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Condensation of Quinolin-6-amine with 5-(*p*-Methoxyphenyl)-cyclohexane-1,3-dione and Substituted Benzaldehydes

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Abstract—New 12-aryl-9-(*p*-methoxyphenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-ones having two asymmetric carbon atoms (C^9 and C^{12}) were synthesized by three-component condensation of quinolin-6-amine with 5-(*p*-methoxyphenyl)cyclohexane-1,3-dione and substituted benzaldehydes. According to the ^{1}H NMR data, the products are mixtures of diastereoisomers.

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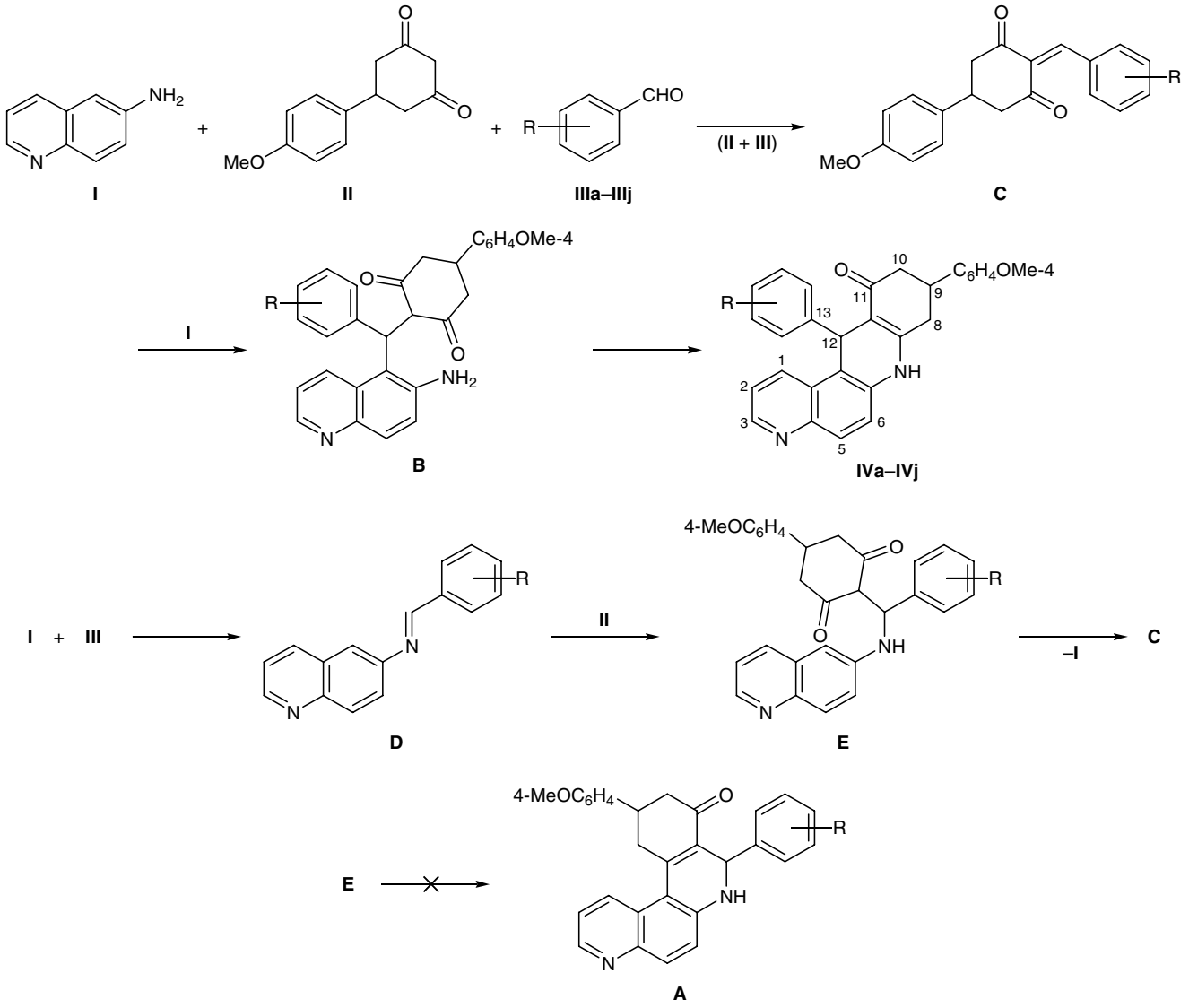
Three-component condensations of aromatic amines with aldehydes and CH acids are widely used in the synthesis of fused heterocycles of the aza- and diazaphenanthrene series, which attract interest as potential biologically active compounds [1–4]. Among the CH acids involved in these condensations, specific attention is given to cyclic β-dicarbonyl compounds, in particular derivatives of cyclohexane-1,3-dione (dihydroresorcinol) whose high reactivity originates from the presence of enolizable carbonyl groups and adjacent methylene groups. We previously showed that cyclohexane-1,3-dione and 5-phenylcyclohexane-1,3-dione react with quinolin-6-amine and substituted aromatic aldehydes to give fused 4,7-phenanthrolinone derivatives [5, 6].

