Twice-distilled water was used. The hydrochloric acid concentration was established by means of 4-amino-pyridine [8]. The ethanol was purified by the method in [6], and the concentrations of the alcohol solutions were established with a pycnometer. The general method for the investigation was as follows. The necessary concentrations of the solvent and the investigated compounds were created in a volumetric flask. The absorption spectra of the protonated and deprotonated particle were recorded, and the analytical wavelength (λ_{an}) was determined [7]. The optical densities at λ_{an} were determined for solutions containing various amounts of hydrochloric acid. The molar absorption coefficients for the particles were determined from the Bouguer—Lambert—Beer law, and the σ and pK values were calculated from the formula presented above. The data were treated statistically by the usual method [9] with fixed reliability $\alpha = 0.95$ for no less than seven experiments.

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MASS SPECTROMETRIC STUDY OF 2-AZAFLUORENES

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The fragmentation of 2-azafluorene and its methyl- and phenyl-substituted derivatives was studied. It is shown that ejection of an RCN fragment ($R = CH_3$, C_6H_5) by the molecular ions leads to a more intense peak if R is in the 3 position of the azafluorene ring. It was established that, in contrast to the dissociative ionization of fluorene, all of the ions of which are formed from the $(M - H)^+$ fragment, the fragmentation of 2-azafluorene and its derivative also takes place from the molecular ion. Randomization of the deuterium atoms attached to C_9 with the remaining hydrogen atoms was observed.

The mass spectral behavior of many classes of nitrogen-containing heterocyclic compounds is currently being studied quite adequately [1, 2]. However, the dissociative ionization of 2-azafluorenes has not been previously examined in the literature, although the fragmentation of fluorene, the hydrocarbon analog of the compounds studied in the present research, has been subjected to a quite detailed study [3, 4].

The present paper is devoted to the establishment of the fundamental regularities in the fragmention of 2-azafluorenes under the influence of electron impact, to the study of the dependence of their dissociative ionization on the position and character of the substituents in the pyridine and benzene rings of the molecules of these substances, and to an examination of the problem of exchange of hydrogen and deuterium atoms in the molecular ion of 9,9-D_2-2-azafluorene.
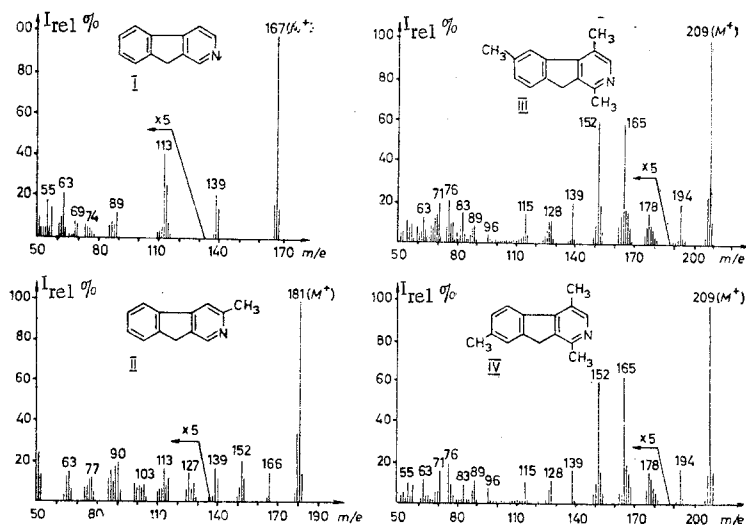
Fig. 1. Mass spectra of 2-azafluorene (I), 3-methyl-2-aza-fluorene (II), 1,4,6-trimethyl-2-azafluorene (III), and 1,4,7-trimethyl-2-azafluorene (IV) recorded at 70 ev.
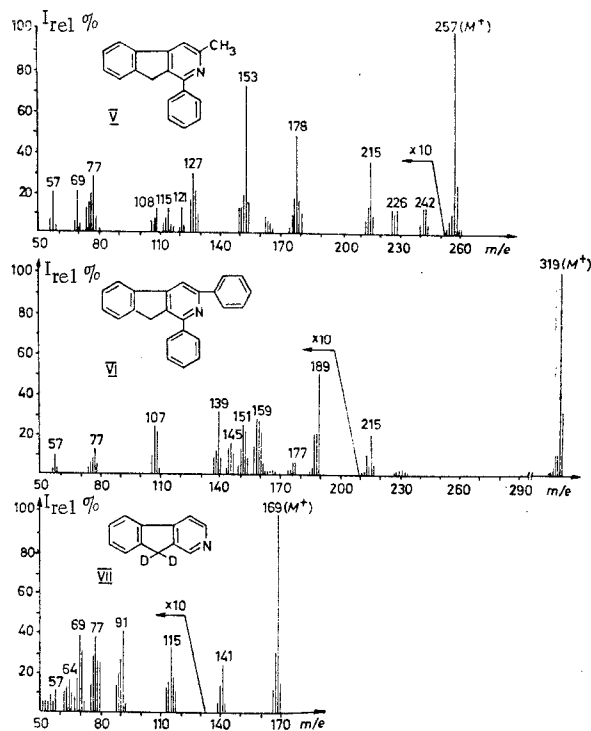

