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Phendione and Anisylhydroresorcinol in the Synthesis of 1,7-Phenanthroline Derivatives

N. G. Kozlov[a], A. B. Tereshko[a], E. V. Koroleva[b], Zh. B. Ignatovich[b], and K. N. Gusak[a]

[a]*Institute of Physical Organic Chemistry, National Academy of Sciences of Belarus, Minsk,220072 Belarus*
e-mail: loc@ifoch.bas-net.by
[b]*Institute of New Materials Chemistry, National Academy of Sciences of Belarus, Minsk, Belarus*

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Abstract—Condensation of 5-phenyl-1,3-cyclohexanedione and 5-(*p*-methoxyphenyl)-1,3-cyclohexanedione with 5-quinolylamine and aldehydes of aromatic, heteroaromatic, and cyclohexene series provided new 7-aryl(heteryl, cyclohexenyl)-10-phenyl- or (*p*-methoxyphenyl)-7,10,11,12-tetrahydro-9H-benzo[*b*][1,7]phenanthrolin-8-ones containing two asymmetrical atoms C^7 and C^{10}. ^{1}H NMR spectroscopy revealed the presence of diastereomers in the target reaction products.

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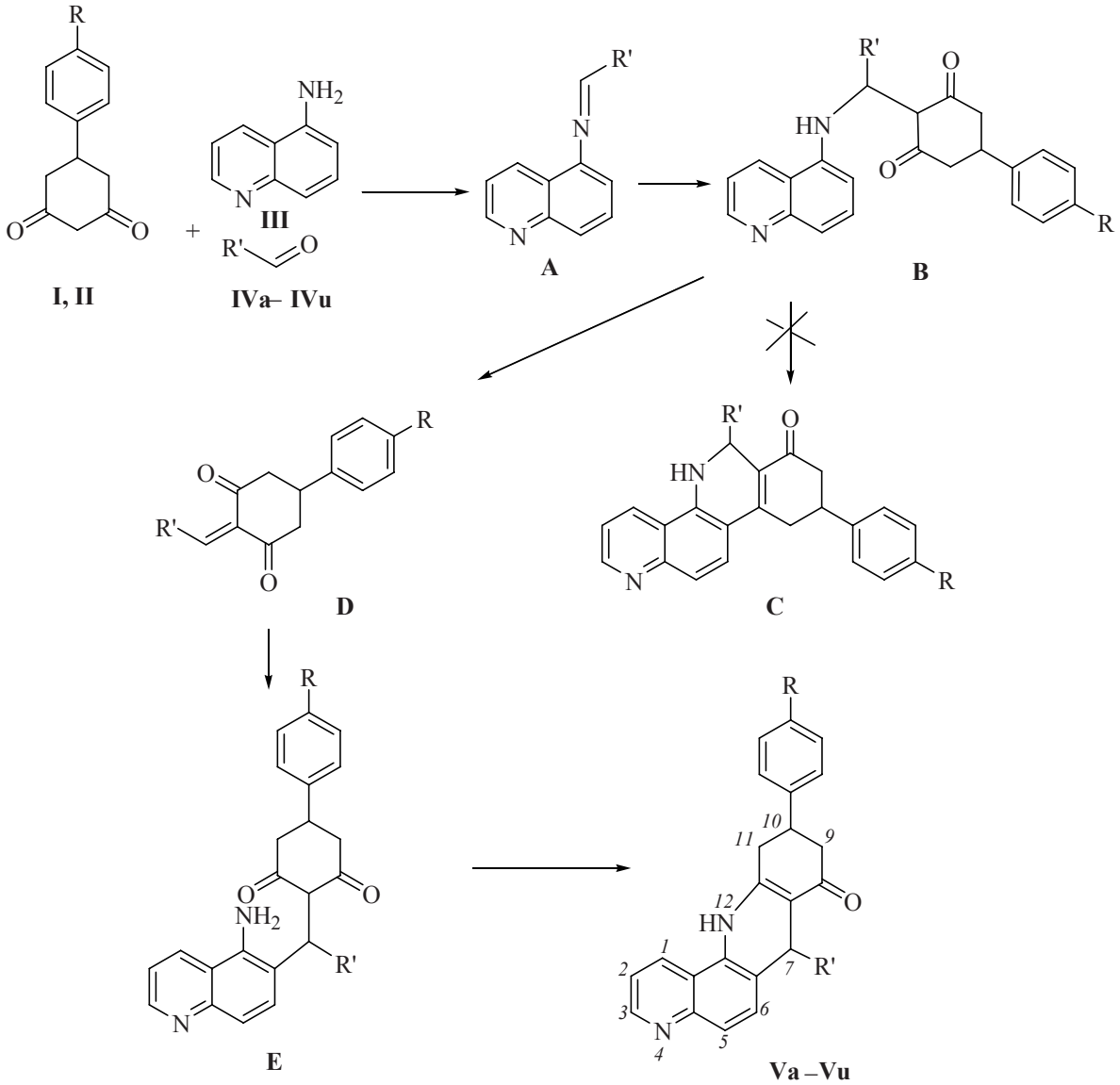
The application of cyclic β-diketones in the preparation of fused nitrogen heterocycles is well documented [1–4]. We showed formerly [3–7] that the reaction of derivatives of 1,3-cyclohexanedione with 2-naphthyl- or 6- quinolylamine and aromatic aldehydes resulted in aza- and diazaphenanthrenes fused to the cyclohexanone ring which were analogs of alkaloid floxacrine [8], ergoalkaloids [9], bactericidal substances [10], enzymes inhibitors [11]. Among the cyclic β-diketones employed in the synthesis of azaheterocycles a special place belongs to mono-substituted 1,3-cyclohexanediones, in particular, to 5-phenyl-1,3- cyclohexanedione (phendione) and 5-(*p*-methoxyphenyl)-1,3-cyclohexanedione (anisylhydroresorcinol) since their molecules contain an asymmetrical carbon atom that is introduced into the structure of the final reaction product and produces a significant effect on the biological activity of the latter.

