fact that $[M-HCN]^+$ and $[M-H, -HCN]^+$ frag-

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*The J value is the relative intensity of the $[M-CH_3]^+$ ion peak.

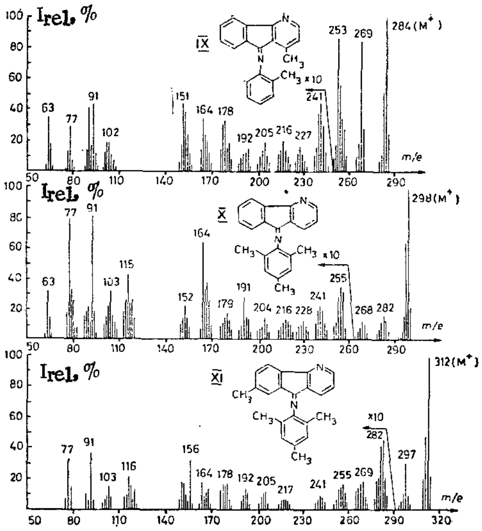


Fig. 3. Mass spectra of N-(1-methyl-4-aza-9-fluorenylidene)-o-toluidine (IX), N-(4-aza-9-fluorenylidene)mesidine (X), and N-(7-methyl-4-aza-9-fluorenylidene)mesidine (XI).

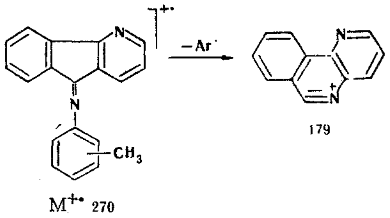
TABLE 2. Data from the High-Resolution Mass Spectra of III, IV, and VI

Compound	Exptl. value	Calc. value	Error	Composition of the ion	Compound	Exptl. value	Calc. value	Error	Composition of the ion
III	242,0960	242,0969	−0,9	$C_{18}H_{12}N$	IV	179,0725	179,0735	−1,0	$C_{13}H_9N$
	227,0738	227,0734	0,4	$C_{17}H_9N$		178,0651	178,0656	−0,5	$C_{13}H_8N$
	178,0660	178,0656	0,4	$C_{13}H_8N$		167,0725	167,0734	−0,9	$C_{12}H_9N$
	177,0580	177,0578	0,2	$C_{13}H_7N$		166,0663	166,0656	0,7	$C_{12}H_8N$
	167,0740	167,0734	0,6	$C_{12}H_9N$		151,0417	151,0421	−0,4	$C_{11}H_5N$
	166,0660	166,0656	0,4	$C_{12}H_8N$		140,0618	140,0625	−0,7	$C_{11}H_8$
	165,0582	165,0578	0,4	$C_{12}H_7N$		139,0538	139,0547	−0,9	$C_{11}H_7$
	152,0507	152,0500	0,7	$C_{11}H_6N$	VI	242,0974	242,0969	0,5	$C_{18}H_{12}N$
	151,0430	151,0421	0,9	$C_{11}H_5N$		241,0900	241,0891	0,9	$C_{18}H_{11}N$
	140,0620	140,0625	−0,5	$C_{11}H_8$		167,0742	167,0734	0,8	$C_{12}H_9N$
	139,0549	139,0547	0,2	$C_{11}H_7$		166,0666	166,0656	1,0	$C_{12}H_8N$
	138,0452	138,0469	−1,7	$C_{11}H_6$		152,0503	152,0500	0,3	$C_{11}H_6N$
IV	242,0958	242,0969	−1,1	$C_{18}H_{12}N$		140,0620	140,0625	−0,5	$C_{10}H_6$
	227,0742	227,0734	0,8	$C_{17}H_9N$		139,0539	139,0547	−0,8	$C_{11}H_7$
	193,0772	193,0765	0,7	$C_{13}H_9N_2$		138,0460	138,0469	−0,9	$C_{11}H_6$
	192,0690	192,0687	0,3	$C_{13}H_8N_2$					

ments are absent in the mass spectrum of their hydrocarbon analog (I). In the case of the dissociative ionization of Schiff bases that contain a pyridine ring [5] this process was associated with splitting out of an HCN molecule containing the nitrogen atom of the azomethine group.