With a view to synthesize new representatives of this class of compounds, in the present work we were the first to examine the condensation of quinolin-6-amine (**I**) with 5-(*p*-methoxyphenyl)cyclohexane-1,3-dione (**II**) (which was prepared from diethyl malonate and *p*-methoxybenzylideneacetone according to the procedure reported in [7]), and aromatic aldehydes **IIIa**–**IIIj**. The latter included benzaldehyde, 4-methoxybenzaldehyde, 3,4-dihydroxybenzaldehyde, 2,4- and 3,4-dimethoxybenzaldehydes, 4-hydroxybenzaldehyde, methyl 4-formylbenzoate, 4-hydroxy-3-methoxybenzaldehyde, and methyl 4-formyl-2-methoxybenzoate. These aldehydes are either naturally occurring compounds or available from natural sources and are accessible and low-toxic reagents. The use of 5-(4-methoxyphenyl)cyclohexane-1,3-dione in the condensation ensures introduction into the resulting fused heterocycle of a methoxy group that constitutes an important structural fragment of many alkaloids [8, 9]. Substituted benzaldehydes endow the products with other pharmacophoric groups, such as acetoxy, hydroxy, and methoxycarbonyl, which extend the spectrum of biological activity of 4,7-phenanthroline derivatives [10, 11].

The condensation was carried out by heating equimolar mixtures of the reactants in butyl alcohol in the absence of a catalyst. As follows from the results of previous studies [2–6], three-component condensations of compounds **I**, **II**, and **IIIa**–**IIIj** could give rise to two kinds of products, 5-aryl-2-(*p*-methoxyphenyl)-1,2,3,4,5,6-hexahydrobenzo[*a*][4,7]phenanthrolin-4-ones like **A** and 12-aryl-9-(*p*-methoxyphenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-ones **IVa**–**IVj**. Detailed analysis of the ^{1}H NMR spectra of the isolated products showed that their structure is similar to the structure of the condensation products obtained previously from quinolin-6-amine, aromatic aldehydes, and cyclohexane-1,3-dione [5, 6], i.e., they are benzo[*b*][4,7]phenanthrolin-11-one derivatives **IV** (Scheme 1).

The benzo[*b*][4,7]phenanthrolinone system arises from intramolecular cyclization of intermediate aminodiketone **B** which can be formed along two pathways.

Scheme 1.



R = H (**a**), 4-HO (**b**), 3,4-$(HO)_2$ (**c**), 2-MeO (**d**), 4-MeO (**e**), 2,4-$(MeO)_2$ (**f**), 3,4-$(MeO)_2$ (**g**), 3-MeO-4-HO (**h**), 3-MeO-4-MeCOO (**i**), 4-MeOCO (**j**).

