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Synthesis of New Methyl Derivatives of Aza- and Diazaphenanthrene

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Abstract—By condensation of acetone with 2-naphthylamine and 3-(4-fluorophenyl)-1*H*-pyrazole-4-, pyridine-3-, quinoline-2-, quinoline-6-carbaldehyde and 4-(2-fluorobenzyloxy)benzaldehyde new 3-aryl(heteryl)-1-methylbenzo[f]quinolines were synthesized. Reactions of acetone with 6-quinolylamine and aromatic aldehydes provided 3-aryl-1-methyl-4,7-phenanthrolines. Intermediate reaction products were isolated: 4-phenyl- or (3-pyridyl)-4-(2-naphthylamino or 6-quinolylamino)butan-2-ones.

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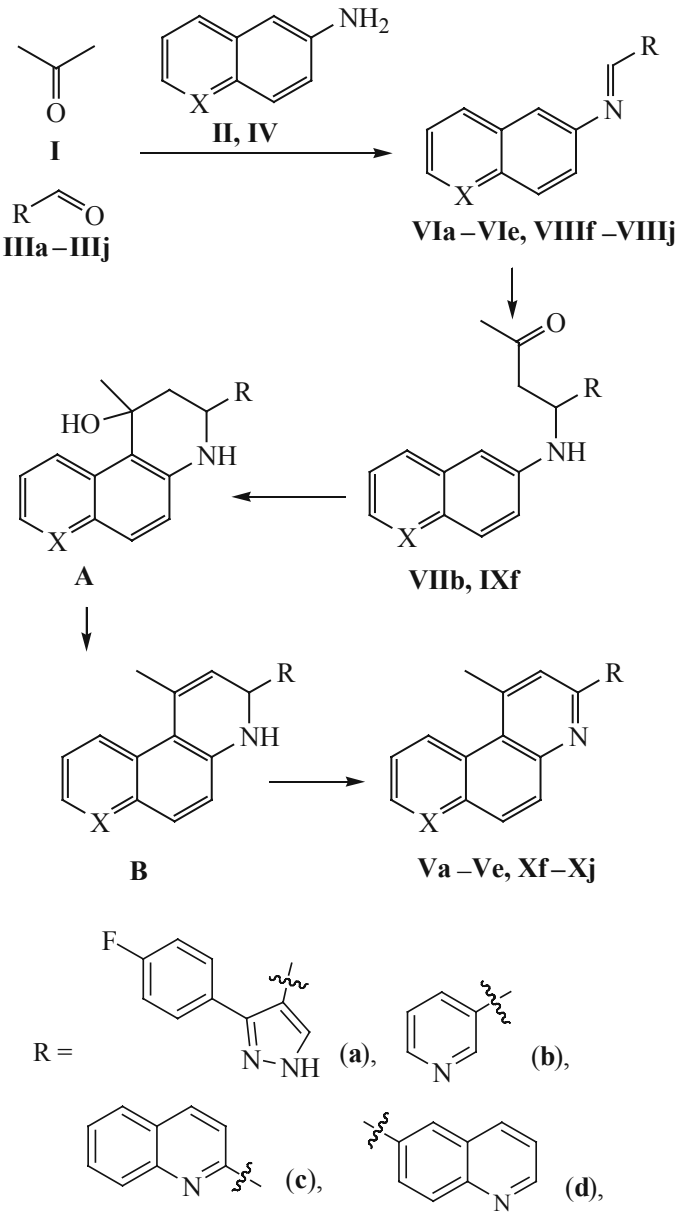
The interest to methyl derivatives of aza- and diazaphenanthrene is due to the high and versatile biological activity inherent to a number of members of this class compounds [1, 2], and also the opportunity of their application to the synthesis of difficultly available and therefore poorly understood aldehydes, styryls, and dyes of the aza- and diazaphenanthrene series [3–6].

The known method of the preparation of methyl-substituted nitrogen heterocycles consisting in a reaction of an aromatic amine with α,β-unsaturated carbonyl compounds (methyl vinyl ketone,crotonaldehyde) or their precursors (acetone, formaldehyde, paraformaldehyde) (Doebner–Miller procedure) did not find extensive application in the synthesis of azaphenanthrenes proceeding from naphthyl- or quinolylamines due to the low yield of the target products caused by the low activity of the initial amines in this reaction and by prevalence of condensations and polymerization of the initial carbonyl compounds.

