MASS SPECTROMETRIC STUDY OF 4-AZAFLUORENES

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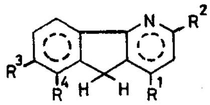
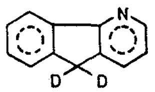
The dissociative ionization of 4-azafluorene and its methyl and phenyl derivatives was investigated. The relative intensity of the $[M - CH_3]^+$ ion peak depends on the position of the CH_3 group in the 4-azafluorene ring. It was established that the loss of an RCN particle (R = H, CH_3, and C_6H_5) for unsubstituted 4-azafluorene takes place from the M^+ and $[M - H]^+$ ion, exclusively from the $[M - H]^+$ ion for the methyl-substituted compounds, and from the $[M - H]^+$ and $[M - 2H]^+$ fragments for the phenyl-substituted derivatives. Randomization of the deuterium ions in the 9,9'-d_2-4-azafluorene molecular ion was observed.

Methods for the synthesis of azafluorenes are currently being developed, and their structures and chemical and spectral properties are under investigation [1-3]. The mass spectral study of azafluorenes with a nitrogen atom in different positions and their derivatives began with an investigation [4] of the dissociative ionization of 2-azafluorene and its C-alkyl(aryl) derivatives. In order to establish the differences in the principal pathways of fragmentation of 4-azafluorenes under the influence of electron impact as a function of the presence, position, and character of the substituents in the present research we studied the mass spectra of 4-azafluorene (I) and methyl- (II-IV), methylphenyl- (V), phenyl- (VI, VII), and 9,9'-d_2-substituted 4-azafluorenes (VIII). As in the case of 2-azafluorenes, the molecular-ion peaks have the maximum intensities in the mass spectra of I-VIII (Figs. 1 and 2). The most stable M^+ ion with respect to fragmentation (W_M) is observed for unsubstituted 4-azafluorene (Table 1); its W_M value coincides with the W_M value for 2-azafluorene [4]. The introduction of methyl and phenyl substituents in the azafluorene ring leads to a certain decrease in the W_M value; this is due to an increase in the number of pathways for fragmentation of the molecular ions of II-VIII.

Ions with the same mass numbers as in the fragmentation of the isomeric 2-azafluorene are formed in the mass spectrum of unsubstituted 4-azafluorene. However, the relative intensities of the peaks of the $[M - H]^+$ (m/e 166*) and $[M - H - HCN - C_2H_2]^+$ (113) fragments and of the peaks of ions in the low-mass region (89 and 63) for 4-azafluorene are lower by a factor of 1.5 to two and the relative intensity of the peak of the doubly charged M^{++} ion is higher by a factor of approximately two as compared with the M^{++} peaks in the mass spectrum of 2-azafluorene (9 and 5%, respectively).





VIII

I $R^1 = R^2 = R^3 = R^4 = H$; II $R^1 = CH_3$, $R^2 = R^3 = R^4 = H$; III $R^1 = R^2 = R^4 = H$, $R^3 = CH_3$
IV $R^1 = R^2 = R^3 = H$, $R^4 = CH_3$; V $R^1 = C_6H_5$, $R^2 = CH_3$, $R^3 = R^4 = H$;
VI $R^1 = R^3 = R^4 = H$, $R^2 = C_6H_5$; VII $R^1 = R^2 = C_6H_5$, $R^3 = R^4 = H$

As in the case of the fragmentation of unsubstituted 2-azafluorene, the formation of the $[M - H]^+$ fragment in the dissociative ionization of 4-azafluorene probably occurs through elimination of a hydrogen atom from the 9 position, as a result of which a stable fragment with a closed system of conjugated π bonds is formed. Loss of hydrogen from the CH_3 radical is also observed in the case of methyl-substituted 4-azafluorenes II-IV, as evidenced by the considerable increase (by a factor of approximately two) in the relative intensity of the $[M - H]^+$ ion peak in their mass spectra and the appearance of an $[M - 2H]^+$ fragment (Scheme 1).

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*Here and subsequently, the numbers that characterize the ions determine the ratio of the mass to the charge.

