MASS SPECTROMETRIC STUDY OF METHYL-SUBSTITUTED 4-AZAPHENANTHRENES AND THEIR NITRATION PRODUCTS

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The mass spectral behavior of five derivatives of the 4-azaphenanthrene series – 1,3-dimethyl- (I), 2,3-dimethyl- (II), 1,2,3,-trimethyl- (III), 1,2,3-trimethyl-8-nitro- (IV), and 1,3-dimethyl-6,7-dinitro-4-azaphenanthrene (V) – was studied. The stabilities of the molecular ions with respect to gragmentation (W_M) are higher by a factor of two or more for the methyl-substituted I-III than for nitro derivatives IV and V. The intensity of the $[M - H]^+$ ion peak in the mass spectra of I-V does not depend on the number of methyl groups but only on their positions: the presence of a CH_3 group in the 2 position leads to an $[M - H]^+$ ion that is 1.5 times more intense than when there is a methyl group in the 1 position. The molecular ions of I-V do not eliminate HCN molecules; this constitutes evidence for the absence of randomization of their methyl groups. The presence of a CH_3 substituent in the 1 or 2 position does not affect the intensity of the $[M - CH_3]^+$ ion peaks, while the simultaneous presence of CH_3 groups attached to the C_1 and C_2 atoms increases the intensity of the $[M - CH_3]^+$ fragment peak by a factor of two. In the mass spectra of nitro derivatives IV and V, $[M - O]^+$, $[M - OH]^+$, $[M - NO]^+$, and $[M - NO_2]^+$ fragments are observed in the first step of the fragmentation of the M^+ ion, whereas the $[M - CO]^+$ ion peak characteristic for the dissociative ionization of 1-nitronaphthalene is also observed for 8-nitro-substituted IV.

Numerous studies of the dissociative ionization of one-ring and two-ring N-heteroaromatic compounds have been reflected in the literature [1, 2]. However, the data on the fragmentation of polynuclear nitrogen heterocycles are limited, and no data at all are available for the azaphenanthrene series. In the present research we investigated the mass spectral behavior of five compounds of this series – 1,3-dimethyl- (I), 2,3-dimethyl- (II), 1,2,3-trimethyl- (III), 1,2,3-trimethyl-8-nitro- (IV), and 1,3-dimethyl-6,7-dinitro-4-azaphenanthrene (V) – in order to ascertain the relationship between their fragmentation and the position and number of substituents in them.

The molecular ion peaks in the mass spectra of azaphenanthrenes I-V (Table 1) have the maximum intensities; this is typical for polynuclear heteroaromatic systems [3]. The presence of rather intense peaks of doubly charged M^{2+} ions (Table 2) confirms the condensed structure of the M^+ ions of these compounds [4]. The stabilities of the molecular ions with respect to fragmentation (W_M) for methyl-substituted I-III are higher by a factor of more than two as compared with methyl nitro derivatives IV and V. As the number of CH_2 groups increases from two to three in the I and II molecules, the W_M value decreases somewhat, while the transition from one nitro group to two in IV and V has no effect on the W_M value.

The fragmentation of I-III is represented by a scheme in the case of I. In the mass spectra of these compounds one observes $[M - nH]^+$ ions (n = 1-4), the formation of which is characteristic for aryl-substituted N-heteroaromatic compounds [3, 5]. The presence of nitro groups in IV and V decreases the probability of the appearance of these ions. It follows from a comparison of the mass spectra of azaphenanthrenes I-III that the intensity of the $[M - H]^+$ ion does not depend on the number of methyl groups in the pyridine ring but rather is determined only by their position. The presence in II of a methyl group attached to C_2 increases the intensity of the $[M - H]^+$ ion peak by a factor of ~ 1.5 as compared with I. The presence of three CH_3 groups in the III molecule practically does not change the intensity of the $[M - H]^+$ ion peak as compared with the mass spectrum of II. Consequently, elimination of a hydrogen atom by the molecular ions of 4-azaphenanthrenes I-III