We showed in [7] that the three-component condensation of acetone, aromatic aldehydes, and 2-naphthylamine led to the formation of 3-aryl-1-methylbenzo[*f*]quinolines, and therewith the acetone molecule provided the methyl group to the structure of the azaheterocycle. The variation of two other components of the reaction mixture, aldehyde and amine, provides an opportunity to obtain previously unknown methyl-substituted azaphenanthrenes, potential biologically active compounds and key intermediates in the synthesis of new heterocycles with practically useful properties.

In this study we for the first time brought into the condensation with acetone (**I**) and 2-naphthylamine (**II**) aldehydes of the heterocyclic series, 3-(4-fluorophenyl)-*1H*-pyrazole-4-carbaldehyde (**IIIa**), pyridine-3- (**IIIb**), quinoline-2- (**IIIc**), quinoline-6-carbaldehyde (**IIId**), and also 4-(2-fluorobenzyloxy)benzaldehyde (**IIIe**). Besides in the condensation of acetone (**I**) and substituted benzaldehydes **IIIf–IIIj** we for the first time investigated a heterocyclic amine, 6-aminoquinoline (**IV**).

The condensation of acetone (**I**), 2-naphthylamine (**II**), and aldehydes **IIIa–IIIe** was carried out by boiling the reagents in ethanol solution in the presence of concn. HCl. Thus we obtained in 35–50% yield previously unknown 3-heteryl-1-methylbenzo[*f*]quinolines **Va–Vd** and 1-methyl-3-[4-(2-fluorobenzyloxy)phenyl]benzo[*f*]-quinoline (**Ve**). In keeping with previous studies [8, 9] the reaction proceeds via the stage of azomethine **VIa–VIe** formation that further reacts with methyl ketone by the known mechanism [9] with the addition of the CH-acid to the C=N bond of the azomethine, the cyclization of the adduct **VII** obtained involving the C^1 atom of the naphthalene skeleton, the subsequent dehydration of cyclic alcohol **A,** and the dehydrogenation of dihydro derivative **B** into tolally aromatic benzo[*f*]quinoline **Va–Ve**. In the presence of the catalyst (HCl) benzo[*f*]-quinoline hydrochlorides were obtained that were



4-$C_6H_4CH_2O(2\text{-}FC_6H_4)$ (**e**), Ph (**f**), 4-FC_6H_4 (**g**), 4-ClC_6H_4 (**h**), 4-BrC_6H_4 (**i**), 4-HOC_6H_4 (**j**); X = CH (**II, V–VII**), N (**IV**, **VIII–X**).

converted into free bases **Va–Ve** by treating with ammonium hydroxide.

To prove the involvement of azomethines in the process of building benzoquinoline structure we performed the condensation of amine **II** with aldehydes **IIIa–IIIe**, and brought the obtained Schiff bases **VIa–VIe** into the condensation with acetone under the above described conditions. As a result of the reaction the methylbenzoquinolines **Va–Ve** cleanly formed in 42–56% yields.

The reaction carried out under mild conditions (without heating) by maintaining the reaction mixture at room temperature for 24 h or at heating for 10–15 min at 40–60°C in the presence of a minimal quantity of the catalyst (2–3 drops of concn. HCl per 10 mmol of reagent) 3-pyridinecarbaldehyde (**IIIb**), and also its azomethine **VIb** was converted into an intermediate reaction product, aminoketone **VIIb** that at boiling in ethanol in the presence of concn. HCl gave 1-methyl-3-(3-pyridyl)-benzo[*f*]quinoline (**Vb**). Quinolinecarbaldehydes, substituted pyrazole and benzaldehyde **IIIa, IIIc–IIIe**, and also the corresponding azomethines **VIa, VIc–VIe** in the temperature range 20–60°C do not react with acetone apparently because of the larger volume of substituent R and sterical hindrances to the ketone interaction with the Schiff base. This components were involved into the reaction only at the boiling point of the solvent (80°C), but we failed to isolate intermediate products in this case since they were fast converted into final reaction products **Va, Vc–Ve**.

