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MASS-SPECTROMETRIC INVESTIGATION OF SOME 2,6-DIMETHYLOXAZOLO[4,5-d]-PYRIMIDINE DERIVATIVES

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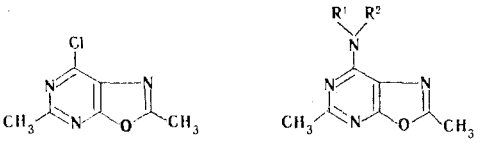
The fragmentation of the molecular ions of 4-chloro- and 4-alkylamino-2,6-dimethyloxazolo[4,5-d]pyrimidines involves splitting out or fragmentation of the substituent in the 4 position or cleavage of the oxazole ring. The compositions of the fragment ions were determined on the basis of the high-resolution mass spectra.

Oxazolo[4,5-d]pyrimidines are oxygen analogs of purines, and this is responsible for the heightened interest of pharmacologists in them. At the same time, the principles of the mass-spectrometric fragmentation of these compounds are virtually unknown.*



I

II–V

II $R^1=H$, $R^2=CH_3$; III $R^1=R^2=CH_3$; IV $R^1=R^2=C_2H_5$; V $R^1=CH_3$, $R^2=CH_2C_6H_5$

We studied the behavior of a series of substituted oxazolo[4,5-d]pyrimidines I-V under electron impact by determining the compositions of the most important ions on the basis of the high-resolution mass spectra.

An analysis of the mass spectra obtained (Table 1) and the intensities of the peaks of the characteristic ions (Table 2) makes it possible to note that an increase in the size of the substituents in the amino group decreases the stabilities of the molecular ions.

The principal processes of dissociative ionization of the molecules of I-V involve the loss by their molecular ions of one hydrogen atom (pathway A, Schemes 1 and 2) or splitting out of the substituent from the 4 position (pathway B). In the case of I the more electronegative group, viz., the chlorine atom, is split out to give the cation of the heterocycle.

*Only the partial mass spectra of six 4-monoalkylaminooxazolo[4,5-d]pyrimidines without a detailed discussion of the scheme of their fragmentation are presented in [1].

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TABLE 1. Mass Spectra* of I-V

Compound	m/z values (relative intensities, %)
I	185 (33), 184 (11), 183 (100), 182 (13), 157 (5), 155 (14), 148 (24), 143 (6), 141 (18), 116 (5), 115 (10), 114 (14), 108 (11), 107 (87), 106 (14), 103 (7), 102 (5), 101 (22), 100 (10), 99 (7), 80 (5), 79 (32), 78 (11), 66 (10). W_M=23
II	179 (14), 178 (100), 177 (10), 163 (5), 150 (34), 149 (32), 137 (20), 135 (8), 109 (10), 108 (16), 95 (8), 56 (20)
III	193 (18), 192 (78), 191 (9), 178 (7), 177 (57), 164 (19), 163 (100), 150 (12), 149 (8), 136 (25), 122 (25), 108 (20), 107 (10), 94 (24), 66 (19)
IV	221 (14), 220 (54), 206 (11), 205 (56), 192 (26), 191 (100), 178 (16), 177 (85), 164 (5), 163 (6), 150 (20), 149 (5), 136 (24), 135 (5), 109 (7), 108 (22), 107 (24), 73 (15), 72 (41), 58 (45)
V	269 (22), 268 (87), 267 (14), 254 (22), 253 (100), 240 (14), 239 (40), 238 (12), 212 (12), 211 (8), 210 (5), 198 (6), 192 (12), 191 (14), 178 (12), 177 (74), 176 (13), 170 (12), 163 (16), 150 (10), 149 (16), 148 (17), 135 (17), 134 (13), 133 (13), 122 (8), 121 (23), 120 (80), 108 (8), 107 (32), 106 (8), 105 (92), 104 (9), 91 (56), 79 (21), 78 (14), 77 (45)

*The ion peaks with intensities >5% are presented.