In this study aiming at the preparation of new fused diazaphenanthrene derivatives containing in the molecule asymmetric center we for the first time investigated the three-component condensation of phendione (**I**) and anisylhydroresorcinol (**II**) with 5-quinolylamine (**III**) and aromatic (heteroaromatic), cyclohexene aldehydes **IVa–IVu**. The condensation was carried out by heating a mixture of equimolar quantities of reagents in *n*-butanol without catalyst.

The condensation proceeded through the stage of azomethine **A** formation and its reaction at the C=N bond with the CH-acid function of the dicarbonyl compound. The resulting aminodiketone **B** may undergo cyclization into a system of 1,2,5,6-tetrahydro-4*H*-benzo[*c*][1,7]-phenanthrolin-8-one **C**. However it was established by spectral investigation that the reaction products were 7-aryl(heteryl, cyclohexenyl)-10-phenyl- or (*p*-methoxyphenyl)-7,10,11,12-tetrahydro-9H-benzo[b][1,7]-phenanthrolin-8-ones **Va–Vu**. Evidently intermediate **B** eliminated aromatic amine **III** and generated α,β-unsaturated diketone **D** where the double bond was strongly activated by the conjugation with two carbonyl groups. Further ketone **D** reacted with the aromatic ring of the 5-quinolylamine (**III**) molecule yielding aminodiketone **E** that suffered cyclization into a derivative of benzo[*b*][1,7]-phenanthrolin-8-one **Va–Vu**.

As we showed formerly [6, 7] the same route took the condensation of isomeric 6-quinolylamine, 1- and 2-naphthylamines (carbocyclic analogs of 5- and 6-aminoquinoline) with arylaldehydes and cyclic 1,3-diketones; therewith the participation of azomethines in the process of azaheterocycles was considered to be proved. Therefore similarly to the event of the formerly studied analogs the transformation of intermediate **B** (the adduct of azomethine and cyclic 1,3-diketone) into aminodiketone

Scheme 1.



R = H (**I, Va–Vp**), 4-OMe (**II, Vq–Vu**); **IV, V**: R' = 3-HOC_6H_4 (**a**), 3,4-$OCH_2OC_6H_3$ (**b**), 4-EtOC_6H_4 (**c**), 4-PrOC_6H_4 (**d**), 3,4,5-$(MeO)_3C_6H_2$ (**e**), 2,3-$Cl_2C_6H_3$ (**f**), 2-BrC_6H_4 (**g**), 2-IC_6H_4 (**h**), 2-$CF_3C_6H_4$ (**i**), 4-*i*-PrC_6H_4 (**j**), 4-PhC_6H_4 (**k**), 4-MeC_6H_4 (**l**), 4-$PhCH_2OC_6H_4$ (**m**), cyclohexen-4-yl (**n**), 4-MeSC_6H_4 (**o**), 2-(3-methyl)thienyl (**p**), 4-FC_6H_4 (**q**), 2-MeOC_6H_4 (**r**), 2,4-$(MeO)_2C_6H_3$ (**s**), 3-MeO,4-HOC_6H_3 (**t**), 3-pyridyl (**u**).

E may be regarded as a rearrangement occurring by a migration of the 2-arylmethyl-1,3-cyclohexanedione fragment into the electron-reach α-position of the amine ring.

It should be noted that compounds **C** forming as a rule in the reaction of arylamines with aldehydes and cyclic monoketones in the presence of acid catalyst [12] were not obtained even as impurities to the products of benzo[*b*]fusion **Va–Vu** in the condensation of diketones **I, II** with amine **III** and aldehydes **IVa–IVu**.