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TABLE 1. Mass Spectra of 4-Azaphenanthrenes I-V

Compound	m/e values (intensities of the ion peaks in percent relative to the maximum peak)
I	209 (1,8), 208 (17), 207 (100), 206 (9,0), 205 (5,0), 204 (4,0), 203 (1,4), 193 (0,7), 192 (3,5), 191 (5,5) 190 (4,0), 189 (0,7), 181 (0,8), 180 (2,0), 179 (1,8), 178 (3,5), 177 (3,0), 176 (1,6), 168 (0,9), 167 (2,0), 166 (2,5), 165 (7,5), 164 (3,0), 163 (3,0), 153 (1,5), 152 (2,5), 151 (2,0), 150 (1,7), 149 (1,1), 140 (2,0), 139 (2,1), 137 (0,6), 127 (2,0), 126 (1,5), 125 (1,0), 115 (0,9), 104 (2,0), 103 (1,4), 102 (2,5), 90 (2,0), 89 (2,0), 88 (2,0), 87 (1,0), 82 (2,0), 77 (1,7), 76 (3,2), 75 (1,7), 74 (1,2), 63 (2,0), 51 (1,8)
II	209 (1,8), 208 (17), 207 (100), 206 (15), 205 (8,0), 204 (6,2), 203 (1,2), 194 (0,6), 193 (2,0), 192 (4,0), 191 (4,8), 190 (3,2), 189 (0,7), 181 (0,4), 180 (2,0), 179 (1,6), 178 (2,3), 177 (1,3), 176 (0,8), 168 (0,4), 167 (1,0), 166 (2,8), 165 (10), 164 (3,2), 163 (4,0), 162 (0,6), 154 (0,4), 153 (0,8), 152 (1,4), 151 (1,0), 150 (0,8), 149 (0,6), 140 (1,2), 139 (2,4), 138 (0,5), 137 (0,6), 128 (0,4), 127 (0,8), 126 (1,2), 115 (1,2), 104 (0,8), 103 (0,7), 102 (1,4), 90 (0,8), 89 (1,4), 88 (0,8), 87 (1,0), 83 (1,0), 82 (2,0), 77 (0,7), 76 (1,2), 75 (1,2), 74 (0,8), 63 (1,6), 51 (1,2)
III	223 (1,1), 222 (11), 221 (100), 220 (13), 219 (2,5), 218 (1,5), 217 (0,9), 207 (2,0), 206 (8,0), 205 (4,0), 204 (4,5), 203 (1,5), 194 (1,9), 193 (1,9), 192 (2,0), 191 (3,0), 190 (3,1), 189 (2,5), 181 (3,5), 180 (4,0), 179 (8,0), 178 (8,0), 177 (3,0), 176 (3,0), 167 (1,0), 166 (2,5), 165 (5,0), 164 (2,0), 163 (2,5), 153 (1,5), 152 (4,5), 151 (2,7), 150 (1,4), 149 (1,3), 140 (1,2), 139 (2,4), 128 (1,0), 127 (2,2), 126 (1,6), 115(1,5), 103 (1,5), 102 (2,5), 91 (2,0), 89 (5,5), 77 (1,9), 76 (4,0), 75 (4,0), 69 (2,7), 63 (4,0), 51 (1,3)
IV	268 (1,2), 267 (12), 266 (100), 265 (6,5), 251 (0,6), 250 (1,9), 249 (3.9), 239 (1,5), 238 (6.0), 237 (3,8), 236 (16,5), 235 (1,1), 234 (0,5), 224 (1,0), 223 (1,0), 222 (3,5), 221 (12), 220 (34), 219 (5,0), 218 (11), 217 (2,4), 216 (2,0), 215 (1,0), 211 (0,9), 210 (2,2), 209 (12), 208 (84), 207 (4,5), 206 (4,5), 205 (10), 204 (13), 203 (3,5), 202 (2,0), 196 (2,4), 195 (2,2), 194 (2,5), 193 (4,5), 192 (3,5), 191 (3,6), 190 (4,1), 189 (1,5), 188 (0,7), 183 (1,0), 182 (0,8), 181 (0,9), 180 (2,2), 179 (2,2), 178 (5,7), 177 (4,0), 176 (5,5), 175 (2,3), 174 (0,8), 168 (1,0), 167 (1,5),166 (2,6), 165 (5,6), 164 (2,7), 163 (4,0), 162 (0,8), 154 (1,2), 153 (2,0), 152 (6,2), 151 (4,8), 150 (2,7), 149 (0,9), 141 (0,9), 140 (1,4), 139 (2,5), 138 (1,0), 137 (0,9), 128 (1,1), 127 (1,4), 126 (2,0), 125 (1,0), 115 (1,2), 104 (1,0), 103 (1,2), 102 (4,5), 91 (0,7), 90 (0,9), 89 (4,0), 88 (5,0), 87 (2,4), 77 (2,4), 76 (5,0), 75 (3,5), 74 (1,5), 63 (3,5), 51 (2,5)
V	299 (1,5), 298 (13), 297 (100), 296 (1,0), 295 (0,5), 281 (1,0), 280 (1,9), 271 (1,3), 270 (0,7), 269 (0,6), 268 (0,9), 267 (3,8), 253 (1,8), 252 (11), 251 (62), 250 (5,7), 240 (1,9), 239 (7,5), 223 (2,0), 222 (2,5), 221 (11), 220 (1,9), 209 (5,0), 208 (1,0), 207 (2,9), 206 (9,0), 205 (40), 204 (17), 203 (7,4), 202 (3,5), 201 (1,8), 195 (1,9), 194 (5,5), 193 (28), 192 (9,5), 191 (6,0), 190 (8,5), 189 (1,7), 188 (1,7), 181 (4,0), 180 (1,8), 179 (2,5), 178 (8,5), 177 (7,0), 176 (6,9), 175 (2,0), 167 (2,3), 166 (2,7), 165 (5,5), 164 (6,0), 163 (8,0), 162 (1,8), 154 (1,8), 153 (2,6), 152 (7,8), 151 (7,6), 150 (3,8), 141 (1,2), 140 (2,6), 139 (3,0), 138 (2,0), 137 (1,8), 128 (1,2), 127 (2,0); 126 (3,0), 125 (1,6), 115 (1,5), 114 (1,2), 102 (3,0), 101 (1,9), 89 (3,5), 88 (5,0), 87 (2,9), 86 (1,7), 77 (3,0), 76 (3,5), 75 (4,0), 74 (2,5), 63 (4,6), 51 (3,5)