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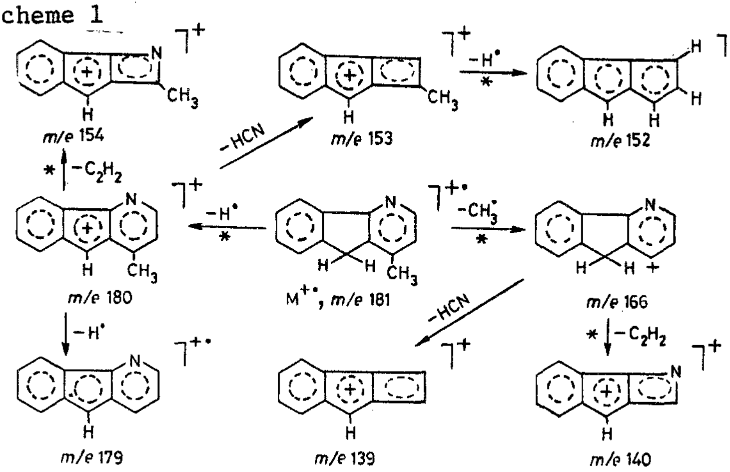
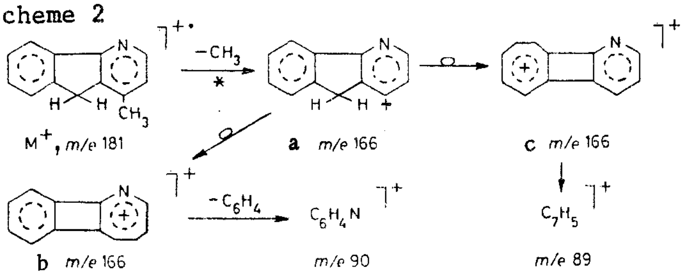
Scheme 1



Peaks of $[M - 3H]^+$ ions are also present in the mass spectra of phenyl-substituted 4-azafluorenes V-VII; this is characteristic for the dissociative ionization of heterocyclic nitrogen compounds that contain a phenyl group [5].

The intensity of the peak of the $[M - CH_3]^+$ fragment is approximately three times higher in the fragmentation of methyl-containing 4-azafluorenes than when the CH_3 group is located in the benzene ring rather than in the pyridine ring of the 4-azafluorene system. The difference in the position of the methyl group in each of these rings has almost no effect on the intensity of the $[M - CH_3]^+$ ion. A fragment with m/e 90, which, according to data from the high-resolution mass spectrum (precise mass 90.0357, empirical formula C_6H_4N), contains a nitrogen atom, is formed in the mass spectrum of II. Its formation can be explained by isomerization of the fragment with m/e 166 from form a to form b (Scheme 2) as a result of expansion of the pyridine ring to an azatropylium ring due to the inclusion of a methylene group and subsequent cleavage of two C—C bonds.

Scheme 2



One cannot exclude the possibility that during randomization of the hydrogen atom in the ion with m/e 166 in the a form a hydrogen deficit arises in the benzene ring rather than in the pyridine ring, and the benzene ring expands to a seven-membered ring to give a fragment in the c form. Fragmentation of ion c with cleavage of two C—C bonds leads to fragment 89 (empirical formula C_7H_5, precise mass 89.0390), which does not contain a nitrogen atom. The existence of this process is indirectly confirmed by the absence (according to data from the high-resolution mass spectra of II-IV) of ion 77 with empirical formula C_5H_3N. Detachment of a C_5H_3N radical in the fragmentation of ion c probably takes place in the form of a neutral particle, and the charge is retained in the C_7H_5 fragment to give ion 89. This type of process is possibly explained by the higher ionization potential of the neutral C_5H_3N particle as compared with the C_7H_5 radical [6].

At the same time, it follows from the high-resolution mass-spectral data that in the fragmentation of III and IV the 90 ions (empirical formula C_7H_5, precise mass 90.0469) do not contain a nitrogen atom, and their appearance therefore cannot be explained by a mechanism that leads to the development of fragment 90 in the mass spectrum of II (Scheme 2). The formation of the C_7H_6 ion is probably due to expansion of the benzene ring to a seven-membered ring through the inclusion of the methyl group in the step involving the formation of the molecular ion [7] with subsequent cleavage of two C—C bonds and localization of the positive charge on the C_7H_6 fragment (Scheme 3).