The substituent R' in the aldehyde molecule somewhat affects the yield of target reaction products **Va**–**Vu**. Benzaldehydes **IVa–IVe, IVo, IVt** containing in the *meta*- and *para*-positions methoxycarbonyl, alkylsulfanyl, hydroxy or alkoxy groups that activate the aldehyde molecule through –*I*- or –*I*- and +*M*-effect furnished high yields (68–79%) of reaction products **Va–Ve, Vo, Vt**. Somewhat lower yield (49–60%) of phenanthrolines **Vp, Vr, Vs** was obtained from *o*-methoxy-substituted benzaldehydes **IVr, IVs** and 3-methyl-2-thiophenecarb-

aldehyde (**IVp**) apparently because of the sterical effect of the *ortho*-substituent. By the same reason decreased the yield (48–59%) of reaction products **Vf–Vi** in the case of *ortho*-halo(or trifluoromethyl)-substituted benzaldehydes **IVf–IVi**. This effect clearly depended on the size of the substituent atoms or group, and the yield decreased in the series Cl > Br > I > CF_3. A sufficiently high yield (70%) of phenanthroline **Vu** was obtained from pyridinecarbaldehyde **IVu**. In this case the enhanced polarization and reactivity of the C=O bond in the aldehyde molecule originated from the *–I*-effect of the nitrogen of the pyridine ring. The decreased yield (43%) of the product of cyclohexenyl derivative **Vn** is due evidently to the side processes of initial aldehyde **IVn** polymerization forming tarry products.

The synthesized benzo[*b*][1,7]phenanthrolinone derivatives **Va–Vu** are highly melting crystalline colorless or light-yellow substances. Their IR spectra contain strong bands at 1695–1585 and 1520–1515 cm^{-1} that should be attributed to the vinylog amide fragment (1580, 1520 cm^{-1}) [1]. Strong bands at 3420 and 1610 cm^{-1} correspond respectively to the stretching and bending vibrations of the secondary amino group. The stretching vibrations of alkyl groups and cycloaliphatic CH bonds are observed in the region 2960–2840 cm^{-1}, of CH bonds in aromatic rings, at 3070–3040 cm^{-1}. The strong band in the region 1240–1230 cm^{-1} in the spectra of compounds **Vb–Ve, Vm, Vq–Vu** corresponds to the absorption of the C–O–C ether fragment. In the spectrum of phenanthroline **Vp** a strong band appears of the stretching vibrations of C–S bond at 1125 cm^{-1}.

^{1}H NMR spectra of compounds **Va–Vu** by the position and multiplicity of the proton signals from the benzophenanthroline skeleton and from aryl substituent are identical to the previously studied spectra of 4,7-phenanthroline analogs [5]. The lack of coupling of the proton of NH group with the proton at the carbon bearing the aryl (heteryl, cyclohexenyl) substituent R', that should have appeared in structure **C** containing a 1,2-dihydropyridine ring, confirms the structure of compounds **Va–Vu** and the presence in their molecules of 1,4-dihydropyridine ring. The proton signals NH and H^7 are observed as singlets at 9.32–9.59 and 5.13–5.61 ppm respectively.

The analysis of the aliphatic part of the spectrum shows that the isolated reaction products exist as mixtures of two isomers with pseudoequatorial and pseudoaxial orientation of phenyl or methoxyphenyl substituent at C^{10} atom in the ratio 2:1.

In the ^{1}H NMR spectra of the reaction products **Va–Vj** the signals of protons attached to C^{10} atom were identified as two multiplets at 3.29–3.40 and 3.41–3.49 ppm. Based on the chemical shift and the half-width of the signal the upfield resonance was assigned to H^{10} proton of the axial orientation, and the downfield resonance, to H^{10} proton of the equatorial orientation. The half-width of the signal of H_a^{10} proton is larger than that of H_e^{10} proton, since the coupling constant value H_a–$H_{a'}$ (~9 Hz) is considerably greater than the value of coupling constant H_a–$H_{e'}$ and H_e–$H_{e'}$ (~6 Hz).

In the spectra of the diastereomer mixtures the above mentioned protons at the nitrogen atom and C^7 atom give rise to two singlets each whose integral intensities correspond to the integral intensities of the signals of protons attached to C^{10} in the isomer with the axially oriented phenyl or methoxyphenyl substituent at the C^{10} atom the signals of proton of NH group and of H^7 atom occur in the region of the shielding of the mentioned substituents and appear in the spectrum in stronger field than in that of the isomer with the equatorially oriented phenyl or methoxyphenyl. From the integral intensities of signals of protons H^7, H^{10}, and NH in the spectra of compounds **Va–Vu** it might be concluded that the ratio of the minor isomer to the dominant one equaled 1:4–1:6, whereas in the case of 4,7-phenanthroline analogs the diastereomers formed in approximately equal quantities [5].

The structure of substituent R' virtually does not affect the chemical shifts of protons of phenanthroline skeleton. Yet it should be noted that the change in the position of the substituent R' in the system of benzophenanthrolinone results in the changes in the positions of some protons. Compared to the spectra of isomeric 4,7-phenanthrolines [5] in the spectra of compounds **Va–Vu** a significant upfield shift (about 0.3 ppm) occurs with the signal of proton H^6 by the replacement of the group NH in the position 7 with the CHR' fragment thus eliminating the anisotropic effect of the electronegative nitrogen atom on the proton H^6, and providing the shielding effect of the aryl (heteryl) substituent. In its turn NH group that is located in compounds **Va–Vu** in the position *12* causes a downfield shift (about 0.45 ppm) of the signal of proton H^1 in the absence of the shielding effect of aryl (heteryl) substituent on this proton. Whereas the above described effect of the NH group on the proton H^1 can exist also in the alternative structure **C**, the influence of the substituent R' on the chemical shift of H^6 proton confirms the structure of compounds **Va–Vu** since it cannot occur in

the structure **C**, where the proton H^1 is removed from the aryl substituent.

