MASS-SPECTROMETRIC INVESTIGATION OF AMINO-1-METHYLNITROPYRAZOLES

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A relationship was established between the structure of amino-1-methylnitropyrazoles and the first stages of their fragmentation under electron impact, viz., the elimination of NO, NO_2, and OH radicals. In contrast to other "ortho" isomers, 4-amino-1-methyl-3-nitropyrazole displays autonomous properties of amino and nitro aromatic compounds as a consequence of weakening of the interaction of the amino and nitro groups along the $C_{(3)}$—$C_{(4)}$ bond and specific redistribution of the electron density in the pyrazole ring.

A nonuniform distribution of the electron density in the pyrazole ring has a decisive effect on the reactivities of substituted pyrazoles in electrophilic-substitution reactions [1, 2] and on the reactivities of bromonitropyrazoles in nucleophilic-substitution reactions [3, 4] and also determines the differences in some physicochemical properties of isomeric 3- and 4-substituted pyrazoles [5, 6]. We have previously synthesized 5-amino-1-methyl-4- (I), 3-amino-1-methyl-4- (II), 4-amino-1-methyl-3- (III), and 4-amino-1-methyl-5-nitropyrazole (IV) [3, 4], which are analogs of o-nitroaniline, the characteristic properties of which were studied by various spectral methods. In the interpretation of the mass spectra of I-IV we used the principles established for the mass spectra of nitroanilines [7] in order to establish the relationship between the peculiarities of the distribution of the electron density in the heteroring of aminonitropyrazole and its fragmentation under electron impact. We examined only the first stages of the fragmentation of the molecular ions (M^+), in which not only the conformation of the starting molecule but also, probably, the electronic system of pyrazole are retained, since the positive charge and the unpaired electron in M^+ of the nitro compounds can be localized to a greater degree on the nitro group [8-11]. In addition, the mass spectra of amino-1-methylnitropyrazoles I-IV (Table 1) do not contain the $[M - H]^+$ ion peaks that are characteristic for 1-methylpyrazole [12], in the M^+ of which the positive charge is localized in the π system of the heteroring.

The primary stages in the fragmentation of the M^+ of aromatic nitro compounds involve the elimination of the nitro and nitroso groups. The latter process is preceded by partial isomerization of the molecular ion to give an aryl nitrite ion. In the case of nitroanilines the presence of an amino group in the ortho and para positions relative to the nitro group facilitates this isomerization and stabilizes the $[M - NO]^+$ ions through resonance [7, 8].

TABLE 1. Mass Spectra of I-VI

Compound	m/z values (relative intensities, %)
I	142 M+ (100), 126 (4,4), 125 (2,7), 113 (5,4), 112 (100), 96 (4,4), 95 (3,4), 69 (7,9), 57 (54,4), 54 (11,6), 53 (29,9), 52 (76,1)
II	142 M+ (100), 126 (3,1), 125 (1,8), 113 (2,2), 112 (33,5), 96 (5,3), 95 (3,9), 81 (5,0), 69 (7,9), 54 (9,7), 53 (14,1), 52 (22,5)
III	142 M+ (100), 126 (6,8), 125 (6,8), 115 (6,8), 112 (11,4), 107 (11,4), 96 (36,4), 95 (18,2), 83 (11,4), 81 (15,9), 71 (11,4), 70 (13,6), 69 (15,9), 61 (11,4), 60 (13,6), 56 (11,4)
IV	142 M+ (100), 125 (37,7), 124 (10,1), 113 (8,7), 112 (13,0), 97 (10,1), 96 (4,3), 95 (14,5), 93 (10,0), 85 (27,5), 83 (47,8), 69 (37,7), 68 (55,1), 57 (21,7), 55 (26,1), 53 (53,6)
V	163 (34,6), 161 M+ (100), 146 (14,2), 144 (40,0), 90 (19,2), 89 (24,2), 88 (78,4), 87 (32,0), 86 (71,9), 80 (14,7), 63 (14,5), 61 (45,2), 53 (6,8), 52 (17,5), 51 (14,2)
VI	127 M+ (100), 111 (3,4), 97 (35,5), 85 (1,2), 83 (2,0), 80 (3,0), 79 (2,4), 66 (1,0), 55 (1,9), 54 (3,8), 53 (2,1), 52 (4,8)

