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MASS SPECTRA OF ISOMERIC THIENO[2,3-b]- AND THIENO[3,2-b]PYRIDINES

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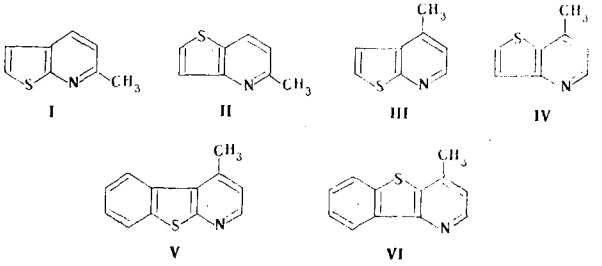
The mass spectra of six isomeric thieno- and thionaphthenopyridines were studied for the first time, and the pathways of fragmentation of the molecular ions, which made it possible to isolate the peaks of the fragment ions that characterize the destruction of the pyridine and thiophene rings, were traced. It is shown that the character and type of conjugation of the heterorings can be distinguished by analyzing the mass-spectral data. The relationship between the intensity of the peak of the doubly charged molecular ion and the number of π electrons in the system and the π-donor character of the heteroring was illustrated by means of the literature data on the mass spectrometry of heteroaromatic systems with one heteroatom.

Methyl-substituted thieno- and benzothienopyridines (I-VI) were previously obtained [1, 2] as starting materials in the synthesis of spectral sensitizers for silver halide photographic emulsions.



In the present research for the first time we undertook a mass-spectrometric study of the indicated heterocyclic systems in order to elucidate those relationships between their structure and dissociative ionization processes that could be used in the solution of analytical problems, particularly with respect to distinguishing isomers.

Compounds I-VI are condensed aromatic systems, and their stability with respect to electron impact (W_M) is therefore quite high (see Table 1). As expected, the highest W_M values are reached in the case of benzothienopyridines V and VI; the selectivity of the fragmentation of the molecular ion increases markedly (the $S_1/_2$ value decreases sharply). The differences in the W_M values for V and III (20.3) and VI and IV (13.4) are substantially greater than for naphthalene and benzene (4.8 [3]). This is explained by the fact that in our case the p and d electrons of the heteroatoms participate, in addition to the π electrons of the aromatic system, in the redistribution of the electron density on passing from III to V (or from IV to VI).

Compounds I-VI undergo fragmentation under electron impact in the same way, and the principal pathways are similar to those in the fragmentation of methylpyridines [4] and thiophenes [5].

A comparison of the ion currents due to dissociative ionization of the compounds of the type peculiar to pyridine or thiophene (Σ_1 and Σ_2 in Table 1, respectively) makes it possible to assume a structure with localization of the charge on the nitrogen atom of the pyridine ring for the molecular ion. Quantum-chemical calculations made for I [6] indirectly confirm this assumption. They show that the greatest electron density is concentrated on the nitrogen atom. It is therefore natural to assume that in the formation of the molecular ion

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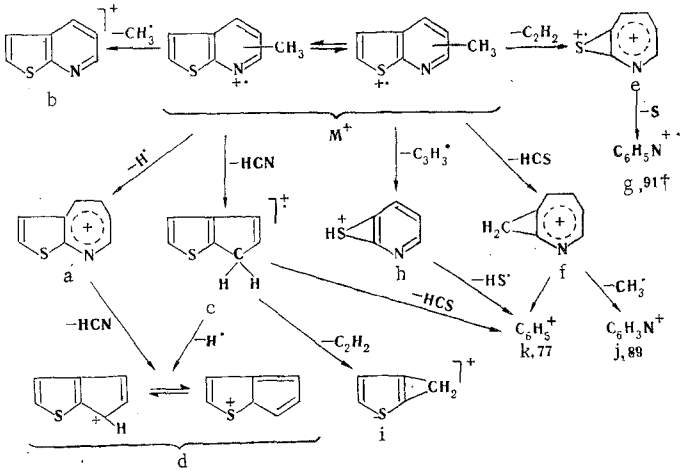
TABLE 1. Intensities of the Peaks of the Principal Fragment Ions in the Mass Spectra of I-VI (in percent of the maximum peak in the spectrum) and Some Analytical Characteristics