The electronic spectra of compounds **Va–Vu** contain in the UV region absorption bands with a pronounced vibronic structure [λ_{max}, nm (log ε): 203–205 (4.70–4.80), 220–223 (4.55–4.62), 262–264 (4.44–4.46), 294–298 (3.98–4.01), 378–382 (3.96–4.06)]. Molecules of benzo-[*b*]phenanthrolinones **Va–Vj** contain four independent chromophore fragments: quinoline ring, enone conjugated system, and aryl(heteryl) substituents. We believe that the appearing in the spectra strong bands at 203–205 and 262–264 nm belong to the system of 5-quinolylamine (**II**) [UV spectrum, λ_{max} , nm (log ε): 202 (4.30), 260 (4.72), 354 (3.42)]. The observed in the spectra of phenanthrolines **Va–Vu** increased intensity of the first band and the appearance of bands at 220–223 and 294–298 nm evidently are due to the effect of aryl (heteryl) substituents. The absorption band in the long-wave region of the spectrum (378–382 nm) according to [13] is due to the presence of a carbonyl group. The substituents in the benzene ring of compounds **Va–Vm, Vo, Vq–Vt** do not materially affect the position and the intensity of the absorption bands. In the spectra of cyclohexenyl- and thienyl-substituted compounds **Vn,Vp** the smoothing is observed of the vibronic structure in the short-wave region of the spectrum: in the spectrum of thienyl derivative **Vp** the band 220–223 nm appears as a shoulder, and in the spectrum of cyclohexenyl derivative **Vn** this band is absent.

In the mass spectra of benzophenanthrolinones **Va–Vu** molecular ion peaks are observed $[M]^+$ ($I_{rel.}$ 15–42%). The most abundant ion (100%) in the spectra is the peak of ion $[M - R]^+$ (*m/z* 325 for phenanthrolines **Va–Vp** and 355 for compounds **Vq–Vu**). In the spectra of all phenanthrolines appears a peak of ion with *m/z* 193 (I_{rel} 14–31%) corresponding to the elimination from ion $[M - R]^+$ of a fragment $PhCHCH_2CO$ for compounds **Va–Vp** and a fragment *p*-$MeOC_6H_4CHCH_2CO$ for methoxy derivatives **Vq–Vu**.

EXPERIMENTAL

Mass spectra were measured on an instrument Finnigan MAT INCOS-50 with ionizing electrons energy 70 eV and on a GC-MS instrument HP 5890/5972 in the electron impact mode at the energy 70 eV, column HP-5MS [30 m long, internal diameter 0.25 mm, film of the stationary phase (5% PLMe Silicone) 0.25 μm thick], vaporizer temperature 250°C. IR spectra were recorded on a Fourier spectrophotometer Nicolet Protege-460. UV spectra were taken on a spectrophotometer Specord UV-Vis from the solutions of compounds in ethanol ($c \times 10^{-4}$ mol l^{-1}). ^1H NMR spectra were registered on spectrometers AC-Bruker 500 (500 MHz) and Tesla BS-567 (100 MHz) in DMSO-d_6, internal reference TMS. The melting points were measured on a Koeffler heating block.

Phendione (**I**) and anisylhydroresorcinol (**II**) were obtained from malonic ester and benzylidene- and *p*-methoxybenzylideneacetone respectively by procedure [14].

7-Aryl(heteryl, cyclohexenyl)-10-phenyl- or (*p*-methoxyphenyl)-7,10,11,12-tetrahydro-9*H*-benzo-[*b*][1,7]phenanthrolin-8-ones Va–Vu. A solution of 5 mmol of phendione (**I**) for compounds **Va–Vp** or anisyl-hydroresorcinol (**II**) for phenanthrolines **Vq–Vu**, 5 mmol of 5-quinolylamine (**III**), and 5 mmol of an appropriate aldehyde **IVa–IVu** in 10 ml of 1-butanol was boiled for 3–4 h. The crystals precipitated on cooling were filtered off, washed with ether to remove unreacted initial compounds, dried, and recrystallized from a mixture ethanol–benzene, 1:2.

7-(3-Hydroxyphenyl)-10-phenyl-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-one (Va). Yield 70%, mp 276–277°C. ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.51 m (2H, H^{11}), 2.97 m (2H, H^9), 3.32 m, 3.41 m (1H, H^{10}), 5.16 s, 5.23 s (1H, H^7), 6.74 m, 7.05 m, 7.22 m, 7.34 m (9H, H_{arom}), 7.40 d.d (1H, H^2, ^3J 7.9, ^4J 4.0), 7.49 d, 7.56 d (2H, $H^{5,6}$, ^3J 8.8), 8.61 s (1H, OH), 8.81 d (1H, H^3, ^3J 4.0), 8.89 d (1H, H^1, ^3J 7.9), 9.35 s, 9.44 s (1H, NH). Found, %: C 80.22; H 5.19; N 6.49. $C_{28}H_{22}N_2O_2$. Calculated, %: C 80.36; H 5.30; N 6.69.