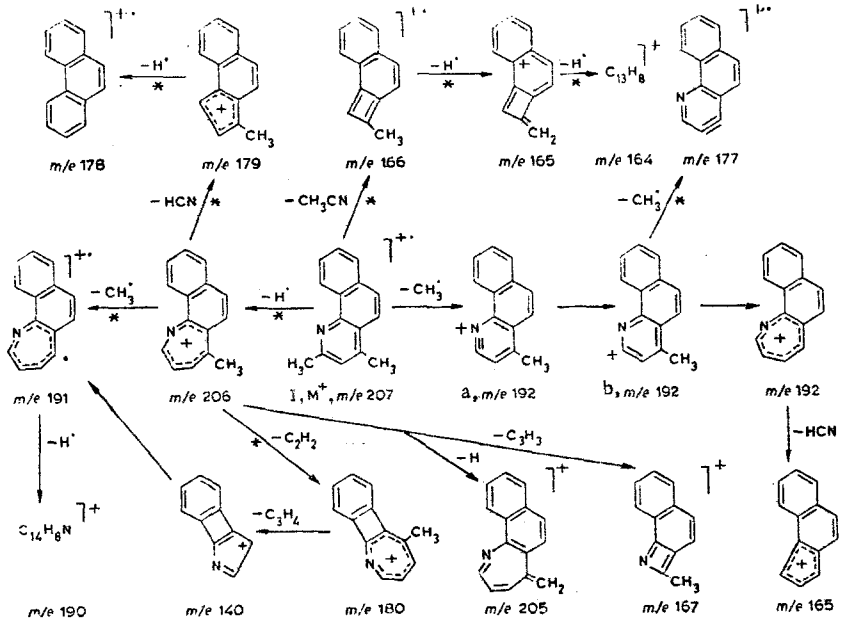
TABLE 2. Stabilities of the Molecular Ions with Respect to Fragmentation (W_M, %) and Relative Intensities (%) of the Peaks of the Characteristic Fragments in the Mass Spectra of Methyl- and Nitromethyl-Substituted 4-Azaphenanthrenes I-V