Ions	Arbitrary designation of the ions in the scheme	Compounds					
		I	II	III	IV	V	VI
M^+		100	100	100	100	100	100
M^{2+}		6,4	4,4	1,3	3,5	5,3	4,9
Fragmentation of the pyridine ring							
$[M-H]^+$	a	26,8	22,7	39,9	22,2	19,5	13,7
$[M-CH_3]^+$	b	3,7	7,6	1,7	4,9	—	0,7
$[M-HCN]^+$	c	19,6	9,0	16,0	8,1	4,7	3,4
$[M-HCN, -H]^+$ or $[M-H, -HCN]^+$	d	19,0	8,1	15,4	8,1	14,3	8,1
Σ_1		69,1	47,4	73,0	43,3	38,5	25,9
Fragmentation of the thiophene ring							
$[M-C_2H_2]^+$	e	2,6	2,4	3,1	2,1	0,9	0,7
$[M-HCS]^+$	f	7,4	5,5	14,1	4,9	1,2	1,2
$[M-C_2H_2, -S]^+$	g	2,6	1,5	3,5	1,1	0,5	0,4
Σ_2		12,6	9,4	20,7	8,1	2,6	2,3
$[M-C_3H_3]^+$	h	3,7	2,3	3,6	3,7	0,4	0,6
$[M-HCN, -C_2H_2]^+$	i	3,2	8,1	3,8	5,0	1,2	1,0
$[M-HCS, -CH_3]^+$	j	2,6	1,1	3,8	1,0	1,7	0,8
$[M-HCS, -HCN]^+$	k	5,8	3,4	11,8	4,0	2,8	1,8
m/z 91		2,6	1,5	3,5	1,1	0,2	0,4
m/z 89		2,6	1,1	3,8	1,0	1,8	1,0
m/z 77		5,8	3,4	11,8	4,0	1,1	1,1
Analytical characteristics							
W_M		22,1	21,2	16,3	26,3	36,6	39,7
$S_{1/2}$		11	16	10	11	3	4

the positive charge will be localized on the nitrogen atom. The scheme of the fragmentation of I-IV can then be represented as follows*:



On passing from thienopyridines I-IV to benzothienopyridines V and VI the probability of the formation of e, f, and h ions should decrease as a consequence of blocking of the thiophene ring by the benzene ring; this was confirmed experimentally. The detachment of an HCS· particle that occurs in the fragmentation of V and VI is evidently similar to the elimination of a molecule of HCN from acridine [7].

An analysis of the data obtained makes it possible to use the parameters of the mass spectra to distinguish the isomers. Thus the relative Σ_2 value makes it possible to form a judgment as to which position of the pyridine ring is occupied by the methyl group. In the case of 4-methyl-substituted derivatives (III and IV) it is higher by a factor of 1.3 to 2.5 than for their 2-methyl isomers (I and II). In the case of isomers with

*The pathways of fragmentation of the molecular and fragment ions were confirmed by the corresponding metastable transitions.

†The mass-to-charge ratios (m/z).

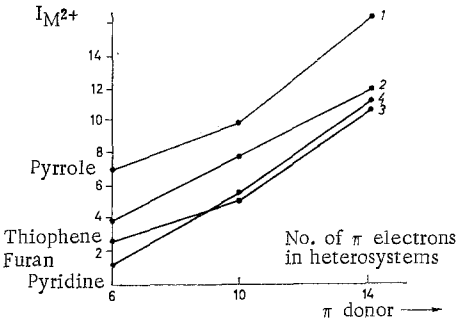


Fig. 1. Change in the intensity of the doubly charged molecular ions as the number of π electrons in the system changes: 1) pyrrole – 7.0 [12a], indole – 9.7 [13a], carbazole – 16.3 [12b]; 2) thiophene – 3.9 [12c], benzothiophene – 7.9 [12d], dibenzothiophene – 12.0 [14]; 3) furan – 2.6 [13b], benzofuran – 5.1 [12e], dibenzofuran – 10.7 [12f]; 4) pyridine – 1.0 [12g], quinoline – 5.4 [12h], acridine – 11.1 [12i].

conjugated pyridine and thiophene rings of the [2, 3-b] type (I and III) the peaks of the c, d, and k ions are 1.5-3 times more intense than for the isomers with conjugation of opposite character (II and IV).