TABLE 2. Intensities of the Peaks of the Characteristic Ions in the Mass Spectra of II-V (Σ_{40}, %)

Compound	W_M	F_1	F_2	$F_3 + F_3'$	$F_4 + F_4'$	$F_5 + F_5'$	F_6	F_7
II	37,0	3,2	<1,0	4,8	21,3	2,5	—	5,2
III	22,0	2,1	<1,0	13,0	24,9	5,7	2,0	5,7
IV	11,0	—	6,1	16,1	14,6	4,0	2,2	3,9
V	11,0	1,5	8,9	19,2	4,8	1,3	9,0	<1,0

However, in the case of II-V the charge is localized primarily in the amine fragment, which has an appearance potential that is lower than that of the heterocycle. Peaks of F_2 ions with m/z values* of 44, 72, and 120, respectively, the intensities of which increase sharply as the R^1 and R^2 groups become more complex, and products of the subsequent fragmentation of these fragments, viz., ions with m/z 57 ($CH_2{=}\overset{+}{N}{-}C_2H_5$), 105 ($C_6H_5CH{=}\overset{+}{N}H$), 91 ($C_7H_7^+$), and 77 ($C_6H_5^+$), appear in the mass spectra of III-V as a result of this. The overall fraction of the peaks of such ions in the mass spectra of IV is 13.8%, whereas it reaches 30% in the mass spectrum of V.

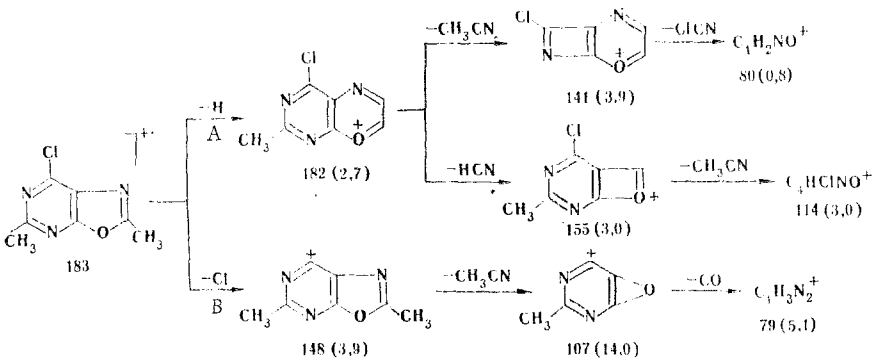
In addition to the indicated fragmentation pathways, two other pathways of the fragmentation of their molecular ions, viz., splitting out of one of the radicals of the amino group (pathway C) and cleavage of the N–heterocycle bond with transfer of one of the radicals to the remaining heteroring (pathway D, Scheme 2), are characteristic for II-V. This type of fragmentation has frequently been observed in series of amino-substituted purines and pyrimidines [2-4].

The data from the high-resolution mass spectra (HRMS) confirm the loss of a CH_3N fragment in the case of II and III and of a C_2H_5N fragment in the case of IV. It should only be noted that in the latter case, in addition to the F_3 ions, the $[M-CH_3,-C_2H_4]^+$ fragments ($C_8H_9N_4O$) typical for diethylamines constitute 20% of the ions with mass number 177. The two-step character of their formation from the molecular ion was confirmed by the corresponding metastable ions.†

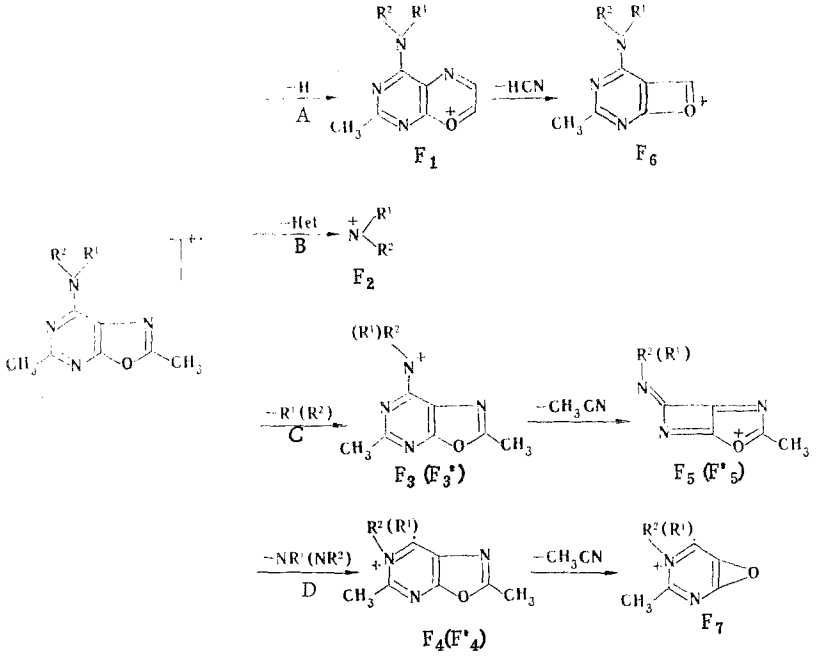
*Here and subsequently, the mass numbers of the ions (m/z) are presented.