7-(3,4-Methylenedioxyphenyl)-10-phenyl-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-one (Vb). Yield 77%, mp 287–288°C. ^1H NMR spectrum, δ, ppm (*J*, Hz): 2.53 m (2H, H^{11}), 2.93 m (2H, H^9), 3.30 m, 3.42 m (1H, H^{10}), 5.16 s, 5.23 s (1H, H^7), 5.88 m (2H, OCH_2O), 6.76 m, 7.07 m, 7.23 m, 7.33 m (8H, H_{arom}), 7.42 d.d (1H, H^2, ^3J 7.9, ^4J 4.1), 7.47 d, 7.54 d (2H, $H^{5,6}$, ^3J 8.9), 8.80 d (1H, H^3, ^3J 4.1), 8.89 d (1H, H^1, ^3J 7.9), 9.37 s, 9.43 s (1H, NH). Found, %: C 77.87; H 4.79; N 6.09. $C_{29}H_{24}N_2O_3$. Calculated, %: C 78.01; H 4.97; N 6.27.

10-Phenyl-7-(4-ethoxyphenyl)-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-one (Vc). Yield 68%, mp 172–173°C. ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.18 t, 4.07 q (OEt), 2.48 m (2H, H^{11}), 2.96 m

(2H, H^9), 3.36 m, 3.45 m (1H, H^{10}), 5.18 s, 5.25 s (1H, H^7), 6.90 m, 7.05 m, 7.16 m, 7.32 m (9H, H_{arom}), 7.41 d.d (1H, H^2, ^3J 8.0, ^4J 4.1), 7.46 d, 7.54 d (2H, $H^{5,6}$, ^3J 8.9), 8.83 d (1H, H^3, ^3J 4.1), 8.89 d (1H, H^1, ^3J 8.0), 9.36 s, 9.43 s (1H, NH). Found, %: C 80.52; H 5.72; N 6.10. $C_{30}H_{26}N_2O_2$. Calculated, %: C 80.69; H 5.87; N 6.27.

7-(4-Propoxyphenyl)-10-phenyl-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-one (Vd). Yield 69%, mp 281–282°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.95 t, 1.63 q, 3.74 t (OPr), 2.51 m (2H, H^{11}), 2.97 m (2H, H^9), 3.36 m, 3.48 m (1H, H^{10}), 5.21 s, 5.28 s (1H, H^7), 6.91 m, 7.05 m, 7.15 m, 7.33 m (9H, H_{arom}), 7.42 d.d (1H, H^2, ^3J 7.9, ^4J 4.1), 7.47 d, 7.56 d (2H, $H^{5,6}$, ^3J 8.8), 8.81 d (1H, H^3, ^3J 4.1), 8.91 d (1H, H^1, ^3J 7.9), 9.35 s, 9.43 s (1H, NH). Found, %: C 80.67; H 5.96; N 5.93. $C_{31}H_{28}N_2O_2$. Calculated, %: C 80.84; H 6.13; N 6.08.

7-(3,4,5-Trimethoxyphenyl)-10-phenyl-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]-phenanthrolin-8-one (Ve). Yield 74%, mp 268–269°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.51 m (2H, H^{11}), 3.02 m (2H, H^9), 3.39 m, 3.47 m (1H, H^{10}), 3.60 s (2OMe), 3.71 s (OMe), 5.20 s, 5.28 s (1H, H^7), 6.98 m, 7.08 m, 7.25 m (7H, H_{arom}), 7.43 d.d (1H, H^2, ^3J 7.9, ^4J 4.1), 7.46 d, 7.55 d (2H, $H^{5,6}$, ^3J 8.9), 8.81 d (1H, H^3, ^3J 4.1), 8.90 d (1H, H^1, ^3J 7.9), 9.41 s, 9.49 s (1H, NH). Found, %: C 75.42; H 5.55; N 5.46. $C_{31}H_{28}N_2O_4$. Calculated, %: C 75.59; H 5.73; N 5.69.

7-(2,3-Dichlorophenyl)-10-phenyl-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-one (Vf). Yield 59%, mp 234–235°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.49 m (2H, H^{11}), 2.97 m (2H, H^9), 3.32 m, 3.41 m (1H, H^{10}), 5.18 s, 5.25 s (1H, H^7), 6.43 m, 6.85 m, 7.23 m (8H, H_{arom}), 7.41 d.d (1H, H^2, ^3J 7.9, ^4J 4.1), 7.54 d, 7.64 d (2H, $H^{5,6}$, ^3J 9.0), 8.78 d (1H, H^3, ^3J 4.1), 8.87 d (1H, H^1, ^3J 7.9), 9.49 s, 9.55 s (1H, NH). Found, %: C 71.17; H 4.08; Cl 14.75; N 5.66. $C_{28}H_{20}Cl_2N_2O$. Calculated, %: C 71.34; H 4.28; Cl 15.04; N 5.94.