In examining the mass spectra of I-VI we attempted to elucidate a criterion of a more general nature that makes it possible to evaluate the character of the annelation of the rings in the conjugated heterocyclic systems. With this in mind, we turned to a comparison of the intensities of the doubly charged molecular ions (M^{++}), the formation of which is characteristic for the mass-spectrometric fragmentation of heteroaromatic systems [8]. Starting from the assumptions advanced in [9], one should expect that the stability of M^{++}, i.e., the intensity of its peak in the spectra of compounds with two heteroatoms, should be higher, the greater the distance between these heteroatoms. This relationship is not observed in our case, and the data obtained consequently cannot be interpreted unambiguously.

We would also like to note the increase in the intensity of the M^{++} peak on passing from a two-ring (I-IV) to a three-ring (V and VI) system, i.e., when the number of π electrons in the molecule increases. Our analysis of the literature data showed that this relationship is general in character in the series of heteroaromatic compounds and can be represented graphically (see Fig. 1). Curves 1, 2, and 3 in the graph are situated one under the other in the same sequence as the decrease in the π-surplus character in the pyrrole–furan–thiophene series [10] and their benzo and dibenzo derivatives. At the same time, each of the curves reflects an increase in the intensity of the M^{++} peak vis-a-vis a decrease in the π-surplus character in series of heterocycles with one heteroatom. The graph also clearly illustrates the previously noted [11] symbatic character in the change in the intensity of this peak and the π-donor character of the system.

EXPERIMENTAL

The mass spectra were obtained with a Varian MAT-311A spectrometer by direct introduction of the samples into the ion source under standard conditions of operation of the apparatus; the ionizing voltage was 70 eV, the cathode emission current was 1.5 mA, the ionization-chamber temperature was 30-40°C lower than the melting points of the samples, and the relative error in the measurement of the intensities of the peaks was 5-7%.

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MASS SPECTRA OF DERIVATIVES OF BENZALDEHYDE SELENAZOLYLHYDRAZONES

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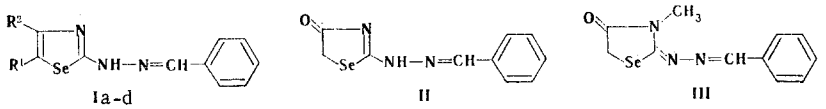
The mass spectra of benzaldehyde selenazolylhydrazones Ia-d and benzaldehyde selenazolidenehydrazones II and III were studied. Splitting out of benzonitrile as a result of a rearrangement of the McLafferty type is characteristic for the fragmentation of the M^+ ions of Ia-d. The subsequent fragmentation of the $M - C_6H_5CN$ ion occurs due to ejection of the SeH group or a molecule of carbodiimide from the selenazole ring or due to cleavage of ring side substituents. The principal fragments in the mass spectra of II and III are formed as a result of the ejection of groups of SeH and SeCHCO atoms.

In a continuation of our research [1, 2] on the synthesis and analysis of derivatives of benzaldehyde heterylhydrazones that have high biological activity, in the present research we studied the principal pathways in the fragmentation of benzaldehyde selenazolylhydrazones Ia-d and benzaldehyde selenazolidenehydrazones II and III under the influence of electron impact.



Ia-d II III

Ia $R^1=H$, $R^2=C_6H_5$; b $R^1+R^2=(CH_2)_4$; c $R^1+R^2=(CH_2)_5$; d $R^1=H$, $R^2=CH_2Cl$

The mass spectra of analytically valuable derivatives of carbonyl compounds, viz. nitro- and, particularly, dinitrophenylhydrazones, have been investigated in greatest detail [3]. Their spectra are characteristic and make it possible in a number of cases to determine the position and character of the substituents in the residue of the carbonyl compound from the mass numbers of the fragment ions [4]. The processes of dissociative ionization of arylhydrazones of aromatic aldehydes and ketones that are accompanied by skeletal rearrangements have been examined in quite some detail [5, 6]. It has been established that for all of the compounds mentioned above one of the chief processes in the fragmentation of their molecular ions (M^+) is cleavage of the nitrogen–nitrogen bond.

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