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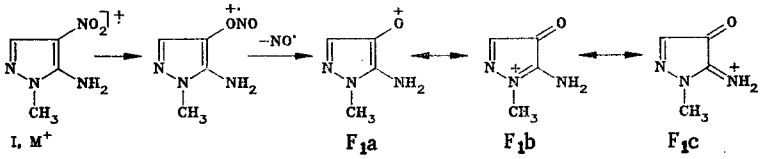
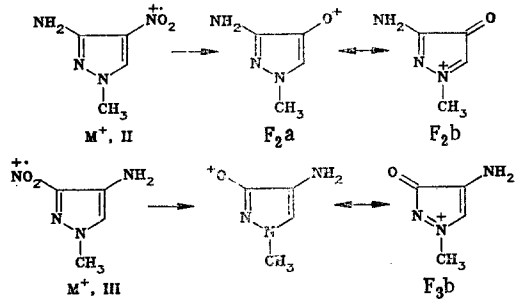
TABLE 2. Relative Intensities of the Peaks of the Characteristic Ions (%) in the Mass Spectra of I-IV

Compound	W_M	$[M-NO]^+$	$[M-NO_2]^+$	$[M-HCN]^+$	$[M-OH]^+$	$I_{[M-NO]^+}/I_{[M-NO_2]^+}$
I	20,0	100	4,4	0,4	2,7	25,0
II	33,0	33,5	5,3	1,0	1,8	5,2
III	16,6	11,4	36,4	6,8	6,8	0,3
IV	13,0	13,0	4,3	—	37,7	3,0

In the mass spectra of aminonitropyrazoles I-IV one observes a peak of $[M - NO]^+$ ions, the maximum relative intensity of which was recorded in the spectrum of I (Table 2). This is evidently due to the high electron-donor character of the 5-amino-1-methyl-4-pyrazolyl radical, which is associated with the π-surplus character of the 4 position in the pyrazole ring and effective transmission of the electronic effect of the amino group along the $C_{(4)}$—$C_{(5)}$ bond, which has a high π order [13]. In this case the positive charge in the $[M - NO]^+$ ion can be localized on the $N_{(1)}$ atom of the heteroring (the F_{1b} fragment) and on the amino group (the F_{1c} fragment).



On passing to 3-amino-4-nitropyrazole II, the intensity of the $[M - NO]^+$ ion peak decreases (Table 2); this is due to a decrease in the electron-donor character of the 3-amino-1-methyl-4-pyrazolyl radical as compared with the 5-amino-1-methyl-4-pyrazolyl radical as a consequence of the difference in the $C_{(3)}$—$C_{(4)}$ and $C_{(5)}$—$C_{(4)}$ bond orders, viz., the bonds along which the mesomeric effect of the amino group is transmitted to the cationic center. For the same reason, in the case of isomer II, the contribution of the fragment of the F_{1c} type to resonance stabilization of the $[M - NO]^+$ ion should be considerably smaller than for I.



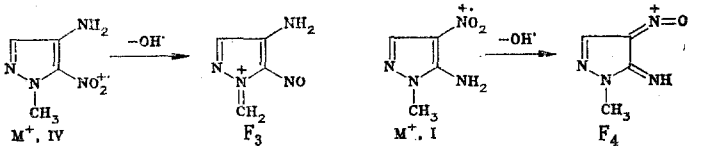
The low intensity of the $[M - NO]^+$ ion peaks in the mass spectrum of 4-amino-3-nitropyrazole III constitutes evidence for the small degree of electron-donor character of the 4-amino-1-methyl-3-pyrazolyl radical, which does not favor nitro-nitrite rearrangement, and for the smaller degree of stabilization of the $[M - NO]^+$ ion by the $N_{(1)}$ atom because of the electron-acceptor character of the $N_{(2)}$ atom of the pyrazole ring (the F_{3b} fragment).

A comparison of the data from the mass spectra of nitrobenzene and nitroanilines makes it possible to conclude that the intensity of the $[M - NO]^+$ ion peak increases as the intensity of the $[M-NO_2]^+$ ion peak decreases. This principle is observed on passing from the spectra of I, II, and IV to the spectrum of 4-amino-3-nitropyrazole III (Table 2), which is distinguished by the presence of a rather intense peak at 115.* The fragment formed in the elimination of a molecule of HCN from M^+, which is characteristic for a number of arylamines [14], corresponds to this peak.

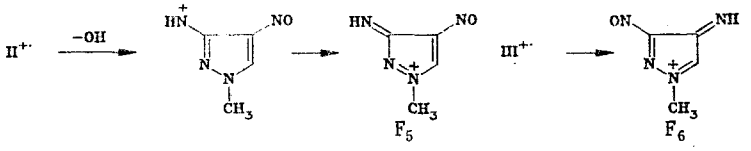
*The numbers that characterize the ions are the m/z values.