According to the first of these, initial reaction of diketone **II** with aldehyde **III** gives 2-arylmethylidenecyclohexan-1,3-dione **C** which takes up quinolin-6-amine (**I**) molecule at the exocyclic double bond via attack by the electron-rich carbon atom in position *5* of the quinoline ring of **I**. An alternative pathway includes initial condensation of amine **I** with aldehyde **III** to produce Schiff base **D**; the subsequent addition of dione **II** at the C=N bond of Schiff base **D** gives aminodiketone **E**. The latter in alcoholic medium undergoes hydramine splitting into initial quinolin-6-amine (**I**) and 2-arylmethylidenecyclohexane-1,3-dione **C**, and the reaction then follows the same path as above. Taking into account the known ability of aminoketones like **E** to undergo hydramine splitting in acidic alcoholic medium [12] and ready reactions of Schiff bases with CH acids to form phenanthrolines [13], we believe that the second pathway is the most probable. Here, enolized β-diketone **II** acts as acid catalyst.

Another theoretically possible cyclization version of the adduct derived from Schiff base and CH acid, as in reactions of *N*-arylmethylideneamines with cyclic ketones [2, 14], did not occur in the condensation of aminoquinoline **I** with diketone **II** and aldehydes **IIIa**–**IIIj**, and benzo[*a*][4,7]phenanthroline derivatives like **A** were not detected in the reaction mixtures even in

trace amounts. Martinez et al. [4] interpreted the migration of the arylmethylidenecyclohexanedione fragment in the three-component condensation of naphthalen-2-amine with aldehydes and 5,5-dimethylcyclohexane-1,3-dione (dimedone) as rearrangement of intermediate aminodiketone **E** ($CHC_6H_4OMe \equiv CMe_2$), which is analogous to the Hoffmann–Martius rearrangement of *N*-alkyl- and *N*,*N*-dialkylanilines hydrohalides and trialkyl(phenyl)ammonium salts on heating [15].

The yield of benzo[*b*][4,7]phenanthrolinones **IVa**–**IVj** depends to some extent on the substituent R in the aldehyde component. Benzaldehydes **IIIi** and **IIIj** having electron-withdrawing groups (CO_2Me, AcO; *–M* effect) in the *para* position or hydroxy compounds **IIIb**, **IIIc**, and **IIIh** (*–I* effect) give rise to 76–80% of the corresponding phenanthrolines. Introduction of a methoxy group (*–I*, *+M* effect) into the *para* position of the benzene ring reduces the yield of phenanthrolines **IVe** and **IVg** to (62–64%) due to weakening of the reactivity of the aldehyde carbonyl group. However, the yields of phenanthrolines **IVd** and **IVf** from 2-methoxy- and 2,4-dimethoxybenzaldehydes **IIId** and **IIIf** are fairly high (86–89%) despite steric effect of the *ortho* substituent. Presumably, the *ortho*-methoxy group in aldehydes **IIId** and **IIIf** activates them via the *–I* effect most strongly due spatial proximity of the substituent to the reaction center.

Benzo[*b*][4,7]phenanthrolinone derivatives **IVa**–**IVj** are colorless or light yellow high-melting substances. They showed in the IR spectra strong absorption bands at 1600–1580 and 1520–1515 cm^{-1}, which should be attributed to the vinylogous amide fragment (1580, 1520 cm^{-1}) [4]. Stretching vibrations of alkyl and cycloalkyl C–H bonds appear in the region 2960–2880 cm^{-1}, and aromatic C–H bonds give rise to absorption at 3060–3040 cm^{-1}. A strong band at 1240–1230 cm^{-1} corresponds to the ether and ester C–O–C fragments. In the IR spectra of phenanthrolines **IVi** and **IVj** we observed a strong absorption band at 1755 and 1740 cm^{-1}, respectively, due to stretching vibrations of the ester carbonyl group.