Compound	W_M	M^+	$[M-H]^+$	$[M-CH_3]^+$	$[M-H, -HCN]^+$	$[M-CH_2CN]^+$	$[M-CH_3, -HCN]^+$
I	50	8,6	9,0	3,5	1,8	2,5	7,5
II	50	6,8	15	4,0	1,6	2,8	10,0
III	42	6,8	13	8,0	1,9	4,0	8,0
IV	22	1,0	6,5	0,6	6,0	—	1,0
V	21	1,5	1,0	0,1	0,6	—	—

occurs with the highest probability from the methyl group attached to the C_3 atom and with the lowest probability from the methyl group attached to the C_1 atom. These facts also constitute evidence for the absence of randomization of the methyl substituents in the molecular ions of I-III. The indicated regularity is also observed for methyl nitro derivatives IV and V. The intensities of the $[M - CH_3]^+$ fragment peaks in the mass spectra of dimethyl-4-azaphenanthrenes I and II are approximately identical (Table 2), i.e., they do not depend on the position of the methyl groups in the pyridine ring. However, when there is a third methyl group in the same ring (III), the intensity of the $[M - CH_3]^+$ ion peak increases by a factor of two; this constitutes evidence for the mutual effect of the methyl groups attached to the C_1 and C_2 atoms on the probability of their detachment.

The molecular ions of 4-azaphenanthrenes I-V do not eliminate an HCN molecule; this also attests to the absence of randomization of the methyl groups in them. Loss of HCN particles by the $[M - H]^+$, $[M - 2H]^+$; and $[M - CH_3]^+$ fragments is observed in the mass spectra of I-III. In the case of the $[M - H]^+$ ion this process can be explained by the formation of an azatropylium ring. In addition, the $[M - H]^+$ ion loses a C_2H_2 molecule and a C_3H_3 radical; this was established by means of the high-resolution mass spectrum of 1,3-dimethyl-4-azaphenanthrene I, in which the empirical formulas ($C_{13}H_{10}$ and $C_{12}H_9$) of the $[M - H - C_2H_2]^+$ and $[M - H - C_3H_3]^+$ fragments are confirmed by measurement of their precise masses (180.0820 and 167.0726, respectively). Elimination of an HCN molecule by the $[M - CH_3]^+$ ion evidently occurs as a result of randomization of the hydrogen atom in this ion, which leads to structure b (see the scheme below). One also cannot exclude the possibility that detachment of a CH_3 radical from the M^+ ion, which takes place with the highest probability from the ortho position, is accompanied by expansion of the pyridine ring to a seven-membered azatropylium ring; this is also explained by the loss of an HCN molecule by the $[M - CH_3]^+$ ion. Splitting out of an acetonitrile (CH_3CN) residue is observed only for the molecular ions of methyl-substituted 4-azaphenanthrenes I-III.