Fig. 2. Mass spectra of 1-phenyl-3-methyl-2-azafluorene (V), 1,3-diphenyl-2-azafluorene (VI), and 9,9-D_2-2-azafluorene (VII) recorded at 70 eV.

To solve this problem we investigated the mass spectra of seven compounds of the 2-azafluorene series (see Figs. 1 and 2).

The mass spectra of I-VII are characterized by molecular ion peaks with maximum intensities. The stabilities (W_M) of the M^+ ions with respect to fragmentation are given in Table 1. The W_M value is lowered appreciably (II-IV) when methyl substituents are introduced in the 2-azafluorene ring. Replacement of the methyl substituent by a phenyl substituent in the 1 position leads to an increase in the W_M value for V as compared with methyl-substituted II-IV. The introduction of a second phenyl substituent in the 3 position (VI) lowers the W_M value.

| Compound	W_M	$(M-H)^+$	$(M-CH_3)^+$	$(M-HCN)^{+\cdot}$	$(M-H-HCN)^+$	$(M-CH_3CN)^{+\cdot}$	$(M-H-CH_3CN)^+$	$(M-C_6H_5CN)^{+\cdot}$	$(M-H-C_6H_5CN)^+$
I	0,42	17,4	—	12,8	21	—	—	—	—
II	0,21	35	14	2,5	12,5	11	18	—	—
III	0,29	20	18	0,3	0,7	1,8	3,7	—	—
IV	0,31	15	18	0,2	0,7	1,8	3,5	—	—
V	0,37	12	1,3	—	—	0,66	3,6	1,3	7
VI	0,27	11	—	—	—	—		3,6	

The formation of $(M-H)^+$ and $(M-2H)^{+\cdot}$ ions in the mass spectra of II-IV is evidently due to the loss of a hydrogen atom by the methylene and methyl groups, since the latter contain hydrogen atoms that are similar to those of the benzyl grouping [5]. The presence of the $(M-H)^+$ ion and the absence of an $(M-2H)^{+\cdot}$ ion of appreciable intensity in the mass spectrum of 2-azafluorene may serve as a confirmation of this. This process can be represented by scheme 1 in the case of 3-methyl-2-azafluorene. The mass spectra of V and VI contain, in addition to $(M-H)^+$ and $(M-2H)^{+\cdot}$ ions, $(M-3H)^+$, $(M-4H)^{+\cdot}$, and $(M-5H)^+$ fragments. This fact is characteristic for fragmentation under the influence of electron impact of phenyl-substituted pyridines [6].

The appearance of the $(M-15)^+$ ion in the mass spectra of II-V is due to the presence of a methyl group in the molecules of these compounds, since a peak of this sort of ion is not observed in the mass spectra of I and VI. It is seen from the data in Table 1 that the introduction of a second and third methyl group in the molecule gives rise to an increase in the intensity of the peaks of the $(M-15)^+$ ions.

Scheme 1

M^+, m/e 181 m/e 180

m/e 179 m/e 179
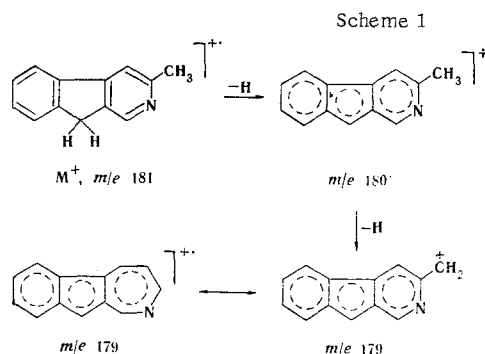
This makes it possible to make an assumption regarding the loss of a CH_3 fragment both from the pyridine ring and from the benzene ring of the molecular ions of III and IV. The presence of a phenyl group in the 1 position leads to a sharp decrease in the intensity of the $(M-15)^+$ ion. This fact is apparently associated with stabilization of the molecular ion by this group, which gives rise to a decrease in the probability of the fragmentation of molecular ion M^+ due to splitting out of the $\overset{\cdot}{C}H_3$ radical.