7-(2-Bromophenyl)-10-phenyl-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-one (Vg). Yield 54%, mp 271–272°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.52 m (2H, H^{11}), 2.87 m (2H, H^9), 3.33 m, 3.42 m (1H, H^{10}), 5.22 s, 5.30 s (1H, H^7), 6.94 m, 7.02 m, 7.31 m, 7.40 m (9H, H_{arom}), 7.46 d.d (1H, H^2, ^3J 8.0, ^4J 4.2), 7.52 d, 7.61 d (2H, $H^{5,6}$, ^3J 8.9), 8.80 d (1H, H^3, ^3J 4.2), 8.89 d (1H, H^1, ^3J 8.0), 9.43 s, 9.49 s (1H, NH). Found, %: C 69.65; H 4.18; Br 16.40; N 5.58. $C_{28}H_{21}BrN_2O$. Calculated, %: C 69.86; H 4.40; Br 16.60; N 5.82.

7-(2-Iodophenyl)-10-phenyl-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-one (Vh). Yield 51%, mp 256–257°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.53 m (2H, H^{11}), 2.86 m (2H, H^9), 3.34 m, 3.43 m (1H, H^{10}), 5.21 C, 5.29 C (1H, H^7), 6.92 m, 7.01 m, 7.30 m, 7.40 m (9H, H_{arom}), 7.45 d.d (1H, H^2, ^3J 8.1, ^4J 4.2), 7.53 d, 7.62 d (2H, $H^{5,6}$, ^3J 8.9), 8.81 d (1H, H^3, ^3J 4.2), 8.89 d (1H, H^1, ^3J 8.1), 9.42 c, 9.49 c (1H, NH). Found, %: C 63.48; H 3.83; I 23.80; N 5.14. $C_{28}H_{21}IN_2O$. Calculated, %: C 63.65; H 4.01; I 24.04; N 5.30.

7-(2-Trifluoromethylphenyl)-10-phenyl-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-one (Vi). Yield 48%, mp 181–182°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.50 m (2H, H^{11}), 2.85 m (2H, H^9), 3.35 m, 3.45 m (1H, H^{10}), 5.21 s, 5.30 s (1H, H^7), 6.93 m, 7.01 m, 7.30 m, 7.41 m (9H, H_{arom}), 7.44 d.d (1H, H^2, ^3J 8.0, ^4J 4.2), 7.53 d, 7.61 d (2H, $H^{5,6}$, ^3J 8.8), 8.79 d (1H, H^3, ^3J 4.2), 8.88 d (1H, H^1, ^3J 8.0), 9.44 s, 9.51 s (1H, NH). Found, %: N 5.67. $C_{29}H_{21}F_3N_2O$. Calculated, %: N 5.95.

7-(4-Isopropylphenyl)-10-phenyl-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-one (Vj). Yield 64%, mp 282–283°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.52 m (2H, H^{11}), 2.72 m (*i*-Pr), 2.88 m (2H, H^9), 3.32 m, 3.43 m (1H, H^{10}), 5.21 s, 5.30 s (1H, H^7), 6.92 m, 7.01 m, 7.29 m, 7.41 m (9H, H_{arom}), 7.45 d.d (1H, H^2, ^3J 8.0, ^4J 4.2), 7.53 d, 7.62 d (2H, $H^{5,6}$, ^3J 8.9), 8.80 d (1H, H^3, ^3J 4.2), 8.88 d (1H, H^1, ^3J 8.0), 9.42 s, 9.48 s (1H, NH). Found, %: C 83.53; H 6.19; N 6.18. $C_{31}H_{28}N_2O$. Calculated, %: C 83.75; H 6.35; N 6.30.

7-(4-Biphenylyl)-10-phenyl-8,9,10,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-one (Vk). Yield 60%, mp 321–322°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.53 m (2H, H^{11}), 2.98 m (2H, H^9), 3.29 m, 3.43 m (1H, H^{10}), 5.18 s, 5.25 s (1H, H^7), 6.79 m, 7.09 m, 7.22 m, 7.35 m (14H, H_{arom}), 7.44 d.d (1H, H^2, ^3J 8.0, ^4J 4.1), 7.52 d, 7.60 d (2H, $H^{5,6}$, ^3J 8.9), 8.82 d (1H, H^3, ^3J 4.1), 8.90 d (1H, H^1, ^3J 8.0), 9.34 s, 9.43 s (1H, NH). Found, %: C 85.17; H 5.29; N 5.67. $C_{34}H_{26}N_2O$. Calculated, %: C 85.33; H 5.48; N 5.85.