The ^1H NMR spectra of **IVa**–**IVj** in the resonance regions corresponding to protons of the benzophenanthroline skeleton and aryl substituent resemble those reported previously for the condensation products of quinolin-6-amine with cyclohexane-1,3-dione and aromatic aldehydes [5]; the latter were unambiguously assigned the structure of benzo[*b*][4,7]phenanthrolinones rather that isomeric structure **A**. Analysis of two-dimensional ^1H and ^{13}C NMR spectra using COSY, NOESY, HSQC, and HMBS techniques showed coupling between the NH proton and C^8; such a coupling is impossible in structure **A**. In addition, no coupling was observed between 7-H, on the one hand, and C^{12} and C^{13}, on the other, though such coupling should occur in structure **A**. The ^1H NMR spectra of **IVa**–**IVj** contain a signal at δ 3.64–3.89 ppm from protons of the methoxy group, and the presence of methoxy group in the *para* position leads to extension of the upfield part of the corresponding aromatic multiplet.

As follows from the spectral pattern in the aliphatic proton region, isolated compounds **IVa**–**IVj** are mixtures of two stereoisomers with pseudoequatorial and pseudoaxial orientation of the methoxyphenyl substituent on C^9 at a ratio of 2:1. The 9-H signal appears as two multiplets at δ 3.07–3.14 and 3.15–3.22 ppm; taking account their halfwidths, the upfield signal was assigned to the axial proton, and the downfield, to the equatorial. The halfwidth of the 9-H_{ax} signal is greater than that of the 9-H_{eq} signal since $J_{ax,ax'} \approx 9$ Hz is considerably larger than $J_{ax,eq'}$ and $J_{eq,eq'}$ (~6 Hz).

In the ^1H NMR spectra of diastereoisomer mixtures **IVa**–**IVj**, protons on the nitrogen atom and C^{12} resonated as singlets whose intensities corresponded to those of the signals from 9-H. The NH and 12-H protons in the isomer with axial orientation of the methoxyphenyl substituent on C^9 are shielded by the latter; therefore, their signals are located in a stronger field relative to the corresponding signals of the isomer with equatorial methoxyphenyl group. The methoxy group also gives rise to two singlets belonging to different diastereoisomers.

The substituent R almost does not affect the position of signals from protons in the phenanthroline fragment. A downfield shift of the 1-H signal was observed only for 2-methoxy- and 2,4-dimethoxyphenyl-substituted derivatives **IVd** and **IVf**, where shielding by the phenyl ring is weakened due to *–I* effect of the 2-methoxy group. These data can be regarded as an evidence in support of the assumed structure, for the 1-H proton in alternative structure **A** is distant from the aryl substituent. Analogous effects of substituents having electronegative atoms on the signal of 2-H (spatially close to the phenyl groups) were observed in the spectra of 1,3-diaryl-4,7-phenanthrolines [13].

Condensation product **IVa** derived from benzaldehyde (**IIIa**) was isolated as a mixture of colorless and brown crystals that can be readily separated both manually and by fractional crystallization from ethanol–benzene (1:3).

The electronic absorption spectra of compounds **IVa–IVj** are characterized by the presence of several maxima with clearly defined vibrational structure in the ultraviolet region, λ_{max}, nm: 203–205, 215–218, 246–248, 282–285, 294–298, 336–339, 377–381. Molecules **IVa–IVj** include four independent chromophores: quinoline ring, conjugated enone system, and two aryl substituents (R-phenyl and *p*-methoxyphenyl). We believe that the strong absorption bands at λ_{max} 203–205 and 246–248 nm and less intense band at λ_{max} 282–285 nm belong to the 6-aminoquinoline system [UV spectrum of **I**, λ_{max}, nm (log ε): 206 (4.08), 247 (4.35), 279 (3.59)]. Increased intensity of the first band and appearance of absorption bands at λ 215–218 and 297–298 nm in the spectra of phenanthrolines **IVa–IVj** are likely to result from the effect of the methoxyphenyl and R-phenyl substituents. According to [16], long-wave absorption bands (λ_{max} 337–339, 379–380 nm) originate from the presence of a carbonyl group. Substituents in the phenyl group of **IVa–IVj** almost do not affect the position and intensity of absorption bands in their electronic spectra.

