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1,3-Cyclohexanedione in the Synthesis of Fused Derivatives of 4,7-Phenanthroline

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Abstract—12-Aryl(heteryl,cyclohexenyl)-8,9,10,12-tetrahydro-7*H*-benzo[b][4,7]phenanthrolin-11-ones were synthesized by condensation of 1,3-cyclohexanedione with 6-quinolylamine and aldehydes of aromatic, heterocyclic, and cyclohexene series.

Application of cyclic β-diketones to preparation of condensed nitrogen-containing heterocycles is well known [1–4]. In extension of our attempts to develop new approaches to the synthesis of previously unknown 4,7-phenanthroline derivatives with conceivable biological activity [5–7] we report here on the study of a reaction between 1,3-cyclohexanedione (**I**) with 6-quinolylamine (**II**) and aldehydes from aromatic **IIIa–t**, heterocyclic **IIIu–w**, and cyclohexene **IIIx** series.

The condensation was carried out by heating at reflux in 1-butanol equimolar amounts of reagents without catalyst. As a result individual derivatives of 4,7-phenanthroline **IVa–x** were obtained in 52–93% yield (Table 1).

Three-component condensation of a cyclic β-diketone with arylamine and aldehyde presumably can take several routes. Depending on the reacting order of the components form some or other isomeric final products. Martinez *et al.* [2] established by an example of condensation of 2-naphthylamine (a carbocyclic analog of 6-quinolylamine) with dimedone and aromatic aldehydes that reaction products were derivatives of benzo[*a*]acridin-11-one (analogs of compounds **IVa–x**, X = CH) and not benzo[*a*]phenanthridin-4-ones **A** (X = CH) as was suggested in [8]. This fact rejected the version of the process occurring through azomethines formation followed by their reaction with diketone. Referring to the low solubility of the reaction products in organic solvents preventing preparation of solutions with concentration suitable for registering NMR spectra Martinez *et al*. [2] made the conclusion on the structure of compounds synthesized mainly from the data of the X-ray diffraction analysis.

In reaction we studied between 1,3-cyclohexanedione (**I**), 6-quinolylamine (**II**), and aldehydes **IIIa–x** the formation of one of two isomers, namely, 12-R-8,9,10,12-tetrahydro-7*H*-benzo-[*b*][4,7]phenanthrolin-11-one (**IVa–x**) was established from NMR spectra recorded from 5–10% solutions of compounds in DMSO-d_6.

^{1}H NMR spectra of compounds **IVa–x** (Table2) are identical to the previously reported [9] spectra of 4,7-phenanthrolines in location and multiplicity of the signals from aromatic protons of the phenanthroline skeleton. The methine proton H^{12} of dihydropyridine ring appears as a singlet at 5.42–6.04 ppm. It is displased downfield with respect to the usual position of methine protons in cyclic compounds [10] due to the anisotropic effect of the neighboring aromatic ring. This effect is confirmed by the fact that in the spectrum of phenanthroline **IVx** containing cyclohexenyl substituent instead of aryl one the signal of H^{12} proton is the least shifted downfield (5.42 ppm) in the series of phenanthrolines **IVa–x**.

The assignment of the other signals in the ^{1}H NMR spectra was performed with the use of two-dimensional spectra in COSY mode that revealed a number of closed spin systems in the resonance regions of aromatic and aliphatic protons. The assignment of signals within these closed spin systems was carried out on the strength of their chemical shifts and multiplicity, and also taking into account spectra recorded in NOESY, HSQC, and HLCC mode (Table3). The combined analysis of all kinds of

Table 1. Yields, melting points, and elemental analyses of 4,7-phenanthroline derivatives **IVa–x**