Since the interaction of the amino and nitro groups along the $C_{(3)}$—$C_{(4)}$ bond of pyrazole is weakened because of its low degree of double-bond character, the dual character of the pyrazole ring is manifested to a greater degree for aminonitropyrazoles II and III: excess π-electron density in the 4 position and a deficit of π-electron density in the 3 position. Thus, upon electron impact, 4-amino-3-nitropyrazole III displays autonomic properties of an amino compound (elimination of HCN) and of a nitro atomatic compound (the highest relative intensity of the $[M - NO_2]^+$ ion peak); this indicates the relatively weak interaction of the amino and nitro groups with the π-electron system of pyrazole. On the other hand, in 3-amino-4-nitropyrazole II the substituents interact quite effectively with the heteroring, and this leads to high stability of the M^+ ion (33%), which exceeds the stabilities of the M^+ ions of its isomers (13-20%).

As in the spectrum of o-nitroaniline [7], $[M - OH]^+$ ion peaks are present in the spectra of all of the amino-1-methylnitropyrazoles. In the mass spectrum of 4-amino-5-nitropyrazole IV this peak has the highest relative intensity as compared with the remaining isomers (Table 2). The reason for this is the participation of a hydrogen atom of the methyl group in the $M^+ - OH^\cdot$ process; this is confirmed by data from the mass spectrum of 1-methyl-5-nitro-4-chloropyrazole (V) [15], in which the relative intensity of the $[M - OH]^+$ ion peak reaches 40%, as well as by data from the mass spectrum of 2,4-diamino-5-nitro-6-methylpyrimidine, in which the detachment of a hydroxy group takes place with the participation of a hydrogen atom of the methyl group [8], despite the fact that an amino group is also located in the ortho position relative to the nitro substituent. In the case of aminonitropyrazoles I-III, in which the nitro and methyl groups are located in "meta" positions, the detachment of an OH radical is possible only with the participation of a hydrogen atom of the amino group; the absence of an $[M - OH]^+$ peak at 110 in the mass spectrum of 1-methyl-4-nitropyrazole (VI) confirms this assumption. The different relative intensities of the $[M - OH]^+$ ion peaks in the spectra of I-III are evidently associated with differences in their modes of stabilization.



In the case of 5-amino-4-nitropyrazole I, owing to interaction of the amino and nitro groups along the $C_{(4)}$—$C_{(5)}$ bond, one may assume that the $[M - OH]^+$ ion is stabilized as a result of the formation of a quinoidlike structure of the F_4 type. In the case of II and III, in which the substituents interact along the $C_{(3)}$—$C_{(4)}$ bond, the existence of structures of the F_4 type after the elimination of an OH radical is unlikely, and the $[M - OH]^+$ ions are evidently stabilized through interaction of the positively charged nitrogen atom of the exocyclic NH group with the π system of the pyrazole ring (the F_5 and F_6 fragments).



In our opinion, evidence for this is provided by the higher intensity of the $[M - OH]^+$ ion peak in the mass spectrum of 4-amino-3-nitropyrazole III than in the spectrum of 3-amino-4-nitropyrazole II and the similar ratio of the intensities of the peaks of the F_{3b} and F_{2b} fragments, in which the positive charge is localized on the $N_{(1)}$ atom of the heteroring.

EXPERIMENTAL

The mass spectra were obtained with Hewlett—Packard 5985 quadrupole chromatographic mass spectrometer with direct introduction of the samples into the ionization region at an ionizing voltage of 70 V and an input temperature 15-20°C below the melting points of the samples. Automatic processing of the data was used.

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SOME TRANSFORMATIONS OF DIMETHYLAMINOVINYLPYRIMIDINES

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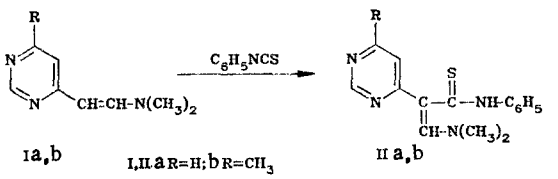
The reaction of enamines of the pyrimidine series with phenyl isothiocyanate, arenediazonium salts, and benzylamine was studied. The corresponding thioamides, pyrimidinylacetaldehydes, and benzylaminovinylpyrimidine were obtained.

The previously described [1] enamines of the pyrimidine series are reactive compounds. The reaction of dimethylaminovinylpyrimidines I with carboxylic acid chlorides, which led to the production of phenacyl- and acetonylpyrimidines, was studied in [2].

Continuing our investigation of enamines of the pyrimidine series, in the present research we studied the reaction of I with electrophilic agents and transamination.

4-(2-Dimethylaminovinyl)pyrimidines Ia,b react with phenyl isothiocyanate to give thioamides IIa,b.

The IR spectra of IIa,b contain an absorption band at 1110 cm^{-1} (NH—CS) but do not contain an absorption band at 2500-2600 cm^{-1} (SH); this confirms the thione form of thioamides



Ia,b I,II a R=H; b R=CH3 IIa,b

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