Phenanthrolinones **IVa–IVj** showed the molecular ion peaks $[M]^+$ in the mass spectra with a relative intensity I_{rel} of 20 to 35%. The base peak (100%) in the mass spectra of **IVa–IVj** was that belonging to the $[M - C_6H_4R]^+$ ion (*m*/*z* 355). Also, a fairly abundant ion (I_{rel} 21–27%) with *m*/*z* 193 was present; it resulted from elimination of the *p*-$MeOC_6H_4CHCH_2CO$ fragment from $[M - C_6H_4R]^+$.

EXPERIMENTAL

The mass spectra (electron impact, 70 eV) were recorded on a Finnigan MAT INCOS-50 instrument and a Hewlett–Packard HP 5890/5972 GC–MS system (HP-5MS column, 5% of phenylmethylsilicone, 30 m× 0.25 mm, film thickness 0.25 μm; injector temperature 250°C). The IR spectra were obtained on a Nicolet Protege-460 spectrometer with Fourier transform. The ^{1}H NMR spectra were measured on Bruker AC-500 (500 MHz) and Tesla BS-567 (100 MHz) spectrometers from solutions in DMSO-d_6 using tetramethylsilane as internal reference. The melting points were determined on a Kofler hot stage.

5-(*p*-Methoxyphenyl)cyclohexane-1,3-dione (**II**) was synthesized according to [7].

12-Aryl-9-(4-methoxyphenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-ones IVa–IVj (*general procedure*). A solution of 5 mmol of quinolin-6-amine (**I**), 5 mmol of diketone **II**, and 5 mmol of the corresponding aldehyde **IIIa–IIIj** in 10 ml of butan-1-ol was heated for 3–4 h under reflux. The mixture was cooled, and the precipitate was filtered off, washed with diethyl ether to remove unreacted initial compounds, dried, and recrystallized from ethanol–benzene (1:3) (compounds **IVa–IVh**) or ethanol (**IVi**, **IVj**).

9-(4-Methoxyphenyl)-12-phenyl-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (IVa). Yield 72%. UV spectrum, λ_{max}, nm (log ε): 204 (4.60), 217 (4.69), 246 (4.37), 285 (4.08), 298 (4.14), 339 (4.01), 380 (3.92).

Axial isomer. mp 270–271°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.51 m (2H, 8-H), 2.85 m (2H, 10-H), 3.22 m (1H, 9-H), 3.70 s (3H, MeO), 5.83 s (1H, 12-H), 6.67–7.29 m (9H, H_{arom}), 7.33 d.d (1H, 2-H, ^3J = 7.9, ^4J = 2.9), 7.54 d and 7.88 d (1H each, 5-H, 6-H, ^3J = 8.8), 8.36 d (1H, 1-H, ^3J = 7.9), 8.69 d (1H, 3-H, ^3J = 4.9), 9.70 s (1H, NH). Found, %: C 80.27; H 5.39; N 6.24. $C_{29}H_{24}N_2O_2$. Calculated, %: C 80.56; H 5.56; N 6.48.

Equatorial isomer. mp 315–316°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.51 m (2H, 8-H), 2.85 m (2H, 10-H), 3.14 m (1H, 9-H), 3.74 s (3H, MeO), 5.90 s (1H, 12-H), 6.67–7.29 m (9H, H_{arom}), 7.33 d.d (1H, 2-H, ^3J = 7.9, ^4J = 2.9), 7.54 d and 7.88 d (1H each, 5-H, 6-H, ^3J = 8.8), 8.36 d (1H, 1-H, ^3J = 7.9), 8.69 d (1H, 3-H, ^3J = 4.9), 10.00 s (1H, NH). Found, %: C 80.32; H 5.27; N 6.41. $C_{29}H_{24}N_2O_2$. Calculated, %: C 80.56; H 5.56; N 6.48