7-(4-Methylphenyl)-10-phenyl-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-one (Vl). Yield 59%, mp 245–246°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.22 C (3H, Me), 2.49 m (2H, H^{11}), 2.98 m (2H, H^9), 3.38 m, 3.46 m (1H, H^{10}), 5.19 s, 5.26 s (1H,

H^{7}), 6.92 m, 7.07 m, 7.17 m, 7.34 m (9H, H_{arom}), 7.40 d.d (1H, H^{2}, ^{3}J 7.9, ^{4}J 4.2), 7.48 d, 7.55 d (2H, H^{5,6}, ^{3}J 8.9), 8.82 d (1H, H^{3}, ^{3}J 4.2), 8.90 d (1H, H^{1}, ^{3}J 7.9), 9.32 s, 9.40 s (1H, NH). Found, %: C 83.47; H 5.58; N 6.54. $C_{29}H_{24}N_2O$. Calculated, %: C 83.63; H 5.81; N 6.73.

7-(4-Benzyloxyphenyl)-10-phenyl-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-one (Vm). Yield 67%, mp 264–265°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.50 m (2H, H^{11}), 3.02 m (2H, H^{9}), 3.34 m, 3.44 m (1H, H^{10}), 4.98 m (2H, OCH_2Ph), 5.18 s, 5.24 s (1H, H^{7}), 6.76 m, 7.08 m, 7.21 m, 7.33 m (14H, H_{arom}), 7.42 d.d (1H, H^{2}, ^{3}J 8.0, ^{4}J 4.1), 7.51 d, 7.59 d (2H, H^{5,6}, ^{3}J 8.8), 8.83 d (1H, H^{3}, ^{3}J 4.1), 8.91 d (1H, H^{1}, ^{3}J 8.0), 9.36 s, 9.43 s (1H, NH). Found, %: C 82.47; H 5.36; N 5.38. $C_{35}H_{28}N_2O_2$. Calculated, %: C 82.65; H 5.55; N 5.51.

10-Phenyl-4-cyclohexenyl-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-one (Vn). Yield 43%, mp 161–162°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 0.92–2.03 m (7$H_{cycloaliph.}$), 2.49 m (2H, H^{11}), 2.97 m (2H, H^{9}), 3.31 m, 3.42 m (1H, H^{10}), 4.77 d, 5.40 d (CH=CH), 5.18 s, 5.24 s (1H, H^{7}), 7.10 m, 7.22 m, 7.34 m (5H, H_{arom}), 7.42 d.d (1H, H^{2}, ^{3}J 8.0, ^{4}J 4.1), 7.50 d, 7.57 d (2H, H^{5,6}, ^{3}J 8.8), 8.82 d (1H, H^{3}, ^{3}J 4.1), 8.89 d (1H, H^{1}, ^{3}J 8.0), 9.38 s, 9.46 s (1H, NH). Found, %: C 82.55; H 6.29; N 6.64. $C_{28}H_{25}N_2O$. Calculated, %: C 82.73; H 6.45; N 6.89.

7-(4-Methylsulfanyl)-10-phenyl-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-one (Vo). Yield 79%, mp 212–213°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.37 C (3H, SMe), 2.51 m (2H, H^{11}), 3.04 m (2H, H^{9}), 3.40 m, 3.48 m (1H, H^{10}), 5.21 s, 5.28 s (1H, H^{7}), 7.00 m, 7.08 m, 7.24 m (9H, H_{arom}), 7.42 d.d (1H, H^{2}, ^{3}J 7.8, ^{4}J 4.1), 7.48 d, 7.56 d (2H, H^{5,6}, ^{3}J 8.9), 8.83 d (1H, H^{3}, ^{3}J 4.1), 8.92 d (1H, H^{1}, ^{3}J 7.8), 9.34 s, 9.43 s (1H, NH). Found, %: C 77.47; H 5.21; N 6.05; S 6.86. $C_{29}H_{24}N_2OS$. Calculated, %: C 77.65; H 5.39; N 6.24; S 7.15.

7-[(3-Methyl-2-thienyl)-10-phenyl-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-one (Vp). Yield 49%, mp 166–167°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.37 C (3H, Me), 2.52 m (2H, H^{11}), 3.07 m (2H, H^{9}), 3.40 m, 3.49 m (1H, H^{10}), 5.55 C, 5.61 C (1H, H^{7}), 6.61 m, 6.94 m, 7.28 m (7H, $H_{arom, heteroarom}$), 7.34 d.d (1H, H^{2}, ^{3}J 7.8, ^{4}J 4.1), 7.42 d, 7.51 d (2H, H^{5,6}, ^{3}J 8.9), 8.82 d (1H, H^{3}, ^{3}J 4.1), 8.91 d (1H, H^{1}, ^{3}J 7.8), 9.50 C, 9.59 s (1H, NH). Found, %: C 76.52; H 5.07; N 6.42; S 7.27. $C_{27}H_{22}N_2OS$. Calculated, %: C 76.75; H 5.25; N 6.63; S 7.59.

