saturated solution of ammonium chloride, and the ether layer was separated. The solvent and volatile impurities were removed by steam distillation, and the residue was crystallized from ethanol to give 0.52 g (32%) of a product with mp 205-207°C. No melting-point depression was observed for a mixture of this product with a sample of IIa obtained under the conditions of the preceding experiment.

B) A solution of 0.5 g (4 mmoles) of 2-aminobenzaldehyde and 0.6 g (4 mmoles) of cyanoacetic acid anilide in 5 ml of anhydrous ethanol was added to a solution of sodium ethoxide obtained from 0.3 g (4 mmoles) of sodium in 2 ml of anhydrous ethanol, and the mixture was refluxed for 1 h. It was then filtered, and the filtrate was diluted with water. The resulting precipitate was separated and crystallized from alcohol to give 0.58 g (54%) of a product with mp 205-206°C.

2-Acetamidoquinoline-3-carboxylic Acid Anilide (IIIa). A 3-ml sample of acetyl chloride was added dropwise to a solution of 1 g (2 mmoles) of IIa in 10 ml of anhydrous pyridine, and the mixture was heated for 30 min at 70°C. It was then poured into water, and the solidified residue was separated and crystallized from aqueous ethanol. IR spectrum: 1650, 1690 (CO), 3270, 3480 cm^{-1} (NH). PMR spectrum: 1.36 and 2.36 (2s, 3H, CH_3), 7.5 (m, 9H, aromatic protons), 8.06 (s, 1H, pyridine), 9.06 and 10.0 ppm (2H, NH).

2-Benzamidoquinoline-3-carboxylic Acid Anilide (IIIb). A solution of 0.5 g (1 mmole) of amide IIa and 0.3 g (2 mmoles) of benzoyl chloride in 5 ml of pyridine was refluxed for 3 h, after which the mixture was cooled and poured into ice water. The resulting precipitate was removed by filtration and crystallized from methanol. PMR spectrum: 7.3 (14H, aromatic protons), 7.8 (s, 1H, pyridine), 8.8 and 9.01 ppm (2H, NH).

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MASS-SPECTROMETRIC BEHAVIOR OF 9-HYDROXY-10-NITROSOPHENANTHRENE AND ITS DIAZA ANALOGS

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According to mass-spectral data, 9-hydroxy-10-nitrosophenanthrene in the gas phase exists primarily in this tautomeric form rather than in the 9-oxo-10-hydroxyimino tautomeric form, while passing to its 4,5-diaza and, particularly, its 1,8-diaza analogs shifts the equilibrium sharply to favor the o-quinoid form. The character of the fragmentation of the molecular ions of the polycyclic compounds differs markedly from the fragmentation of the acyclic rearrangement product — 2-carboxy-2'-cyanobiphenyl.

It is well known that o-hydroxynitrosoarenes are capable of undergoing cleavage with the formation of derivatives of o-cyanocinnamic acids [1-3]. This is associated with the fact that, according to spectral data, hydroxynitrosoarenes in solutions exist primarily in the o-quinone monooxime tautomeric form [4-6]. It was later established that a similar rearrangement can also be observed in a number of o-hydroxynitrosohetarenes of the indazole [7], benzotriazole [8], and indole [9, 10] series. It was recently found that some oximes are capable of undergoing the Beckman rearrangement also in the gas phase under electron

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TABLE 1. Mass Spectra* of I-IV

Compound	m/z (relative intensity, %)
I	223 (96), 207 (20), 206 (100), 179 (11), 178 (34), 177 (15), 166 (7), 165 (40), 164 (14), 163 (20), 151 (18)
II	255 (100), 209 (18), 208 (77), 195 (17), 180 (41), 167 (23), 166 (10), 153 (14), 140 (27), 113 (9), 103 (10)
III	225 (100), 195 (26), 180 (14), 168 (15), 167 (83), 166 (14), 141 (14), 140 (68), 139 (11), 113 (16), 63 (11)
IV	223 (88), 206 (39), 180 (16), 179 (100), 178 (37), 177 (24), 152 (12), 151 (27), 150 (11), 76 (17), 75 (13)

*The M^+ peak and the 10 most intense peaks of fragment ions are presented.