The condensation of acetone (**I**) with arylaldehydes **IIIf–IIIj** and 6-quinolylamine (**IV**) proceeding by analogous scheme required more stringent conditions. At heating for 1–2 h to 60°C in ethanol in the presence of concn. HCl acetone reacted only with benzaldehyde **IIIf** and 6-quinolylamine (**IV**) or with benzylidene-6-quinolylamine (**VIIIf**), and the reaction stopped here at the stage of aminoketone **IXf** formation. The cyclization of the aminoketone into a derivative of diazaphenanthrene series, 1-methyl-3-phenyl-4,7-phenanthroline (**Xf**), occurred at boiling in ethanol for 6 h in the presence of enhanced amount of the catalyst. Under these conditions the substituted benzaldehydes **IIIg–IIIj** reacted with amine **IV** and acetone forming the corresponding 3-aryl-1-methyl-4,7-phenanthrolines **Xg–Xj** in 22–28% yield. The prolonged heating required for this condensation and the lower yield of the reaction products **Xg–Xj** compared with **Va–Ve** indicated the worse reactivity of 6-quinolylamine than that of 2-naphthylamine caused evidently by decreased nucleophilic activity of the amino group due to the electronegativity of the nitrogen in the quinoline ring of amine **IV**. Bringing into the condensation with acetone preliminary prepared arylmethylene-6-quinolylamines **VIIIg–VIIIj** increased the yield of 4,7-phenanthrolines **Xg–Xj** to 32–38%, but it is still lower than that of the mononitrogen analogs (40–74%) [7] obtained proceeding from 2-naphthylamine also due to the presence of the heterocyclic nitrogen in the molecule of the Schiff bases

VIIIg–VIIIj reducing the polarization and chemical activity of the azomethine bond.

In the IR spectra of aza- and diazaphenanthrenes **Va–Ve** and **Xf–Xj** absorption bands are observed in the region 3070–3030 cm^{-1} [H(C–H)] and 875–865, 840–835, 770–755 cm^{-1} [δ(C–H)]. The secondary amino group present in the pyrazole ring of compound **Va** appeared as a strong band [H(NH)] at 3200 cm^{-1}. In the spectrum of benzoquinoline **Ve** a strong band is observed in the region 1235–1230 cm^{-1} corresponding to the stretching vibrations of the ether bond in the benzoxyphenyl substituent. In the IR spectra of open-chain precursors **VIIb** and **IXf** characteristic bands of the stretching vibrations of carbonyl and amino group are observed respectively at 1695–1650 and 3365–3360 cm^{-1} disappearing after dehydrocyclization the aminoketones into the corresponding azaheterocycles **Vb** and **Xf**.

In the mass spectra of azaphenanthrenes **Va–Ve** and **Xf–Xj** the molecular ion peaks $[M]^+$ are the most abundant (100%), the peaks of fragment ions $[M - H]^+$ and $[M - 2H]^+$ (I_{rel} 23–44%) and peaks of low intensity (I_{rel} 10–14%) $[M - HCN]^+$, $[M - H - HCN]^+$ are characteristic of the nitrogen heteroaromatic compounds.

In the mass spectra of aminoketones **VIIb** and **IXf** the intensity of the molecular ion peak (*m/z* 290) is relatively low (20–22%). The most abundant (100%) are peaks of *m/z* 232 and 56 corresponding to compounds **IVb**, **VIIIf**, and **I** resulting from the rupture of C–C bond and recombination of the fragment ions with a simultaneous disproportionation.

Electron absorption spectra of compounds **Va–Ve** and **Xf–Xj** in the UV region (220–365 nm) have a structure characteristic of benzo[*f*]quinolines and 4,7-phenanthrolines [8, 10]. The long-wave band (331–365 nm) is interpreted as the Clar α-band (L_b according to Platt). In the spectra of benzoquinolines **Va, Vc**, and **Vd** this band suffered a red shift compared to the previously investigated spectra of azaphenanthrenes [8, 10] evidently because of the increased conjugation chain resulting from the introduction of fluorophenylpyrazoline or quinoline substituent. More short-wave bands in the region 281–293 and 220–263 nm are *p*- and β-bands (L_a and B_b) respectively, and the *p*-band is stronger than the β-band, which is characteristic of compounds of angular structure: phenanthrene and its heterocyclic analogs.

In the ^{1}H NMR spectra of compounds **Va–Ve** the protons of the methyl group appear as a singlet at 3.00–3.13 ppm, signals of the aromatic protons are observed in the range 6.60–8.85 ppm. In the spectrum of benzoquinoline **Va** the proton of the NH group and the methine proton of the pyrazoline ring gave rise respectively to a broadened singlet at 13.30 ppm and a singlet at 8.35 ppm. In the spectrum of compound **Ve** the methylene protons of the 2-fluorobenzyloxy group appear as a singlet at 5.22 ppm.