In the fragmentation of 4-azafluorenes I-VII the elimination of neutral particles of the RCN type that is characteristic for nitrogen-containing heteroaromatic compounds is observed in different stages of the fragmentation as a function of the presence, position,

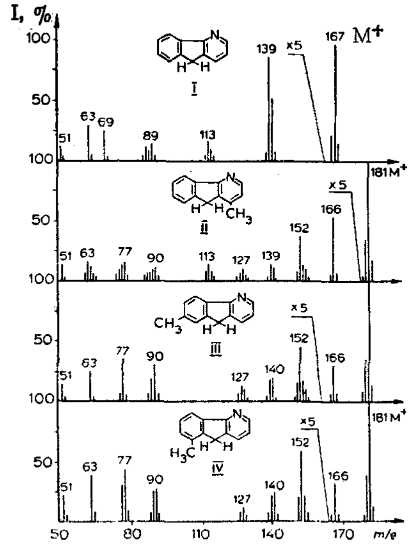


Fig. 1

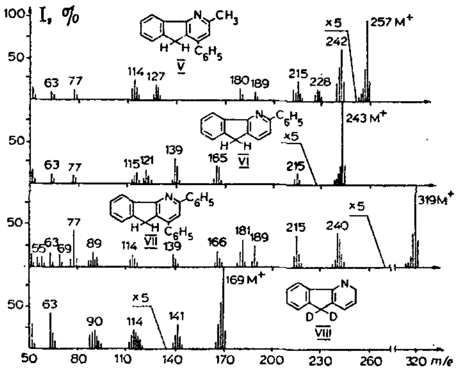


Fig. 2

Fig. 1. Mass spectra of 4-azafluorene (I), 1-methyl-4-azafluorene (II), 7-methyl-4-azafluorene (III), and 8-methyl-4-azafluorene (IV).

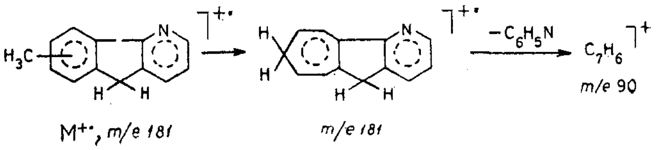
Fig. 2. Mass spectra of 1-phenyl-3-methyl-4-azafluorene (V), 3-phenyl-4-azafluorene (VI), 1,3-diphenyl-4-azafluorene (VII), and 9,9'-d_2-4-azafluorene (VIII).

TABLE 1. Stabilities of the Molecular Ions with Respect to Fragmentation (W_M) and Relative Intensities (%) of Some Characteristic Fragments in the Mass Spectra of 4-Azafluorenes

Compound	W_M	$[M-H]^+$	$[M-CH_3]^+$	$[M-H-HCN]^+$	$[M-H-HCN-H]^+$
I	0,43	20	—	14	—
II	0,31	36,5	13	2,2	9,2
III	0,31	38	27	4,8	12,1
IV	0,31	35	30	4,1	12,1
V	0,25	24	9,2	—	1,6
VI	0,43	13	—	—	3,2
VII	0,30	16	1,4	—	—
VIII	0,30	77	—	—	

and character of substituent R.

Scheme 3



In the dissociative ionization of unsubstituted 4-azafluorene the ejection of a molecule of hydrocyanic acid takes place from both the molecular ion and from the $[M - H]^+$ ion; this is confirmed by the corresponding metastable ions (m* = 117.3 and 115.8) and the precise values of the masses of the resulting $[M - HCN]^+$ fragments (140.0626, empirical formula $C_{11}H_{18}$; 139.0549, empirical formula, $C_{11}H_7$). In the mass spectra of monomethyl-substituted II-IV the loss of an HCN particle occurs exclusively from the $[M - H]^+$ ion, which also eliminates a molecule of acetylene (Scheme 1). The indicated facts are confirmed by data from the high-resolution mass spectra of II-IV (precise mass 154.0656, empirical formula $C_{11}H_8N$; precise mass 153.0705, empirical formula $C_{12}H_9$). In the mass spectrum of 3-methyl-1-phenyl-4-azafluorene V elimination of an HCN particle is observed only from the $[M - 2H]^+$ ion, as a result of which an $[M - 2H - HCN]^+$ fragment with m/e 228 is observed (precise mass

228.0940, empirical formula $C_{18}H_{12}$). In addition, as in the case of II-IV, in the fragmentation of the molecular ion of azafluorene V the $[M - H]^+$ fragment splits out a C_2H_2 molecule to give ion 230 (precise mass 230.0970, empirical formula $C_{17}H_{12}N$). It is interesting to note that the elimination of an HCN molecule in the mass spectrum of 3-phenyl-4-azafluorene VI occurs from the $[M - H]^+$ ion. This fact can be explained by migration of the phenyl group in the $[M - H]^+$ ion or by isomerization of this ion by expansion of the pyridine ring to an azatropylium ring due to inclusion in it of the methyl group from the 9 position. In the case of dissociative ionization of 1,3-diphenyl-4-azafluorene VII an HCN particle is not lost by the $[M - H]^+$ ion; this is evidently due to its stabilization by the phenyl ring attached to the C_1 atom, which hinders the indicated process. The dissociative ionization of phenyl-substituted 4-azafluorenes also leads to the formation of $[M - C_6H_5]^+$ and $[M - C_6H_6]^+$ ions. The appearance of the latter ion is confirmed by the presence of metastable ions for the 243 → 165 and 319 → 241 transitions in the mass spectra of VI and VII ($m^* = 112.3$ and 182.3, respectively). The indicated process is highly likely for compounds that contain a phenyl substituent in the ortho position relative to the nitrogen atom, since in the mass spectrum of V the corresponding 179 ion has a considerably lower intensity.