The presence of one or two nitro groups in the 8 or 6 and 7 positions of the 4-azaphenanthrene rings is responsible for the fragmentation of IV and V that is typical for nitro derivatives of the aromatic and heteroaromatic series. The dissociative ionization of IV displays the properties characteristic for nitroarenes. The $[M - O]^+$, $[M - NO]^+$, and $[M - NO_2]^+$ ion peaks observed in the mass spectrum of this compound are characteristic for nitrobenzenes [6]. The formation of an $[M - OH]^+$ fragment (m/e 249) is characteristic of the mass spectral behavior of substances in which there is a substituent containing a hydrogen atom in the ortho position relative to the nitro group [6, 7]. The development of an $[M - CO]^+$ ion (m/e 238, empirical formula $C_{15}H_{14}N_2O$, precise mass 238.1079) is characteristic for the fragmentation of 1-nitronaphthalene [8]. The peaks of $[M - O]^+$, $[M - NO]^+$, and $[M - NO_2]^+$ ions that are typical for the fragmentation of dinitrobenzenes [9] are present in the mass spectrum of 6,7-dinitro derivative V, but an $[M - CO]^+$ ion peak is absent. The formation of the low-intensity $[M - OH]^+$ fragment in the dissociative ionization of V is apparently due to the removal, in the composition of the OH radical, of the oxygen atom of one of the nitro groups and the adjacent hydrogen atom; this is characteristic of the mass spectral behavior of benzylnitrobenzenes [10].



*The metastable transitions are indicated by asterisks.

Thus the fragmentation, under the influence of electron impact, of 4-azaphenanthrenes containing substituents in the pyridine ring displays elimination of $\dot{H}$ and $\dot{C}H_3$ radicals in the first step of the fragmentation and elimination of $\dot{H}$ and $\dot{C}H_3$ radicals and HCN, CH_3CN, and C_2H_2 molecules in the second step. The fragmentation of mono- and dinitro-substituted (in the benzene ring) 4-azaphenanthrenes IV and V in the first step is associated with splitting out of O, OH, NO, and NO_2 particles, and in the case of the 8-nitro derivative elimination of a CO molecule is also observed.

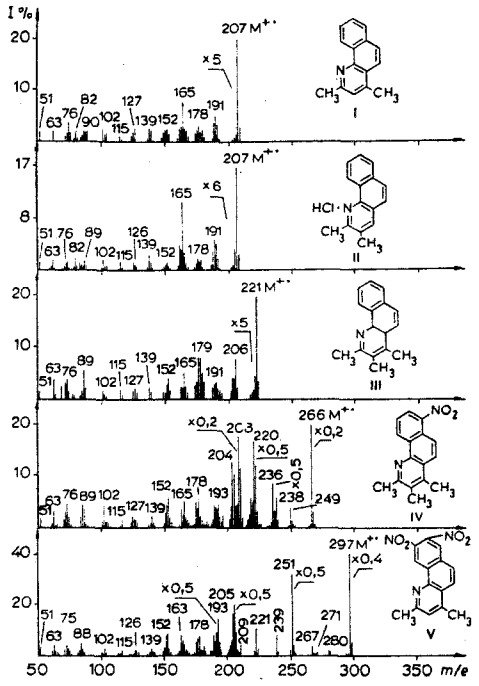


Fig. 1. Mass spectra: 1,3-dimethyl-4-azaphenanthrene (I), 2,3-dimethyl-4-azaphenanthrene (II) hydrochloride, 1,2,3-trimethyl-4-azaphenanthrene (III), 1,2,3-trimethyl-8-nitro-4-azaphenanthrene (IV), and 1,3-dimethyl-6,7-dinitro-4-azaphenanthrene (V).

The nitrogen-free fragments in the mass spectra of I-III, which are formed in the second and later steps of the fragmentation due to the loss of HCN and CH_3CN molecules, subsequently, as usual, split out C_2H, C_2H_2, C_2HCH_3, and C_3H_3 particles. The $[M - O]^+$, $[M - OH]^+$, $[M - NO]^+$, and $[M - NO_2]^+$ fragments in the mass spectra of nitro derivatives IV and V eliminate NO, CO, and CH_3 particles to give ions that subsequently undergo fragmentation in a manner similar to that observed for the similarly constructed fragments formed in the fragmentation of azaphenanthrenes I-III. The dissociative ionization of the molecular ion of V also leads to $[M - NO_2 - NO]^+$, $[M - NO - CO - NO]^+$, $[M - 2NO_2]^+$, and $[M - NO - CO - NO_2]^+$ fragments with m/e 193, the development of which is due to the presence of two nitro groups in the molecule.