In the ^{1}H NMR spectra of aminoketones **VIIb** and **IXf** alongside the signals of methyl group protons at 3.00–3.01 ppm and of aromatic (heteroaromatic) protons in the range 6.72–8.59 ppm signal is present of methylene protons at 3.44–3.51 ppm and a broadened singlet from the proton of the amino group at 4.84–4.93 ppm. The signal of methine proton at the central carbon atom linked to amine, aryl (heteryl), and acetyl fragments is observed as a multiplet at 5.11–5.14 ppm.

The ^{1}H NMR spectra of compounds **Xf–Xj** were interpreted considering the spectral studies on 1,3-diaryl-4,7-phenanthrolines published in [11]. Owing to the poor solubility of methyl derivatives **Xf–Xj** in organic solvents the spectra of the compounds were registered in CF_3COOD. Therefore compared to the spectra of benzoquinolines **Va–Ve** registered in DMSO-d_6 in the spectra of methyl-substituted 4,7-phenanthrolines **Xf–Xj** all the signals suffered a downfield shift caused by the appearance of a positive charge on the nitrogen atoms of the phenanthroline ring due to D^+ addition. The considerable downfield shift of signals from protons H^9 and H^{10} observed in the spectra of methylphenanthrolines **Xf–Xj** as compared to the spectra of 1,3-diaryl-4,7-phenanthrolines [11] where these protons are located under the phenyl ring plane is evidently caused by the anisotropic deshielding resulting from replacement of the arylsubstituent by the methyl group.

EXPERIMENTAL

IR spectra were recorded on a Fourier spectrophotometer Nicolet Protégé-460 from pellets with KBr. Mass spectra were measured on a Finnigan MAT INCOS 50 instrument with the energy of ionizing electrons 70eV, and on a GC-MS device HP 5890/5972 in the electron impact mode at the energy 70eV; column HP-5MS (30 m...0.25 mm, stationary phase film 5% PLMe Silicone, 0.25 μm); vaporizer temperature 250°C. UV spectra of compounds solutions in ethanol (c 10^{-4} mol l^{-1}) were taken on a spectrophotometer Specord UV-Vis. NMR spectra were registered on spectrometers Bruker AC-500 (500 MHz) and Tesla BS-567 (100 MHz) in DMSO-d_6

and CF_3COOD, internal reference TMS. Melting points of compounds were measured on a Koeffler heating block.

Aryl(heteryl)methylene-2-naphthylamines **VIa–VIe** and arylmethylene-6-quinolylamines **VIIIf–VIIIj** were prepared by procedure [12].

3-Aryl(heteryl)-1-methylbenzo[*f*]quinolines Va–Ve. *a*. A mixture of 10 mmol of acetone (**I**), 5 mmol of 2-naphthylamine (**II**), 5 mmol of an appropriate aldehyde **IIIa–IIIe**, 20 ml of ethanol, and 0.5 ml of concn. HCl was boiled for 2 h. On cooling the separated precipitate was filtered off, neutralized with 25% aqueous NH_4OH, washed with water, and recrystallized from a mixture ethanol–benzene, 3:1.

b. A solution of 10 mmol of acetone (**I**), 5 mmol of azomethine **VIa–VIe**, 20 ml of ethanol, and 0.5 ml of concn. HCl was boiled for 1.5 h. Reaction products **Va–Ve** were isolated as described above.

1-Methyl-3-[3-(4-fluorophenyl)-1*H*-pyrazol-4-yl]-benzo[*f*]quinoline (Va). Yield 50% (*a*), 56% (*b*), mp 245–246°C. UV spectrum, λ_{max}, nm (log ε): 225 (4.61), 263 (4.59), 282 (4.74), 336 (3.70), 365 (3.80). ^{1}H NMR spectrum, δ, ppm: 3.05 s (3H, Me), 6.60–7.98 m, 8.80 m ($11H_{arom}$), 8.35 s (1H, =CH–NH), 13.30 br.s (1H, =CH–NH). Found, %: N 11.73. $C_{23}H_{16}FN_3$. Calculated, %: N 11.90.