The appearance of an intense peak of an $[M - H]^+$ fragment in the mass spectrum of VIII, the magnitude of the peak of which is 2.6 times higher than in the mass spectrum of nondeuterated I, indicates randomization of the deuterium atom in the molecular ion of 9,9'-d_2-4-azafluorene. Virtually complete replacement of the hydrogen atoms in the 9 position by deuterium was established from the PMR spectrum of VIII. Consequently, the increase in the intensity of the $[M - H]^+$ ion in the mass spectrum of 9,9'-d_2-4-azafluorene can be explained only by a secondary deuterium effect [8] caused by the formation of molecular ions that contain geminal H and D atoms attached to C_9 due to randomization. A similar fact was also observed in the dissociative ionization of 9,9'-d_2-2-azafluorene [4].

Thus the study of the dissociative ionization of 4-azafluorene and its derivatives showed that the principal fragment ions are formed from both the molecular ion and the $[M-H]^+$ ion, in contrast to the mass-spectral fragmentation of fluorene [9], for which the principal ions are formed exclusively from the $[M - H]^+$ fragment.

EXPERIMENTAL

Compounds I and V-VII were synthesized by the method described in [3, 10], and II-IV were similarly obtained [11]. The deuteration of 4-azafluorene was carried out by refluxing it in an excess amount of a 0.03 N solution of CD_3ONa in CD_3OD on a water bath. The purity and individuality of the compounds were monitored by thin-layer chromatography and the IR, UV, and PMR spectra. The mass spectra were obtained with an MKh-1303 mass spectrometer with a system for direct introduction of the samples into the ion source at an ionizing voltage of 70 V and 30°C. The high-resolution mass spectra were measured with a JMS-01-SG-2 mass spectrometer with automatic processing of the results.

LITERATURE CITED

1. N. S. Prostakov, K. D. Matthew, and V. A. Kurichev, Khim. Geterotsikl. Soedin., No. 5, 876 (1967).
2. N. S. Prostakov, K. D. Matthew, and E. N. Sedykh, Khim. Geterotsikl. Soedin., No. 6, 1072 (1967).
3. N. S. Prostakov, G. A. Vasil'ev, V. P. Zvolinskii, A. V. Varlamov, A. A. Savina, and O. I. Sorokin, Khim. Geterotsikl. Soedin., No. 8, 1112 (1975).
4. V. P. Zvolinskii, P. I. Zakharov, V. K. Shevtsov, V. G. Pleshakov, A. V. Varlamov, G. A. Vasil'ev, K. I. Furnaris, and N. S. Prostakov, Khim. Geterotsikl. Soedin., No. 6, 101 (1977).
5. N. A. Klyuev, R. A. Khmel'nitskii, S. M. Chupakhin, G. A. Mal'tseva, V. P. Rusinov, and I. Ya. Postovskii, Khim. Geterotsikl. Soedin., No. 7, 983 (1975).
6. Handbook of the Energies of Cleavage of Chemical Bonds. Ionization Potentials and Electron Affinities [in Russian], Nauka, Moscow (1974).
7. P. M. Drapper and D. B. McLean, Can. J. Chem., 48, 738 (1970).
8. J. H. Beynon, Mass Spectrometry and Its Applications to Organic Chemistry, Elsevier, Amsterdam (1960).
9. H. Güsten, L. Klasine, J. Marsel, and D. Méliwjevié, Org. Mass. Spectrom., 6, 175 (1972).
10. N. S. Prostakov, A. V. Varlamov, G. A. Vasil'ev, O. G. Kesarev, and G. A. Urbina, Khim. Geterotsikl. Soedin., No. 1, 124 (1977).
11. N. S. Prostakov, V. G. Pleshakov, T. S. Seitembetov, D. A. Fesenko, and L. Olubazho Onasan'ya, Zh. Org. Khim., 13, 1484 (1977).