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MASS-SPECTRAL BEHAVIOR OF 2-AZATRIPTYCENE AND ITS DERIVATIVES

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The mass-spectral behavior of 11 aromatic and partially hydrogenated 2-azatriptycenes was investigated. It was established that the principal fragmentation pathway for these compounds is the formation of $[M-nH]^+$ and $[M-nH]^{2+}$ ions (n = 1-6), as well as pseudoretrodiene fragmentation of the heterocyclic ring with the elimination of the atoms in the 2 and 3 positions.

The mass-spectral behavior of triptycene has been studied frequently [1-3]. It has been established that this compound upon electron impact loses one, two, three, and even four hydrogen atoms. Double charged (M^+, $[M-H]^{2+}$, and $[M-2H]^{2+}$) and even triply charged ions are also formed during fragmentation [1]. The facile formation of polycharged molecular or fragment ions of the $[M-H]^{n+}$, $[M-2H]^{n+}$, and $[M-3H]^{n+}$ type (n = 2, 3) is also characteristic for heteroanalogs of triptycene that contain phosphorus [4], arsenic, and antimony [5], or, simultaneously, nitrogen and phosphorus [6], or nitrogen and arsenic [7] atoms in the bridge positions of the triptycene molecule.

Up until now, the mass-spectral behavior of heteroanalogs of triptycene that contain heteroatoms in the aromatic rings has not been studied. To fill this gap we studied the mass-spectral behavior of a series of 2-azatriptycenes (III-XI). For comparison, we recorded the mass spectra of triptycene (I) itself and 11,12-dimethylene-9,10-dihydro-9,10-ethanoanthracene (II).

It is apparent from an analysis of the mass spectra (Table 1) that intense molecular-ion peaks (the maximum peaks in most cases) are characteristic for all of the investigated compounds except VII. As in the mass spectrum of triptycene itself, peaks of $[M-H]^+$, $[M-2H]^+$, and $[M-3H]^+$ ions, as well as peaks of the corresponding doubly charged ions, were observed in the mass spectra of completely aromatic III-IX. However, whereas the intensities of the single charged fragment $[M-nH]^+$ (n = 1-3) are quite high (up to 42.8% of Σ100),* the intensities of the $[M-nH]^{2+}$ ion peaks do not exceed 2.2% (see Table 2). Peaks of $[M-nH]$ ions ($n \geqslant 2$) are completely absent in the mass spectra of partially hydrogenated X and XI; the $[M-H]^+$ ion is also virtually absent in the mass spectrum of XI. The introduction of two nitrogen atoms in one of the aromatic rings does not lead to an appreciable change in the character of the primary fragmentation. Thus peaks of $[M-nH]^+$ ions (n = 1-3) are also

*The Σ100 symbol denotes the overall intensity of the ion peaks for m/z values from 100 to M^+.

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TABLE 1. Mass Spectra of II-XI*

Compound	m/z values (relative peak intensities, %)
II	230 (31,6), 229 (12,3), 228 (3,4), 215 (12,6), 178 (100), 177 (2,5), 176 (4,7), 152 (3,2), 129 (2,9), 128 (2,7), 115 (11,7)
III	255 (79,8), 254 (100), 253 (5,9), 252 (1,6), 228 (4,2), 227 (2,9), 226 (12,2), 127 (4,3), 113 (4,8), 111 (3), 109 (2)
IV	271 (53,8), 270 (2,7), 255 (32,7), 254 (100), 253 (8), 239 (6,5), 228 (3,4), 226 (9,6), 215 (7,6), 127 (6,5), 113 (7,2)
V	331 (100), 330 (65,3), 254 (4,7), 228 (16,8), 227 (5,9), 226 (16,2), 165,5 (9,5), 165 (8,3), 164 (4,9), 151 (6), 111 (11,3)
VI	331 (66,1), 330 (100), 329 (2,9), 328 (3,3), 254 (3,3), 228 (7,8), 227 (2,3), 226 (8,3), 178 (2,4), 164,5 (5,1), 164 (4,4)
VII	311 (0,2), 296 (2,1), 282 (6), 269 (100), 268 (9,2), 267 (2,6), 239 (1,9), 226 (1,8), 178 (1,2), 134 (1,7), 133,5 (2,8)
VIII	256 (100), 228 (23,1), 227 (32,6), 226 (13), 225 (6), 202 (7,9), 178 (32,6), 125 (6,5), 123 (5,1), 111 (19,7), 109 (9,3)
IX	271 (100), 270 (27), 243 (11), 242 (20), 241 (8), 215 (13), 213 (8,5), 123 (7), 115 (8), 111 (14), 109 (11)
X	331 (100), 302 (76), 258 (24,6), 256 (13), 230 (23,8), 229 (43), 228 (16,9), 216 (13,5), 215 (43,8), 202 (11,6), 178 (63,8)
XI	405 (49,2), 230 (27,6), 229 (69,7), 228 (100), 227 (11,8), 217 (9,4), 216 (54,5), 215 (53), 202 (19,5), 178 (68,2), 119 (28,6)

*The molecular ion and the 10 most intense peaks of the fragment ions for m/z values from 100 to M^+ are presented.