1-Methyl-3-(3-pyridyl)benzo[*f*]quinoline (Vb). Yield 43% (*a*), 49% (*b*), mp 183–184°C. UV spectrum, λ_{max}, nm (log ε): 220 (4.58), 259 (4.53), 281 (4.80), 331 (3.98), 358 (3.86). ^{1}H NMR spectrum, δ, ppm: 3.00 s (3H, Me), 7.01–8.19 m, 8.24 s, 8.74 s, 8.81 m ($11H_{arom, heteroarom}$). Found, %: C 84.19; H 5.03; N 10.40. $C_{19}H_{14}N_2$. Calculated, %: C 84.44; H 5.19; N 10.37.

1-Methyl-3-(2-quinolyl)benzo[*f*]quinoline (Vc). Yield 38% (*a*), 44% (*b*), mp 187–188°C. UV spectrum, λ_{max}, nm (log ε): 226 (4.51), 259 (4.49), 291 (4.78), 340 (3.88), 359 (3.81). ^{1}H NMR spectrum, δ, ppm: 3.04 s (3H, Me), 7.11–8.63 m, 8.85 m ($13H_{arom, heteroarom}$). Found, %: C 86.02; H 4.81; N 8.64. $C_{23}H_{16}N_2$. Calculated, %: C 86.25; H 5.00; N 8.75.

1-Methyl-3-(6-quinolyl)benzo[*f*]quinoline (Vd). Yield 35% (*a*), 40% (*b*), mp 170–171°C. UV spectrum, λ_{max}, nm (log ε): 223 (4.52), 255 (4.41), 286 (4.73), 339 (3.91), 357 (3.68). ^{1}H NMR spectrum, δ, ppm: 3.02 s (3H, Me), 7.00–8.22 m, 8.64 m, 8.80 m ($13H_{arom, heteroarom}$). Found, %: C 86.11; H 4.76; N 8.59. $C_{23}H_{16}N_2$. Calculated, %: C 86.25; H 5.00; N 8.75.

1-Methyl-3-[4-(2-fluorobenzyloxy)phenyl]benzo-[*f*]quinoline (Ve). Yield 45% (*a*), 46% (*b*), mp 135–136°C. UV spectrum, λ_{max}, nm (log ε): 222 (4.60), 261 (4.58), 290 (4.83), 339 (4.02), 360 (3.91). ^{1}H NMR spectrum, δ, ppm: 3.13 s (3H, Me), 5.22 s (2H, OCH_2), 7.10 d, 7.20 m, 7.60 m, 7.70 s, 7.96 m, 8.15 d, 8.78 m ($15H_{arom}$, ^3J 7.4 Hz). Found, %: N 3.28. $C_{27}H_{20}FNO$. Calculated, %: N 3.56.

4-(3-Pyridyl)-4-(2-naphthylamino)butan-2-one (VIIb). A solution of 10 mmol of acetone (**I**), 5 mmol of 2-naphthylamine (**II**), and 5 mmol of 3-pyridinecarbaldehyde (**IIIb**) (*a*) or 10 mmol of ketone **I** and 5 mmol of N-(pyridin-3-ylmethylene)-2-naphthalenamine (**VIb**) (*b*) in 20 ml of ethanol with 2 drops of concn. HCl was maintained for 24 h at room temperature or was heated on a water bath at 40–60°C for 15 min. The separated precipitate was filtered off, treated with 25% water solution of NH_4OH, washed with water, and recrystallized from ethanol. Yield 44% (*a*) and 51% (*b*), mp 164–165°C. ^{1}H NMR spectrum, δ, ppm: 3.01 s (3H, Me), 3.44 m (2H, CH_2), 4.93 br.s (1H, NH), 5.14 m (1H, CH), 6.72–7.98 m, 8.65 s ($11H_{arom, heteroarom}$). Found, %: C 78.54; H 5.93; N 9.48. $C_{19}H_{18}N_2O$. Calculated, %: C 78.62; H 6.21; N 9.66.