12-(4-Hydroxyphenyl)-9-(4-methoxyphenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (IVb). Yield 84%, mp 273–274°C. UV spectrum, λ_{max}, nm (log ε): 205 (4.66), 218 (4.69), 247 (4.34), 283 (4.02), 296 (4.10), 337 (3.96), 378 (3.90). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.54 m (2H, 8-H), 2.87 m (2H, 10-H), 3.10 m and 3.19 m (1H, 9-H), 3.71 s and 3.76 s (3H, MeO), 5.70 s and 5.75 s (1H, 12-H), 6.50–7.40 m (9H, 2-H, H_{arom}), 7.52 d and 7.86 d (1H each, 5-H, 6-H, ^3J = 8.9), 8.34 d (1H, 1-H, ^3J = 7.9), 8.66 d (1H, 3-H, ^3J = 4.7), 8.87 s (1H, OH), 9.78 s and 9.87 s (1H, NH). Found, %: C 77.43; H 5.25; N 6.03. $C_{29}H_{24}N_2O_3$. Calculated, %: C 77.67; H 5.36; N 6.25.

12-(2,4-Dihydroxyphenyl)-9-(4-methoxyphenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (IVc). Yield 78%, mp 279–280°C. UV spectrum, λ_{max}, nm (log ε): 203 (4.60), 217 (4.65), 246 (4.32), 284 (4.00), 297 (4.01), 339 (3.91), 380 (3.88).

^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.53 m (2H, 8-H), 2.86 m (2H, 10-H), 3.12 m and 3.18 m (1H, 9-H), 3.70 s and 3.75 s (3H, MeO), 5.79 s and 5.85 s (1H, 12-H), 6.63–7.26 m (7H, H_{arom}), 7.34 d.d (1H, 2-H, ^3J = 7.7, ^4J = 2.8), 7.51 d and 7.80 d (1H each, 5-H, 6-H, ^3J = 9.0), 8.35 d (1H, 1-H, ^3J = 7.7), 8.62 d (1H, 3-H, ^3J = 4.5), 8.80 s (1H, OH), 8.89 s (1H, OH), 9.83 s and 9.94 s (1H, NH). Found, %: C 74.96; H 4.93; N 5.81. $C_{29}H_{24}N_2O_4$. Calculated, %: C 75.00; H 5.17; N 6.03.

12-(2-Methoxyphenyl)-9-(4-methoxyphenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (IVd). Yield 89%, mp 286–287°C. UV spectrum, λ_{max}, nm (logε): 205 (4.68), 218 (4.72), 247 (4.33), 285 (4.09), 296 (4.08), 338 (3.95), 381 (3.84). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.50 m (2H, 8-H); 2.88 m (2H, 10-H); 3.12 m and 3.18 m (1H, 9-H); 3.72 s and 3.74 s (3H, MeO); 2.50 m (2H, 11-H); 2.98 m (2H, 9-H); 3.31 m and 3.39 m (1H, 10-H); 3.70 s (3H, MeO); 3.78 s (3H, MeO); 5.19 s and 5.25 s (1H, 7-H); 6.44 m, 6.86 m, and 7.24 d (7H, H_{arom}, ^3J = 7.7); 7.42 d.d (1H, 2-H, ^3J = 7.9, ^4J = 4.2); 7.55 d and 7.61 d (1H each, 5-H, 6-H, ^3J = 9.1); 8.80 d (1H, 3-H, ^3J = 4.2); 8.88 d (1H, 1-H, ^3J = 7.9); 9.50 s and 9.55 s (1H, NH); 6.02 s and 6.08 s (1H, 12-H); 6.68–7.22 m (8H, H_{arom}); 7.38 d.d (1H, 2-H, ^3J = 8.0, ^4J = 2.9); 7.45 d and 7.80 d (1H each, 5-H, 6-H, ^3J = 9.1); 8.59 d (1H, 1-H, ^3J = 8.0); 8.65 d (1H, 3-H, ^3J = 4.5); 9.80 s and 9.86 s (1H, NH). Found, %: C 77.73; H 5.60; N 5.89. $C_{30}H_{26}N_2O_3$. Calculated, %: C 77.92; H 5.63; N 6.06.