TABLE 2. Stabilities (W_M) of the Molecular ions and Intensities (I, % Σ_{1000}) $[M - nH]^+$ and $[M - nH]^{2+}$ Ion Peaks (n = 1-3) in the Mass Spectra of II-XI

Compound	W_M	$[M-H]^+$	$[M-2H]^+$	$[M-3H]^+$	M^{2+}	$[M-H]^{2+}$	$[M-2H]^{2+}$	$[M-3H]^{2+}$
II	14,4	5,2	1,4	0,6	5,0	0,1	1,0	0,1
III	33,9	38,9	2,3	0,6	0,4	1,7	0,2	0,4
IV	18,4	0,8	0,1	—	0,2	0,2	—	—
V*	30,8	17,1	0,8	0,7	2,5	2,2	0,8	1,3
VI*	31,3	42,8	1,2	1,4	0,7	0,9	2,2	1,9
VII	0,2	0,2	—	—	—	—	—	—
VIII	31,9	1,0	0,2	0,1	0,1	—	0,7	—
IX	30,7	7,4	1,1	—	0,4	1,1	0,4	0,5
X	19,3	1,1	—	—	—	0,2	—	—
XI	9,5	0,1	—	—	—	2,8†	—	0,3

*The intensities of the $[M - 4H]^+$, $[M - 5H]^+$, and $[M - 6H]^+$ ion peaks are, respectively, 0.3, 0.2, and 0.1%.
†The mass number of the $[M - H]^{2+}$ ion coincides with the mass number for the F_3 ion.

observed in the mass spectrum of 2,3-diazatriptycene (VIII). However, oxidation of the nitrogen atom of 2-azatriptycene leads to an appreciable decrease in the intensities of the peaks of the $[M - nH]^+$ ions ($n \geqslant 2$). A similar phenomenon is observed in the case of 3-butyl-2-azatrypticene (VII). Oxidation of the C_3 atom in the 2-azatriptycene (IX) molecule leads only to a decrease in the relative intensities of the peaks of the $[M - H]^*$ and $[M - 2H]^+$ ions. On the other hand, the introduction of a phenyl group in the 1 or 3 position favors the formation of $[M - nH]^+$ ions; the maximum n value reaches six in this case.

In [2] it was assumed that the molecular ion of triptycene exists at least partially in the 9-(1,5-hexadiyn-3-en-1-yl)-9,10-dihydroanthracene form, by the dehydrogenation of which the development of $[M - nH]^+$ ions is also explained. The introduction of heteroatoms in one of the aromatic rings of the symmetrical triptycene molecule leads to "asymmetrization" of the molecular ion; this "asymmetrization" is greater, the more pronounced the electron-donor properties of the resulting heterocyclic ring (compare III and IV).

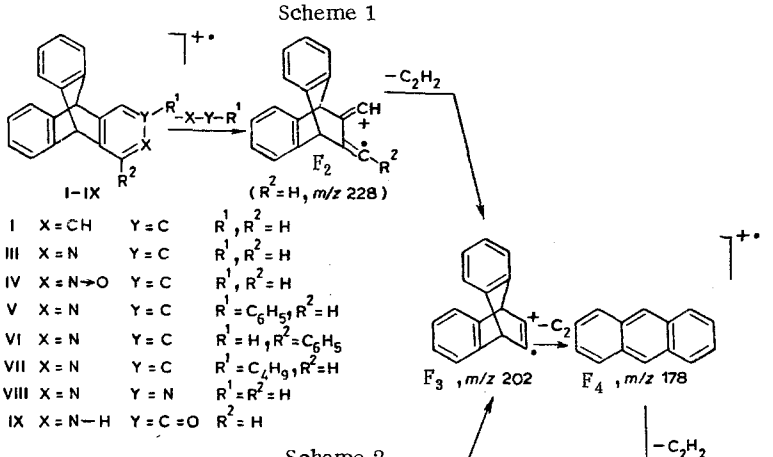
The second pathway in the primary fragmentation of II-XI involves cleavage of the heterocyclic ring with the elimination of the atoms in the 2 and 3 positions of the heteroring

TABLE 3. Intensities of the Peaks of the Characteristic Ions in the Mass Spectra of I-XI (I, $\%\Sigma_{100}$)