4-Phenyl-4-(6-quinolylamino)butan-2-one (IXa). A solution of 10 mmol of acetone (**I**), 5 mmol of benzaldehyde (**IIIf**), and 5 mmol of 6-quinolylamine (**IV**) (*a*) or 10 mmol of ketone **I** and 5 mmol of *N*-(benzylidene)-6-quinolinamine (**VIIIf**) (*b*) in 20 ml of ethanol with 5 drops of concn. HCl was heated on a water bath at 60°C for 2 h. The reaction product was isolated in the same way as described for aminoketone **VIIb**. Yield 40% (*a*) and 43% (*b*), mp 177–178°C. ^{1}H NMR spectrum, δ, ppm: 3.00 s (3H, Me), 3.51 m (2H, CH_2), 4.84 br.s (1H, NH), 5.11 m (1H, CH), 6.76–7.80 m, 8.59 d.d ($11H_{arom, heteroarom}$, ^3J 4.8, ^4J 2.4 Hz). Found, %:C 78.43; H 5.88; N 9.51. $C_{19}H_{18}N_2O$. Calculated, %: C 78.62; H 6.21; N 9.66.

3-Aryl-1-methyl-4,7-phenanthrolines Xf–Xj. *a*. A mixture of 10 mmol of acetone (**I**), 5 mmol of an appropriate aldehyde **IIIf–III**j, 5 mmol of 6-quinolylamine (**IV**), 20 ml of ethanol, and 1 ml of concn. HCl was boiled for 7 h. On cooling the separated precipitate was filtered off, neutralized with 25% aqueous NH_4OH, washed with water, and recrystallized from a mixture ethanol–benzene, 2:1.

b. A solution of 10 mmol of acetone (**I**), 5 mmol of azomethine **VIIIf–VIIIj**, 20 ml of ethanol, and 1 ml of concn. HCl was boiled for 7 h. Reaction products **Xf–Xj** were isolated as described above.

1-Methyl-3-phenyl-4,7-phenanthroline (Xf). Yield 28% (*a*), 38% (*b*), mp 170–171°C. UV spectrum, λ_{max}, nm (log ε): 223 (4.21), 253 (4.42), 283 (4.60), 337 (3.82), 350 (3.77). ^{1}H NMR spectrum, δ, ppm: 3.63 s (3H, Me), 7.56 m, 7.89 m (5H, Ph), 8.62 m (2H, H^2, H^9) 8.94 d, 9.03 d (2H, H^{5,6}, ^3J 8.9 Hz), 9.45 d (1H, H^8, ^3J 4.9 Hz), 10.40 d (1H, H^{10}, ^3J 8.0 Hz). Found, %: C 84.32; H 4.97; N 10.21. $C_{19}H_{14}N_2$. Calculated, %: C 84.44; H 5.19; N 10.37.

1-Methyl-3-(4-fluorophenyl)-4,7-phenanthroline (Xg). Yield 24% (*a*), (34%) (*b*), mp 181–182°C. UV spectrum, λ_{max}, nm (log ε): 225 (4.33), 253 (4.56), 286 (4.68), 338 (3.46), 355 (3.37). ^{1}H NMR spectrum, δ, ppm: 3.65 s (3H, Me), 7.52 m, 8.24 m (4H$_{arom}$), 8.63 m (2H, H^2, H^9) 8.98 d, 9.10 d (2H, H^{5,6}, ^3J 9.0 Hz), 9.50 d (1H, H^8, ^3J 4.8 Hz), 10.44 d (1H, H^{10}, ^3J 8.1 Hz). Found, %: N 9.54. $C_{19}H_{13}FN_2$. Calculated, %: N 9.72.

1-Methyl-3-(4-chlorophenyl)-4,7-phenanthroline (Xh). Yield 27% (*a*), 37% (*b*), mp 216–217°C. UV spectrum, λ_{max}, nm (log ε): 227 (4.24), 255 (4.47), 288 (4.62), 339 (3.45), 356 (3.29). ^{1}H NMR spectrum, δ, ppm: 3.65 s (3H, Me), 7.83 d, 8.11 d (4H$_{arom}$, ^3J 7.9 Hz), 8.62 d.d (1H, H^9, ^3J 7.8, ^4J 4.3 Hz), 8.65 s (1H, H^2), 8.98 d, 9.09 d (2H, H^{5,6}, ^3J 8.8 Hz), 9.48 d (1H, H^8, ^3J 4.3 Hz), 10.43 d (1H, H^{10}, ^3J 7.8 Hz). Found, %: C 74.61; H 4.12; Cl 11.41; N 9.04. $C_{19}H_{13}ClN_2$. Calculated, %: C 74.88; H 4.27; Cl 11.66; N 9.20.