Yet another pathway for fragmentation of the molecular ions of I-VI is due to elimination of HCN, CH_3CN, and C_6H_5CN fragments. The fact that ejection of an HCN molecule is observed primarily from the molecular ion in the case of unsubstituted 2-azafluorene, whereas loss of an HCN molecule occurs primarily from the $(M-H)^+$ ion for methyl-substituted 2-azafluorenes (Table 1) is interesting. This process can be represented by scheme 2 in the case of 3-methyl-2-azafluorene.

Scheme 2

M^+, m/e 181 m/e 154

m/e 180 m/e 153 $C_{12}H_8$ m/e 152
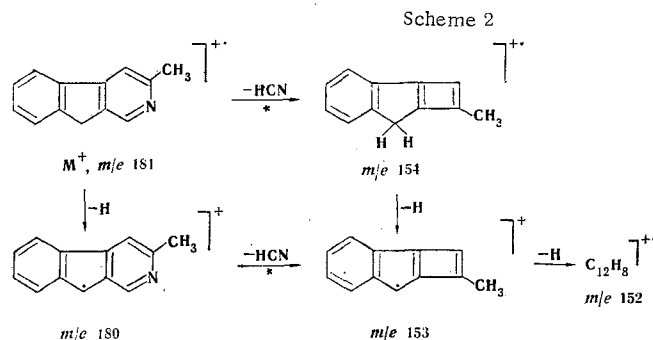
The empirical formulas ($C_{12}H_9$ and $C_{12}H_8$) of the ions with m/e 153 and 152 formed in this case are confirmed by their masses (153.0715 and 152.0605) obtained from the high-resolution spectrum. As seen from Table 1, the loss of an HCN molecule including the CH structural fragment from the 1 position of the azafluorene ring gives a more intense ion than in the case of elimination of this molecule from this group from the 3 position.

In contrast to the ejection of an HCN molecule, the loss of neutral CH_3CN and C_6H_5CN particles is observed primarily from the molecular ion. In this case elimination of a CH_3CN particle for the methyl-substituted compounds leads to the formation of a more intense peak when the CH_3 group is in the 3 position rather than the 1 position of the 2-azafluorene ring (see Table 1). For molecules containing a phenyl group the intensity of the $(M - H - C_6H_5CN)^+$ ion peak is higher when this group is also in the 3 position rather than in the 1 position of the azafluorene ring. It should be noted that the loss of a neutral RCN fragment ($R = H$, CH_3, C_6H_5) leads to a more intense ion as the number of atoms in radical R increases. This process can be represented by scheme 3 for 3-methyl-2-azafluorene.

Scheme 3

$M^{+\cdot}$, m/e 181   m/e 140   m/e 139
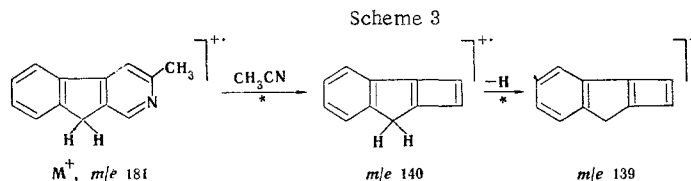
The empirical formulas ($C_{11}H_8$ and $C_{11}H_7$) of the ions with m/e 140 and 139 are confirmed by their masses (140.9585 and 139.0579) obtained from the high-resolution mass spectrum. The subsequent fragmentation of the nitrogen-free fragment proceeds via the pathway characteristic for ions of the same composition in the mass spectra of phenyl-substituted pyridines [6] through the loss of C_2H_2, C_2H, or CR ($R = CH_3$, C_6H_5) particles; this leads to the appearance of ions with m/e 128, 127, 126, 115, 114, and 113.

Thus the dissociative ionization of methyl- and phenyl-substituted 2-azafluorenes is due to the loss by their molecular ions and $(M - H)^+$ ions of the CH_3 group and HCN, CH_3CN, and C_6H_5CN molecules, whereas fragmentation of fluorene under the influence of electron impact occurs exclusively from the $(M - H)^+$ ion due to the loss of C_2H_2, C_4H_2, and C_6H_4 particles.