9,12-Bis(4-methoxyphenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (IVe). Yield 62%, mp 261–262°C. UV spectrum, λ_{max}, nm (logε): 204 (4.67), 217 (4.68), 248 (4.34), 283 (4.13), 295 (4.10), 337 (3.98), 377 (3.82). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.51 m (2H, 8-H), 2.82 m (2H, 10-H), 3.07 m and 3.15 m (1H, 9-H), 3.60 s (3H, MeO), 3.71 s and 3.75 s (3H, MeO), 5.75 s and 5.81 s (1H, 12-H), 6.60–7.26 m (8H, H_{arom}), 7.38 d.d (1H, 2-H, ^3J = 8.1, ^4J = 2.8), 7.50 d and 7.82 d (1H each, 5-H, 6-H, ^3J = 9.0), 8.30 d (1H, 1-H, ^3J = 8.1), 8.62 d (1H, 3-H, ^3J = 4.3), 9.68 s and 9.74 s (1H, NH). Found, %: C 77.68; H 5.39; N 5.72. $C_{30}H_{26}N_2O_3$. Calculated, %: C 77.92; H 5.63; N 6.06.

12-(2,4-Dimethoxyphenyl)-9-(4-methoxyphenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (IVf). Yield 81%, mp 297–298°C. UV spectrum, λ_{max}, nm (logε): 205 (4.60), 218 (4.67), 247 (4.35), 282 (4.14), 294 (4.09), 338 (3.95), 378 (3.81). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.51 m (2H, 8-H), 2.86 m (2H, 10-H), 3.08 m and 3.15 m (1H, 9-H), 3.63 s (3H, MeO), 3.72 s (3H, MeO), 3.86 s and 3.89 s (3H, MeO), 5.93 s and 6.00 s (1H, 12-H), 6.30–7.25 m (7H, H_{arom}), 7.38 d.d (1H, 2-H, ^3J = 7.8, ^4J = 2.9), 7.50 d and 7.80 d (1H each, 5-H, 6-H, ^3J = 9.2), 8.57 d (1H, 1-H, ^3J = 7.8), 8.62 d (1H, 3-H, ^3J = 4.1), 9.73 s and 9.80 s (1H, NH). Found, %: C 75.75; H 5.51; N 5.54. $C_{31}H_{28}N_2O_4$. Calculated, %: C 75.61; H 5.69; N 5.69.

12-(3,4-Dimethoxyphenyl)-9-(4-methoxyphenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-one (IVg). Yield 59%, mp 305–306°C. UV spectrum, λ_{max}, nm (logε): 203 (4.66), 215 (4.70), 247 (4.33), 284 (4.06), 297 (4.05), 338 (3.97), 380 (3.88). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.50 m (2H, 8-H), 2.81 m (2H, 10-H), 3.11 m and 3.17 m (1H, 9-H), 3.51 s and 3.56 s (3H, MeO), 3.66 s (3H, MeO), 3.72 s and 3.76 s (3H, MeO), 5.72 s and 5.80 s (1H, 12-H), 6.50–7.20 m (7H, H_{arom}), 7.32 d.d (1H, 2-H, ^3J = 7.9, ^4J = 2.5), 7.49 d and 7.81 d (1H each, 5-H, 6-H, ^3J = 8.8), 8.35 d (1H, 1-H, ^3J = 7.9), 8.60 d (1H, 3-H, ^3J = 4.3), 9.80 s and 9.90 s (1H, NH). Found, %: C 75.53; H 5.56; N 5.49. $C_{31}H_{28}N_2O_4$. Calculated, %: C 75.61; H 5.69; N 5.69.