†The intensities of the peaks of these ions remain high even when the ionization energy is decreased to 12 eV, which confirms their rearrangement character.

Scheme 1



Scheme 2



The subsequent steps of the fragmentation of the resulting fragment ions are characterized by the elimination of HCN or CH_3CN molecules, while a CO molecule is ejected only in the case of more profound degrees of fragmentation. It should be noted that the overall intensity of the peaks of the ions formed via pathway A is 13.5%* in the case of I, where it is from 15 to 3% in the case of II-V and decreases regularly as the size of the R^1 and R^2 groups increases. At the same time, the fraction of ions formed via pathways C and D is appreciably higher and is greater than 23% in the mass spectrum of I, as compared with from 49 to 25% in the case of II-V, also decreasing on passing from the simpler to the more bulky dialkylamino groups. This indicates the high selectivity of the fragmentation of the investigated compounds.

Thus the observed character of the mass-spectrometric behavior of 4-aminooxazolopyrimidines I-V is associated primarily with the processes of dissociation of the amino group and also with cleavage of the oxazole ring, which makes it possible to assume primary localization of the charge in their molecular ions in the region of the pyrimidine ring.

An analysis of the fragmentation of such compounds makes it possible with confidence to determine the character of the groups attached to the nitrogen atom of the amino group.

*Of the total ion current (Σ_{40},%).

EXPERIMENTAL

The mass spectra were obtained with an MKh-1303 spectrometer with direct introduction of the samples into the ionization region at an ionizing voltage of 50 eV and an inlet temperature 15-20°C lower than the melting point of the sample. The elementary compositions of the fragment ions in the mass spectra of II-V were determined with a JMS-01-SG-2 high-resolution spectrometer (Jeol).

The synthesis of the compounds was published in [5].

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TAUTOMERISM, ELECTRONIC STRUCTURES, AND ELECTRONIC SPECTRA OF INDOLO[2,3-b]QUINOXALINE AND ITS DERIVATIVES

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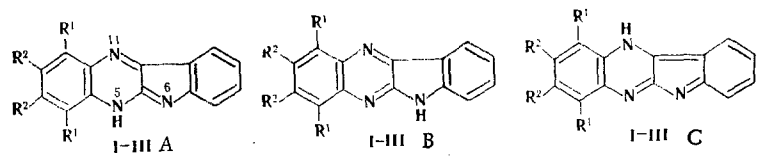
The tautomerism, electronic spectra, and electronic structures of the ground and excited states of indolo[2,3-b]quinoxaline and its 2,3- and 1,4-dibutoxy derivatives were investigated by the Pariser–Parr–Pople (PPP) method. It is shown that these compounds exist primarily in the 6H form; the long-wave $S_{\pi\pi}^*$ transition is due to transfer of π charge from the indole fragment to the quinoxaline fragment, and in the first excited state many of the bonds in the quinoxaline fragment are loosened significantly. The effect of butoxy substituents on the first $S_{\pi\pi}^*$ transition of indolo[2,3-b]quinoxaline was analyzed by means of perturbation theory within the framework of the Hückel MO method.

Continuing the synthesis and study of indolo[2,3-b]quinoxaline derivatives [1,2] we have studied the electronic structures of some indolo[2,3-b]quinoxalines that theoretically may exist in three tautomeric forms A, B, and C:



I–III A I–III B I–III C

I $R^1=R^2=H$; II $R^1=H$, $R^2=n\text{-}C_4H_9O$; III $R^1=n\text{-}C_4H_9O$, $R^2=H$

We have previously shown on the basis of a comparative investigation of the electronic spectra of I-III and their methyl analogs that in neutral solutions they exist primarily in

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