TABLE 2. Intensities of the Peaks* of the Characteristic Ions in the Mass Spectra of I-IV (% Σ_{50})

Compound	M^+ (W_M)	$[M-OH]^+$ (F_1)	$[F_1-CO]^+$	$[F_1-CO-HCN]^+$	$[F_1-CN]^+$	$[M-NO]^+$ (F_2)	$[F_2-CO]^+$	$[F_2-CHO]^+$	$[F_2-CO-HCN]^+$	$[M-CO_2]^+$	$Z_1=\Sigma F_1/F_2$	$Z_2=\Sigma F_1/\Sigma F_2$‡
I†	18,4	19,5	6,0	2,7	0,8	0,4	6,8	2,8	—	—	48,5	3,3
II	22,4	16,4	8,9	2,5	0,2	3,6	4,2	1,9	5,2	—	4,6	1,9
III	21,7	<0,1	2,5	1,0	0,2	5,1	17,0	2,4	13,0	—	<0,02	<0,1
IV	14,7	6,8	5,1	3,7	0,2	—	—	—	—	16,3	—	—

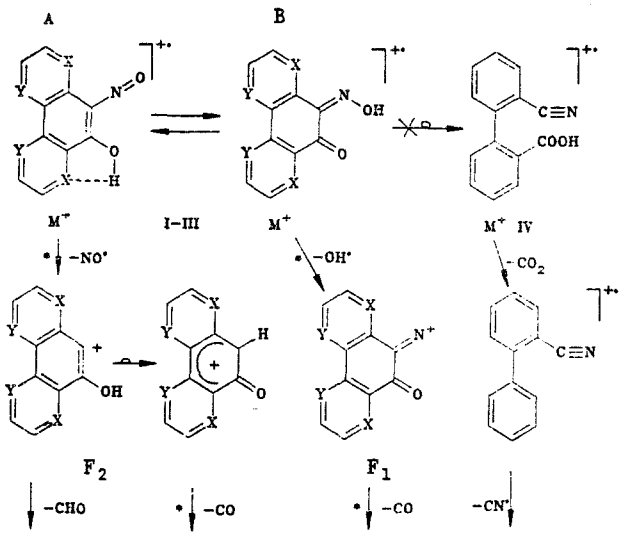
*Taking into account the isotope correction.
†The intensity of the $[F_1 - CHO]^+$ peak of I was 2.5.
‡The sums of the intensities of the peaks of the F_1 (F_2) ions and their fragments.

impact [11, 12]. In particular, a similar process was observed in the mass-spectrometric fragmentation of isatin monooximes [13], while this sort of rearrangement was not noted for the molecular ions (M^+) of 2-hydroxy-1-nitrosonaphthalenes, which exist primarily in the hydroxyimino-o-quinoid tautomeric form [14]; it was established that the introduction of electron-acceptor substituents into the aromatic ring increases the percentage of the hydroxy nitroso tautomeric form of M^+ in the gas phase.

In connection with the information set forth above we made a thorough analysis of the character of the mass-spectrometric fragmentation of 9-hydroxy-10-nitrosophenanthrene (I) and its 4,5- and 1,8-diaza analogs (II, III), as well as 2-carboxy-2'-cyanobiphenyl (IV) – the product of a Beckmann rearrangement of the second sort of I. We accomplished the synthesis of I and II via described methods, whereas III was obtained by nitrosation of 9-hydroxy-1,8-phenanthroline.

It follows from the mass spectra obtained (Tables 1 and 2) that the stability of the M^+ ion of carbocyclic compound I is somewhat lower than the W_M values of diaza derivatives II and III but higher than the W_M value for substituted biphenyl IV. The overall character of the dissociative ionization of I and II is quite monotypic and is associated with the primary loss by their M^+ ions of a hydroxy radical (F_1 ion); this is characteristic for the primary pathway of fragmentation of cyclic and heterocyclic oximes [15]. This ion then loses CO and HCN molecules successively (see the scheme).

This fragmentation pathway characterizes the M^+ ion of the hydroxyimino-o-quinoid tautomeric form B. At the same time, the mass spectra of I-III contain ions, the formation of which is explained by the fragmentation of A – the more aromatic hydroxy nitroso form of the M^+ ion – and is associated with the primary loss by the M^+ ion of a nitroso group (F_2 ion) with the subsequent elimination of a molecule of CO (or a CHO radical) and a molecule of HCN. Thus, in the gas phase I exists, as in the case of solutions in nonpolar solvents [11], primarily in the less aromatic tautomeric form B. However, as expected, annelation of two electron-deficient pyridine rings to the nitrosophenol ring (as in II) apparently leads to a



I X=Y=CH; II X=CH, Y=N; III X=N, Y=CH

shift of the tautomeric equilibrium to favor the more aromatic A structure, since the Z_1 and Z_2 ratios (Table 2) decrease sharply on passing from I to II.