EXPERIMENTAL

The mass spectra of I-V were obtained with an MKh-1303 spectrometer with a system for direct introduction of the samples into the ion source at an ionizing voltage of 70 V and an inlet temperature of 30°C. The high-resolution mass spectra of I and IV were measured with a JMS-01-SG-2 spectrometer with an automatic system for information processing.

The synthesis of I-III was accomplished by the methods in [11, 12]. The synthesis of the remaining azaphenanthrenes will be published in a special communication. The purity and individuality of the compounds were monitored by thin-layer chromatography, and the structures of the compounds were established on the basis of data from the IR, UV, and PMR spectra.

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REACTION OF 2-METHYLENE-3-OXOQUINUCLIDINE WITH NUCLEOPHILIC REAGENTS

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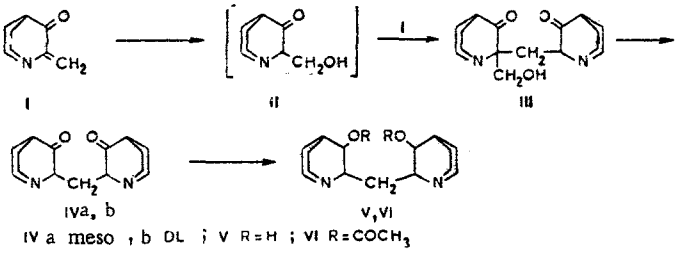
The salts and quaternary derivatives of 2-methylene-3-hydroxyquinuclidine readily add nucleophilic reagents because of the high polarity and polarizability of the carbon–carbon double bond, which are due to the overall electron-acceptor effect of the positively charged nitrogen atom and the carbonyl group. The double bond is substantially deactivated in the base, and the addition of nucleophilic reagents is hindered.

The quinuclidine molecule is a rigidly fixed bicyclic system with a fixed orientation of the free electron pair of the nitrogen atom, as a result of which $p\pi$ electron interactions are sterically impossible in Δ^2-dehydroquinuclidines and quinuclidine derivatives with a semicyclic double bond attached to the α carbon atoms, and, in contrast to ordinary enamines, only the inductive effect of the nitrogen atom is exerted on the double bond vis-a-vis the absence of a +M effect [1].

We have previously shown [2] that in the case of 2- and 3-carboxyl derivatives of quinuclidine with an endocyclic Δ^2-double bond the above-indicated steric and electronic effects are responsible for the rather high polarization of the double bond and that under the conditions of the Michael reaction strong nucleophilic agents add to it to give 2,3-disubstituted quinuclidines.

The present research was devoted to a study of the effect of migration of the double bond from the endocyclic position to the semicyclic position on the reactivities of unsaturated oxoquinuclidine compounds. We used 2-methylene-3-oxoquinuclidine I as the subject of study in reactions with nucleophilic agents. Because of the absence of $p\pi$ conjugation, the polarizability of the carbon–carbon double bond in I is reduced, and, as noted in [3], the addition of nucleophilic reagents such as alcohols to it is hindered. In addition, we showed that when ketone I is heated with an aqueous solution of potassium hydroxide, it is converted to a mixture of meso- and DL-bis(3-oxo-2-quinuclidyl)methanes IVa and IVb.



It may be assumed that IV are formed as a result of a subsequent series of transformations. 2-Hydroxymethyl-3-oxoquinuclidine II, which is formed as a result of the addition of water to the double bond of I, subsequently reacts with a second molecule of olefin I to give 2-hydroxymethylbis(3-oxo-2-quinuclidyl)methane III, which loses a molecule of formaldehyde to give diketone IV. Hydroxy ketone III was isolated when I was

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