12-(4-Hydroxy-3-methoxyphenyl)-9-(4-methoxyphenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]-phenanthrolin-11-one (IVh). Yield 86%, mp 283–284°C. UV spectrum, λ_{max}, nm (logε): 204 (4.67), 216 (4.71), 248 (4.31), 282 (4.13), 295 (4.11), 336 (3.89), 379 (3.82). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.53 m (2H, 8-H), 2.83 m (2H, 10-H), 3.08 m and 3.18 m (1H, 9-H), 3.60 s and 3.65 s (3H, MeO), 3.70 s and 3.74 s (3H, MeO), 5.70 s and 5.74 s (1H, 12-H), 6.42–7.22 m (7H, H_{arom}), 7.31 d.d (1H, 2-H, ^3J = 7.8, ^4J = 2.6), 7.49 d and 7.83 d (1H each, 5-H, 6-H, ^3J = 9.1), 8.34 d (1H, 1-H, ^3J = 7.8), 8.60 s (1H, OH), 8.64 d (1H, 3-H, ^3J = 4.4), 9.76 s and 9.83 s (1H, NH). Found, %: C 75.22; H 5.35; N 5.67. $C_{30}H_{26}N_2O_4$. Calculated, %: C 75.31; H 5.44; N 5.86.

2-Methoxy-4-[9-(4-methoxyphenyl)-11-oxo-7,8,9,10,11,12-hexahydrobenzo[*b*][4,7]phenanthrolin-12-yl]phenyl acetate (IVi). Yield 76%, mp 267–268°C. UV spectrum, λ_{max}, nm (logε): 205 (4.69), 218 (4.72), 246 (4.34), 284 (4.11), 297 (4.11), 338 (4.00), 379 (3.99). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.20 s (3H, MeCO), 2.50 m (2H, 8-H), 2.87 m (2H, 10-H), 3.11 m and 3.22 m (1H, 9-H), 3.60 s (3H, MeO), 3.64 s and 3.69 s (3H, MeO), 5.85 s and 5.91 s (1H, 12-H), 6.56–7.14 m (7H, H_{arom}), 7.28 d.d (1H, 2-H, ^3J = 7.6, ^4J = 2.9), 7.51 d and 7.88 d (1H each, 5-H, 6-H, ^3J =

9.0), 8.36 d (1H, 1-H, ^3J = 7.6), 8.65 d (1H, 3-H, ^3J = 4.7), 9.85 s and 9.94 s (1H, NH). Found, %: C 73.67; H 5.29; N 5.11. $C_{32}H_{28}N_2O_5$. Calculated, %: C 73.85; H 5.38; N 5.38.

Methyl 4-[9-(4-methoxyphenyl)-11-oxo-7,8,9,10,-11,12-hexahydrobenzo[*b*][4,7]phenanthrolin-12-yl]-benzoate (IVj). Yield 77%, mp 175–176°C. UV spectrum, λ_{max}, nm (log ε): 203 (4.65), 218 (4.70), 247 (4.35), 284 (4.12), 296 (4.10), 337 (4.00), 378 (3.92). ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.52 m (2H, 8-H), 2.91 m (2H, 10-H), 3.09 m and 3.18 m (1H, 9-H), 3.68 s (3H, CO_2Me), 3.73 s and 3.77 s (3H, MeO), 5.91 s and 5.99 s (1H, 12-H), 6.68 d and 7.01 d (4H, H_{arom}, ^3J = 7.7), 7.22–7.79 m (7H, 2-H, 5-H, 6-H, H_{arom}), 8.35 d (1H, 1-H, ^3J = 7.7), 8.68 d (1H, 3-H, ^3J = 4.9), 9.90 s and 9.98 s (1H, NH). Found, %: C 75.71; H 5.23; N 5.46. $C_{31}H_{26}N_2O_4$. Calculated, %: C 75.92; H 5.31; N 5.71.

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