The fragmentation of azomethines I-XI is accompanied by the formation of $[M-Ar]^+$ ions (Table 1). Their development is probably accompanied by expansion of the five-membered ring to a pyridine ring (Scheme 3) with a quaternized nitrogen atom.

Scheme 3

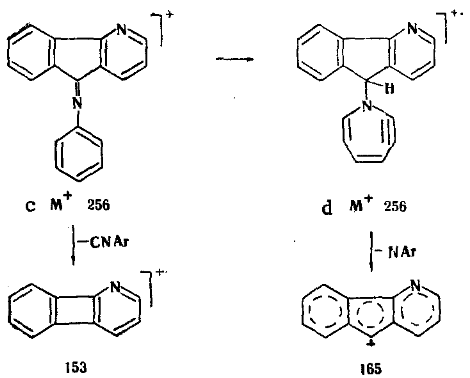


This conclusion can be drawn on the basis of the fact that an $[M-Ph]^+$ fragment is absent in the fragmentation of Schiff bases of the PhN=CHPh type [3], whereas the $[M-Ar]^+$ ion in the mass spectra of compounds of the ArN=CHPy type is formed as a result of cyclization of the exocyclic nitrogen atom to give a pyridine ring nitrogen atom [5].

A peculiarity of the dissociative ionization of azomethines I-XI is the presence in their mass spectra of $[M-Ar]^+$ ion peaks, the elementary composition of which is confirmed by the data from the high-resolution mass spectra (Table 2). Since cleavage of the C=N bond in the M^+ ion is unlikely, it may be assumed that some of the molecular ions undergo rearrangement from the c form to the d form (Scheme 4). The ease of cleavage of the C−N bond in the d ion increases considerably, since the conjugation between the dehydroazatropylium ring and the azafluorene ring is disrupted.

Splitting out of a C=N−Ar group to give $[M-(C=N-Ar)]^+$ fragments, the composition of which was established by means of the high-resolution mass spectra (Table 2), is observed in the fragmentation of I-XI, and the structures of the indicated fragments are evidently analogous to the structure of the $[M-CO]^+$ ions in the mass spectra of azafluorenones [8]. However, the intensity of the peaks of these ion in the fragmentation of the investigated azomethines is considerably lower than in the mass spectra of azafluorenones; this indicates the lower probability of cleavage of the two bonds of the C_9 atom with the pyridine and benzene rings when the exocyclic oxygen atom attached to C_9 is replaced by a nitrogen atom.

Scheme 4



The subsequent fragmentation of the $[M-Nar]^+$ and $[M-CNAr]^+$ ions is accompanied by ejection of $\dot{H}$, $\dot{C}_2H$, and $\dot{C}_3H_2$ radicals and C_2H_2, C_3H_3, and HCN molecules, as in the case of the previously investigated dissociative ionization of azafluorenones [8].

Thus the fragmentation of methyl-substituted N-(4-aza-9-fluorenylidene)-arylamines under the influence of electron impact is characterized by elimination of $\dot{H}$, $\dot{A}r$, $\dot{N}Ar$, and $\dot{C}NAr$ radicals from the molecular ion. The formation of an $[M-CNAr]^+$ fragment is a distinctive feature of the fragmentation of azomethines of the 4-azafluorene series.

EXPERIMENTAL

The mass spectra of I-XI were obtained with an MKh-1303 spectrometer with a system for direct introduction of the samples into the ion source at an ionizing voltage of 70 V and a sample-input temperature of 30°C. The high-resolution mass spectra were measured with a JMS-01-SG-2 spectrometer with an automatic system for information processing. The investigated azomethines were synthesized by the method in [9]. The purity and individuality of the compounds were monitored by thin-layer chromatography. The structures of the compounds were established on the basis of data from the IR, UV, and PMR spectra.

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