3-(4-Bromophenyl)-1-methyl-4,7-phenanthroline (Xi). Yield 22% (*a*), 33% (*b*), mp 183–184°C. UV spectrum, λ_{max}, nm (log ε): 230 (4.28), 256 (4.45), 290 (4.64), 339 (3.95), 362 (3.89). ^{1}H NMR spectrum, δ, ppm: 3.63 s (3H, Me), 7.79 d, 8.14 d (4H$_{arom}$, ^3J 7.8 Hz), 8.61 d.d (1H, H^9, ^3J 8.0, ^4J 4.1 Hz), 8.64 s (1H, H^2), 8.94 d, 9.05 d (2H, H^{5,6}, ^3J 8.9 Hz), 9.49 d (1H, H^8, ^3J 4.1 Hz), 10.42 d (1H, H^{10}, ^3J 8.0 Hz). Found, %: C 65.19; H 3.76; Br 22.63; N 7.79. $C_{19}H_{13}BrN_2$. Calculated, %: C 65.33; H 3.82; Br 22.92; N 8.02.

3-(4-Hydroxyphenyl)-1-methyl-4,7-phenanthroline (Xj). Yield 23% (*a*), 32% (*b*), mp 312–313°C. UV spectrum, λ_{max}, nm (log ε): 236 (4.55), 255 (4.563), 290 (4.69), 320 (4.39), 360 (3.76). ^{1}H NMR spectrum, δ, ppm: 3.66 s (3H, Me), 7.38 d, 8.18 d (4H$_{arom}$, ^3J 7.6 Hz), 8.60 m (2H, H^2, H^9), 8.92 d, 9.02 d (2H, H^{5,6}, ^3J 9.1 Hz), 9.44 d (1H, H^8, ^3J 4.4 Hz), 10.40 d (1H, H^{10}, ^3J 8.1 Hz). Found, %: C 79.57; H 4.81; N 9.63. $C_{19}H_{14}N_2O$. Calculated, %: C 79.72; H 4.90; N 9.79.

Cyclization of aminoketones VIIb and IXf. A mixture of 2.5 mmol of aminoketone **VIIb** or **IXf**, 0.5–1.0 ml of concn. HCl, and 20 ml of ethanol was boiled for 2 h for compound **VIIb** or 6 h for aminoketone **IXf**. The precipitate was worked up as described for compounds **Vb** and **Xf**. Yield of benzo-[*f*]quinoline **Vb** 52%, 4,7-phenanthroline **Xf** 34%.

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REFERENCES

1. Berger, D., Fey, G., Kuhr, M., and Werner, W., EPV Patent 14929, 1980; *Chem. Abstr*., 1981, vol. 94, 43719z
2. Wei, N., Xiaoying, W., and Yulin, Y., *Zhonngguo, Yaolixue, Tongbao*, 1996, vol. 12, p. 354; *Chem. Abstr*., 1997, vol. 126, 99038y.
3. Jastzebska-Glapa, M., Mlochowski, J., and Sliwa, W., *J. Prakt. Chem*., 1977, vol. 319, p. 883.
4. Konyukhov, V.N., P'yankova, L.N., and Pushkareva, Z.V., *Zh. Obshch. Khim.,* 1962, vol. 32, p. 2745.
5. El'tsov, A.V., Nekrasov, S.V., Smirnov, E.V., *Zh. Org. Khim.,* 1972, vol. 8, p. 1309.
6. Mikhailenko, F.A. and Boguslavskaya, A.P., *Ukr. Khim. Zh*., 1971, vol. 37, p. 1031.
7. Kozlov, N.G. and Basalaeva, L.I., *Zh. Org. Khim.,* 2003, vol. 39, p. 765.
8. Gusak, K.N. and Kozlov, N.G., *Zh. Org. Khim.,* 2007, vol. 43, p. 711.
9. Kozlov, N.C., Vorob'eva, G.V., and Bychkova, G.S., *Izv. Akad. Nauk BSSR, Ser. Khim. Nauk*, 1969, p. 796.
10. Kozlov, N.S., Gusak, K.N., Serzhanina, V.A., Gladchenko, L.F., and Krot, N.A., *Khim. Geterotsikl. Soedin*., 1987, p. 1651.
11. Gusak, K.N. and Kozlov, N.G., *Zh. Obshch. Khim.,* 2003, vol. 73, p. 1018.
12. Gusak, K.N., Tereshko, A.B., and Kozlov, N.G., *Zh. Obshch. Khim.,* 2000, vol. 70, p. 320.