10-(*p*-Methoxyphenyl)-7-(*p*-fluorophenyl)-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-one (Vq). Yield 74%, mp 256–257°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.54 m (2H, H^{11}), 2.88 m (2H, H^{9}), 3.34 m, 3.41 m (1H, H^{10}), 5.22 s, 5.29 s (1H, H^{7}), 6.95 d, 7.01 d, 7.32 d, 7.39 m (8H, H_{arom}, ^{3}J 8.2), 7.45 d.d (1H, H^{2}, ^{3}J 8.0, ^{4}J 4.3), 7.53 d, 7.60 d (2H, H^{5,6}, ^{3}J 9.0), 8.81 d (1H, H^{3}, ^{3}J 4.3), 8.87 d (1H, H^{1}, ^{3}J 8.0), 9.40 s, 9.46 s (1H, NH). Found, %: N 6.09. $C_{29}H_{23}FN_2O_2$. Calculated, %: N 6.22.

7-(*o*-Methoxyphenyl)-10-(*p*-methoxyphenyl)-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7] phenanthrolin -8-one (Vr). Yield 62%, mp 243–244°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.55 m (2H, H^{11}), 3.04 m (2H, H^{9}), 3.38 m, 3.44 m (1H, H^{10}), 3.71 s (3H, MeO), 3.79 s (3H, MeO), 5.18 s, 5.25 s (1H, H^{7}), 6.46 m, 6.88 m, 7.23 d, (8H, H_{arom}, ^{3}J 8.0), 7.43 d.d (1H, H^{2}, ^{3}J 7.9, ^{4}J 4.1), 7.50 d, 7.57 d (2H, H^{5,6}, ^{3}J 8.9), 8.76 d (1H, H^{3}, ^{3}J 4.1), 8.80 d (1H, H^{1}, ^{3}J 7.9), 9.37 s, 9.44 s (1H. NH). Found, %: C 77.63; H 5.49; N 5.74. $C_{30}H_{26}N_2O_3$. Calculated, %: C 77.92; H 5.63; N 6.06.

7-(*o,p*-Dimethoxyphenyl)-10-(*p*-methoxyphenyl)-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-one (Vs). Yield 60%, mp 261–263°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.50 m (2H, H^{11}), 2.98 m (2H, H^{9}), 3.30 m, 3.41 m (1H, H^{10}), 3.70 s (3H, MeO), 3.78 s (3H, MeO), 3.93 s (3H, MeO), 5.19 s, 5.25 s (1H, H^{7}), 6.44 m, 6.86 m, 7.24 d, (7H, H_{arom}, ^{3}J 7.7), 7.42 d.d (1H, H^{2}, ^{3}J 7.9, ^{4}J 4.2), 7.55 d, 7.61 d (2H, H^{5,6}, ^{3}J 9.1), 8.80 d (1H, H^{3}, ^{3}J 4.2), 8.88 d (1H, H^{1}, ^{3}J 7.9), 9.50 s, 9.55 s (1H, NH). Found, %: C 75.55; H 5.42; N 5.44. $C_{31}H_{28}N_2O_4$. Calculated, %: C 75.61; H 5.69; N 5.69.

7-(4-Hydroxy-3-methoxyphenyl)-10-(*p*-methoxyphenyl)-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]-phenanthrolin-8-one (Vt). Yield 75%, mp 281–282°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.52 m (2H, H^{11}), 3.09 m (2H, H^{9}), 3.41 m, 3.46 m (1H, H^{10}), 3.65 s (3H, MeO), 3.80 s (3H, MeO), 5.13 s, 5.20 s (1H, H^{7}), 6.52 m, 6.90 m, 7.22 d, (7H, H_{arom}, ^{3}J 8.1), 7.48 d.d (1H, H^{2}, ^{3}J 7.8, ^{4}J 4.0), 7.52 d, 7.60 d (2H, H^{5,6}, ^{3}J 8.8), 8.60 C (1H, OH), 8.83 d (1H, H^{3}, ^{3}J 4.0), 8.90 d (1H, H^{1}, ^{3}J 7.8), 9.45 s, 9.53 s (1H, NH). Found, %: C 75.19; H 5.27; N 5.72. $C_{30}H_{26}N_2O_4$. Calculated, %: C 75.31; H 5.44; N 5.86.

10-(*n*-Methoxyphenyl)-7-(3-pyridyl)-7,10,11,12-tetrahydro-9*H*-benzo[*b*][1,7]phenanthrolin-8-one (Vu). Yield 70%, mp 266–267°C. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 2.58 m (2H, H^{11}), 3.05 m (2H, H^{9}), 3.40 m,

3.49 m (1H, H^{10}), 3.82 s (3H, MeO), 5.26 s, 5.33 s (1H, H^{7}), 6.98 m, 7.26 m, 8.34 s (8H, $H_{arom,heteroarom}$), 7.44 d.d (1H, H^{2}, ^{3}J 7.9, ^{4}J 4.1), 7.53 d, 7.60 d (2H, $H^{5,6}$, ^{3}J 8.9), 8.80 d (1H, H^{3}, ^{3}J 4.1), 8.89 d (1H, H^{1}, ^{3}J 7.9), 9.47 s, 9.54 s (1H. NH). Found, %: C 77.44; H 5.25; N 9.63. $C_{28}H_{23}N_3O_2$. Calculated, %: C 77.60; H 5.31; N 9.70.

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