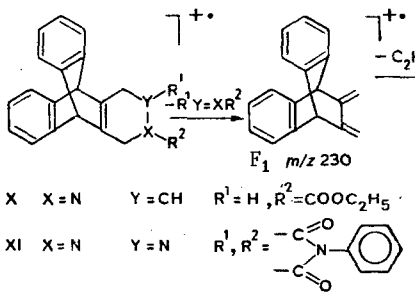
Compound	Intensities of the ion peaks (m/z)				
	F_1 (230)	F_2 (228)	F_3 (202)	F_4 (178)	F_5 (152)
I	—	0,1	0,1	2,3	0,4
II	13,3 (M^+)	1,4	0,7	42,3	1,4
III	—	1,6	0,2	0,5	0,4
IV	—	1,0	0,3	0,7	0,4
V	—	4,4	0,3	0,9	0,8
VI	—	1,2	0,3	1,0	0,3
VII	—	0,5	0,2	0,8	0,2
VIII	—	6,5	1,2	9,1	0,6
IX	—	1,6	0,5	1,0	1,0
X	4,1	2,8	1,9	10,6	0,8
XI	4,0	14,6	2,8	9,9	0,6

(retrodiene or pseudoretrodiene fragmentation) and the formation of the F ion, which subsequently successively loses an acetylene molecule and two carbon atoms (the F_3 and F_4 ions, Scheme 1).

Scheme 1



Scheme 2



Under the influence of electron impact, partially hydrogenated X and XI undergo similar fragmentation to give the F_1 ion (Scheme 2), the subsequent fragmentation of which is in agreement with the character of the dissociative ionization of II. The intensities of the indicated characteristic ions are presented in Table 3. A peculiarity of the mass-spectrometric fragmentation of VII is the elimination by the molecular ion of a propylene molecule, which is characteristic for 2-alkylpyridines [10]. An ion peak with m/z 243 is characteristic for the mass spectrum of pyridone IX; this is associated with the elimination from the molecular ion of a CO molecule (characteristic for 2-pyridone [10]). An ion peak with m/z 258, which correspond to the ejection of a molecule of ethanol, and an ion peak with m/z 256, which indicates the splitting out of a carbethoxy group from the molecular ion, are observed in the mass spectrum of X.

It should be noted that the position of the substituent in the pyridine ring of the 2-azatriptycene molecule has an appreciable effect on the probability of the primary fragmentation of the molecular ion. Thus the $I_{[M-H]}/I_{M^+}$ ratio in the mass spectrum of 3-phenyl-2-azatriptycene (V) is less than one, whereas it is more than one in the mass spectrum of 1-phenyl-2-azatriptycene (VI); this is probably explained by steric factors [11].

Thus, the positive charge in the molecular ions of 2-azatriptycenes is localized primarily in the heterocyclic ring, and this is also responsible for all of the fragmentation pathways discussed above.

EXPERIMENTAL

The investigated compounds were obtained by the methods in [8, 9]. The mass spectra were recorded with an MKh-1303 spectrometer with direct introduction of the substances into the ion source at an ionization energy of 50 eV, an electron emission current of 1.5 mA, and temperatures close to the melting points of the substances.

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FORMATION OF DERIVATIVES OF 5,6-DIHYDROOXAZINO- AND 5,6-DIHYDROOXAZOLO[3,2-b]-1,2,4-TRIAZOLE IN THE REACTION OF 1-OXOALKYL-3,5-DINITRO-1,2,4-TRIAZOLES WITH POTASSIUM CYANIDE

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1,3-Dihydrooxazino- and 1,3-dihydrooxazolo[3,2-b]-1,2,4-triazoles were obtained instead of the expected 3-nitro-5-cyano-1,2,4-triazole derivatives in the reaction of 1-oxoalkyl-3,5-dinitro-1,2,4-triazoles with potassium cyanide. Their formation is due to the fact that primary attack by the cyanide anion is not directed at the ring C_5 atom but rather at the carbonyl group with subsequent intramolecular replacement of the nitro group.

The introduction of a cyano group in the ring of 1,2,4-triazoles can be realized by the Sandmeyer reaction [1]. A second possible method, viz., nucleophilic substitution at the ring carbon atom, has not been investigated, although the reaction of 1-substituted 3,5-dinitro- or 3-nitro-5-halo-1,2,4-triazoles with nucleophilic reagents is an effective method for the modification of the structure of compounds of this class [2, 3]. We attempted to obtain derivatives of 3-nitro-5-cyano-1,2,4-triazoles by the reaction of 1-oxoalkyl-3,5-dinitro-1,2,4-triazoles I and II with potassium cyanide. However, this attempt was unsuccessful.

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