A study of the mass spectrum of 9,9-D_2-2-azafluorene showed that both $(M - D)^+$ and $(M - H)^+$ ions are formed in the fragmentation of this compound and that there is a partial shift of two units of the $(M - HCN)^+$ ion. The complete replacement of the hydrogen atoms of the methylene group by deuterium in the deuteration of 2-azafluorene was established from the PMR spectrum of VII, and the appearance of an intense $(M - H)^+$ fragment in the mass spectrum of VII can therefore be explained only by exchange between the deuterium atoms of the methylene group in the molecular ion of VII and the remaining hydrogen atom of the azafluorene ring.

EXPERIMENTAL

The low-resolution mass spectra of the compounds were recorded with an MKh-1303 spectrometer equipped with a system equipped for direct introduction of the samples into the ionization chamber. The spectra were obtained at ionizing voltages of 70 and 30 V and an admission temperature of 30°. The high-resolution mass spectrum of 3-methyl-2-azafluorene was recorded with a JMS-01 CG-2 spectrometer with an automatic system for information processing.

The synthesis and purification of II, V, and VI were carried out by the methods described in [7, 8]. Compounds I-III were synthesized by a similar method. Compound VII was obtained by heating 2-azafluorene with excess CH_3OD in the presence of CH_3ONa on a boiling-water bath for 10 h. At the end of the reaction, the excess CH_3OD was removed by vacuum distillation. The purity and individuality of the compounds were monitored by thin-layer chromatography and the IR and PMR spectral data.

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DIPOLE MOMENTS AND STRUCTURES

OF 1,5-DIPHENYL-3-ARYL-2-PYRAZOLINES AND THEIR

FORMYL DERIVATIVES

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The dipole moments of 1,5-diphenyl-3-aryl- and 1-(p-formylphenyl)-3-aryl-5-phenyl-2-pyrazolines were measured in benzene solutions at 25°C and were estimated theoretically by a combination of quantum-chemical calculations by the self-consistent-field MO method within the Pariser−Parr−Pople approximation and the vector-additive scheme. It is shown that polarization of the N_1-N_2, N_1-C_{ar}, and C = N bonds makes a significant contribution to the resulting moment of 1,3,5-triphenyl-2-pyrazoline. The introduction of an electron-acceptor aldehyde group in the para position of the N-phenyl ring changes the polarization of these bonds substantially and leads to the appearance of considerable μ interaction. When electron-donor substituents are introduced into the 3-aryl grouping, one observed a similar but weaker effect that changes regularly as the electron-donor properties of the substituents increase.

The polarity of molecules containing a pyrazoline ring has already been the subject of a number of studies [1-5]. However, the data on the moment of the C = N bond in this system have been extremely contradictory up to now. No attempts have been made to take into account the asymmetry of the N_1-N_2 bond. In [2, 3] the application of a vector-additive scheme for the calculation of the dipole moments of 5-aryl- and 5-hetaryl derivatives of 1,3-diphenyl-2-pyrazoline, based on the assumption of the coplanarity of the entire molecule, contradicts the real geometry of these systems (sp^3 hybridization of the heteroring 5-C atom). A more accurate idea of the polarity of triaryl-2-pyrazolines and the factors that determine it would be extremely useful for the elucidation of the character of the electron interactions in such systems and its effect on the physicochemical properties, and, particularly, the spectral-luminescence properties of these compounds.

In the present research we attempted to refine and expand concepts regarding the electronic structures of triaryl-2-pyrazolines. For this we measured the dipole moments (μ_{exp}) in benzene of two systematic series of compounds of this class (see Table 1) and also estimated them theoretically (μ_{calc}) by a combination of a vector-additive scheme with the quantum-chemical calculations of some of the molecules by the self-consistent-field (SCF) MO method within the Pariser−Parr−Pople (PPP) π-electron approximation (see Fig. 1, diagrams a and b).

In previous calculations [2, 3] of the dipole moments of 2-pyrazolines it was assumed a priori that the μ value of the ring is determined primarily by the moment of the C = N bond, thereby ignoring the fact that the conjugation of the amine nitrogen atom with the azomethine group should weaken the polarization of the latter. At the same time, the polarization of the C = N group itself was completely ignored in [6, 7] during an interpretation of the spectral-luminescence properties of triaryl-2-pyrazolines.