According to the mass-spectral data, III in the gas phase exists virtually completely in tautomeric form A (Z_1 and Z_2 < 0.1); this is probably associated with fixing of this structure due to intramolecular interaction of the hydrogen atom of the phenolic hydroxy group with the free sp^2 pair of electrons of the nitrogen atom in the peri position, similar to what has been described in the case of 8-hydroxyquinolines [16, 17].

Finally, the character of the mass-spectrometric fragmentation of acyclic rearrangement product IV differs from that for cyclic compound I with respect to the intensive elimination of a molecule of CO_2, which is characteristic for the fragmentation of aromatic acids with electron-acceptor substituents in the ring [18].

Thus, on the basis of the mass-spectral data one can speak with confidence regarding the primary tautomeric form of the investigated compounds in the gas form and regarding the absence of a Beckmann rearrangement of the second sort under these conditions.

EXPERIMENTAL

The UV spectra of solutions of the compounds in ethanol were obtained with a Specord UV-vis spectrophotometer. The mass spectra were recorded with MKh-1303 and MAT-212 (Varian-MAT) spectrometers at energies of 50 and 70 eV, respectively, with direct introduction of the substances into the ion source. The elementary compositions of the principal ions were determined with an MAT-212 spectrometer with a resolution of $M/\Delta M$ = 10,000. The purity of the substances was determined by TLC on a loose layer of activity II aluminum oxide; the eluent was isopropyl alcohol–10% ammonium hydroxide (4:1), and the chromatograms were developed with iodine vapors.

9-Hydroxy-10-nitrosophenanthrene (I). A suspension of 20.8 g (100 mmoles) of phenanthrenequinone and 6.95 g (100 mmoles) of hydroxylamine hydrochloride was refluxed in a mixture of 250 ml of ethanol and 25 ml of chloroform was refluxed for 1.5 h, after which one-third of the solvent was removed by distillation, and the residual mixture was cooled. The precipitate was separated and crystallized from ethanol to give 19 g (85%) of a product with mp 157°C (mp 158°C [19]) and R_f 0.70. UV spectrum, λ_{max} (log ε): 232 (4.39), 260 (4.52), 316 nm (3.74); in ethanolic 0.01 N KOH solution: 258 (4.61), 404 nm (4.04); in ethanolic 0.01 N HCl solution: 260 (4.49), 320 nm (3.60).

9-Hydroxy-10-nitroso-4,5-phenanthroline (II). A solution of 0.7 g (10 mmoles) of hydroxylamine hydrochloride in 8 ml of water was added dropwise to a refluxing solution of 2.1 g (10 mmoles) of 9,10-dioxo-4,5-phenanthroline in 75 ml of ethanol, after which the mixture was refluxed for another 5 min and then allowed to stand overnight. The resulting precipitate was separated, dried, and crystallized from ethanol to give 1.18 g (52%) of a product with mp 218-220°C (dec.) and R_f 0.52. Found, %: C 63.9; H 3.0; N 18.5. $C_{12}H_7N_3O_2$. Calculated, %: C 64.0; H 3.1; N 18.9.

9-Hydroxy-1,8-phenanthroline. A solution of 4.20 g (20 mmoles) of 9-methoxy-1,8-phenanthroline [20] in 15 ml of hydrobromic acid (48%) was refluxed for 5 h, after which it was cooled, and the precipitate was removed by suction filtration, washed with 20 ml of isopropyl alcohol, and dried to give 3.7 g (51%) of the chromatographically pure dihydrobromide. The latter was dissolved in 10 ml of water and the solution was neutralized with 5% sodium bicarbonate solution. The precipitate was removed by suction filtration, washed with water, and crystallized from isopropyl alcohol to give a product with mp 147-148°C and R_f 0.56. UV spectrum, λ_{max} (log ε): 234 (4.51), 284 nm (4.34). Found, %: N 14.2. $C_{12}H_8N_2O$. Calculated, %: N 14.2.

9-Hydroxy-10-nitroso-1,8-phenanthroline (III). A cooled solution of 3.45 g (50 mmoles) of sodium nitrite in 150 ml of distilled water was added dropwise to a cooled (to 0°C) solution of 17.9 g (50 mmoles) of the dihydrobromide obtained above, and the mixture was stirred for 30 min. The precipitate was removed by suction filtration, washed with distilled water, and dried to give 11 g (97%) of a product with mp 290°C (dec.) and R_f 0.64. UV spectrum, λ_{max} (log ε): 138 (4.42), 288 (4.18), 354 nm (3.65); in ethanolic 0.01 N NaOH solution: 242 (4.26), 288 (4.09), 304 (4.15), 408 nm (3.97). Found, %: 18.5. $C_{12}H_7N_3O_2$. Calculated, %: N 18.8.

2-Carboxy-2'-cyanobiphenyl (IV). A solution of 4.42 g of NaOH in 45 ml of water was added carefully with vigorous stirring to a heated (to the boiling point) solution of 6.2 g (28 mmoles) of phenanthrene I and 7.37 g (42 mmoles) of benzenesulfonyl chloride in 60 ml of dioxane in such a way that the mixture refluxed, after which it was refluxed for another 10-15 min. It was then neutralized with 15% sodium bicarbonate solution, and the dioxane was removed by distillation. A solution of sodium bicarbonate was added again, and the mixture was shaken with activated charcoal and filtered. The filtrate was acidified (with respect to Congo Red) with hydrochloric acid, and the resulting copious precipitate was removed by suction filtration, washed with water, and dried to give 5.5 g (89%) of a product with mp 168-169°C. Recrystallization from toluene gave a product with mp 171°C (mp 172°C [21]) and R_f 0.63 [ethanol–acetic acid (8:1)]. UV spectrum, λ_{max} (log ε): 285 nm.

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SPIRO[4-AZAFLUORENEPYRAZOLENINES] AND THEIR THERMAL REARRANGEMENT TO PYRAZOLOAZAPHENANTHRENES

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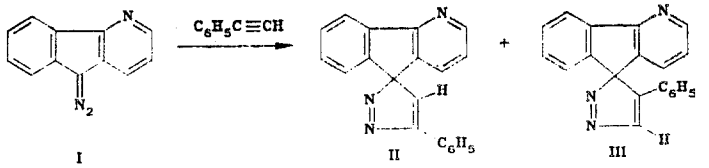
Reaction of 9-diazo-4-azafluorene with phenylacetylene gives spiro[4-azafluorene-9,3'-pyrazolenines], isomeric according to the position of the substituent in the pyrazolenine ring. Their thermal rearrangement to pyrazolo-4-azaphenanthrenes that are isomeric according to ring linkage and position of the substituent in the pyrazole ring has been studied.

The 1,3-dipolar cycloaddition of α,α-disubstituted diazo compounds to alkynes is a method for synthesizing pyrazolenines (3H-pyrazoles). However, in many cases it is not the initial adducts which are separated but products derived from subsequent rearrangement of them – 1H-pyrazoles [1]. The rearrangement of pyrazolenines with a spiro structure proceeds with particular ease [2]. Thus, when 9-diazofluorene is reacted with phenylacetylene, only the product from rearrangement of the initial spiro[fluorene-9,3'-pyrazolenine] is formed, namely, 2H-3-phenylphenanthro[9,10-d]pyrazole [3]. The presence of strong electron-withdrawing substituents at the 4- and 5-positions of the pyrazolenine fragment stabilizes spiropyrazolenines [4]. There is no information in the literature about the effect of substituents in the diazo compound on the stability of the spiropyrazolenines formed.

With the object of synthesizing new spiro compounds containing azafluorene and diazole fragments, we have studied the reaction of 9-diazo-4-azafluorene (1) [5] with phenylacetylene. We attempted to determine the effect of the nitrogen atom in the azafluorene fragment on the stability of the spiroazafluorenepyrazolenines formed and the direction of their thermal rearrangement to isomeric pyrazoloazaphenanthrenes.

The reaction of diazo compound I with phenylacetylene was carried out at 20°C. A 70% yield was obtained for a mixture of 5'- and 4'-phenylspiro[azafluorene-9,3'-pyrazolenines] (II and III), from which compounds II and III were obtained in the ratio 6:1 by chromatographic separation.



I II III

The position of the phenyl substituent in the pyrazolenine fragment of compounds II and III was established from the signal of the pyrazolenine proton in their PMR spectra (Table 1). The shift downfield by 1.38 ppm by the signal from this proton in compound III relative to compound II is due to the electron-withdrawing effect of the nitrogen atom in the pyrazolenine fragment. The predominant formation of isomer II is probably due to steric factors [6]. Rearrangement of compounds II and III to the tautomeric pyrazole form, as often occurs when similar reactions are carried out, does not take place during the reaction.

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