Compd. no.	Yield, %	mp, °C	Found, %			Formula	Calculated, %		
			C (Hlg)	H (S)	N		C (Hlg)	H (S)	N
IVa	72	348–349	81.09	5.76	8.11	$C_{23}H_{20}N_2O$	81.18	5.88	8.24
IVb	78	301–302	77.31	5.57	7.84	$C_{23}H_{20}N_2O_2$	77.53	5.62	7.87
IVc	80	309–310	74.43	5.62	7.04	$C_{24}H_{22}N_2O_3$	74.61	5.70	7.25
IVd	81	307–308	77.48	5.73	7.61	$C_{24}H_{22}N_2O_2$	77.84	5.95	7.57
IVe	76	298–299	78.18	6.29	7.16	$C_{25}H_{24}N_2O_2$	78.13	6.25	7.29
IVf	89	333–334	73.31 (9.63)	4.11	7.64	$C_{22}H_{17}ClN_2O$	73.33 (9.72)	4.22	7.77
IVg	79	318–319	65.24 (19.83)	4.29	6.61	$C_{22}H_{17}BrN_2O$	65.19 (19.75)	4.20	6.91
IVh	75	306–307	58.25 (27.78)	3.49	5.87	$C_{22}H_{17}IN_2O$	58.41 (28.10)	3.76	6.19
IVi	70	319–320	66.61 (18.04)	3.94	6.88	$C_{22}H_{16}Cl_2N_2O$	66.84 (17.97)	4.05	7.09
IVj	52	305–306	66.58 (17.71)	3.86	6.94	$C_{23}H_{17}Cl_2N_2O$	66.84 (17.97)	4.05	7.09
IVk	73	291–292	–	–	6.92	$C_{23}H_{17}F_3N_2O$	–	–	7.11
IVl	84	331–332	63.29 (18.07)	4.31	6.32	$C_{23}H_{19}BrN_2O_2$	63.45 (18.39)	4.37	6.44
IVm	58	292–293	67.01 (15.39)	5.38	8.77	$C_{26}H_{25}Cl_2N_3O$	66.95 (15.23)	5.36	9.01
IVn	83	288–289	72.34	5.23	6.79	$C_{25}H_{22}N_2O_4$	72.46	5.31	6.76
IVo	79	279–280	72.81	5.43	6.29	$C_{26}H_{24}N_2O_4$	72.90	5.61	6.54
IVp	69	261–262	78.04	5.59	5.67	$C_{30}H_{26}N_2O_3$	77.92	5.63	6.06
IVq	85	321–322	74.37	5.58	7.27	$C_{24}H_{22}N_2O_3$	74.61	5.70	7.25
IVr	61	314–315	74.20	5.31 (8.43)	7.39	$C_{23}H_{20}N_2OS$	74.19	5.3 (8.60)	7.53
IVs	93	294–295	71.47	5.38	7.07	$C_{24}H_{22}N_2O_4$	71.64	5.47	6.97
IVt	58	329–330	81.94	6.19	7.18	$C_{26}H_{24}N_2O$	82.11	6.32	7.37
IVu	71	297–298	76.83	5.04	12.65	$C_{21}H_{17}N_3O$	77.06	5.20	12.84
IVv	72	355–356	72.13	4.62 (9.48)	8.25	$C_{20}H_{16}N_2OS$	72.29	4.8 (9.64)	8.43
IVw	80	325–326	72.77	5.11 (8.97)	8.24	$C_{21}H_{18}N_2OS$	72.83	5.2 (9.25)	8.07
IVx	54	284–285	79.95	6.23	8.37	$C_{22}H_{21}N_2O$	80.24	6.38	8.51

two-dimensional NMR spectroscopy was also used in assignment of signals in the ^{13}C NMR spectra (see EXPERIMENTAL).

The similarity of proton spectra of compounds **IVa–x** with respect to location of proton signals from aliphatic rings C and D and with respect to their splitting suggests that these compounds belong to the same series.The choice of one of the two possible isomers was done in the series under study by an example of compound **IVs** using analysis of two-dimensional NMR spectra HSQC and HMBC (Table 3). As a criterion for selection of the structure of **IVs** type (and not type **A** structure) can serve the presence of a sufficiently intense correlation peak NH^7/C^8. The absence of correlation peaks expected for

structure **A,** those of NH[7] with a carbon attached to aryl substituent and with atom C[13] of the aryl substituent proper, if is not a rigorous proof, yet is an essential argument against **A** structure.

In the three-component mixture of reagents **I, II**, and **III** where each one is capable of reacting with the other two routes are preferred: [(**I**)+(**II**) = **B**] and [(**I**)+(**III**) = **C**]. The reaction of enamine **B** with arylaldehyde **III** and of dione **C** with 6-quinolylamine (**II**) affords intermediate **D**, and dehydration of the latter yields compounds **IVa–x**. The reaction occurs under thermo-dynamic control with formation of a 1,4-dihydropyridine ring apparently with an axial position of aryl substituent thus situated out of the plane of the main ring.

Table 2. ^{1}H NMR spectra of benzo[*b*][4,7]phenanthrolinone derivatives **IVa–x,** δ, ppm[a]

Compd. no.	H[1], d (^3J 8.0 Hz)	H[2], d.d (^3J 8.0, ^4J 2.8 Hz)	H[3], d (^3J 4.8 Hz)	H[5], H[6], 2 d (^3J 8.8 Hz)	H[8], m	H[9], m	H[10], m	H[12], s	Aromatic protons of R substituent	NH, s
IVa	8.30	7.31	8.59	7.50, 7.79	2.21	1.97	2.58	5.73	6.90–7.08 m	9.49
IVb	8.62	7.30	8.55	7.46, 7.80	2.20	1.96	2.62	6.04	6.70 t, 6.84 d, 6.98 t, 7.20 d (^3J 7.6 Hz)	9.51
IVc	8.60	7.34	8.62	7.51, 7.82	2.19	1.90	2.57	5.87	6.62 d, 6.81 d (^3J 7.2 Hz), 7.01 s	9.56
IVd	8.28	7.29	8.62	7.49, 7.79	2.22	1.95	2.61	5.79	6.62 d, 7.02 d (^3J 7.8 Hz)	9.48
IVe	8.24	7.24	8.58	7.44, 7.78	2.23	1.94	2.59	5.75	6.57 d, 7.04 d (^3J 7.4 Hz)	9.43
IVf	8.29	7.31	8.61	7.47, 7.79	2.20	1.90	2.58	5.76	6.99–7.20 m	9.53
IVg	8.30	7.29	8.64	7.50, 7.81	2.24	1.91	2.61	5.79	7.14–7.21 m	9.59
IVh	8.33	7.34	8.60	7.52, 7.80	2.21	1.90	2.60	5.85	7.09–7.18 m	9.63
IVi	8.38	7.30	8.61	7.46, 7.79	2.21	1.92	2.61	6.00	7.00 t, 7.14 d, 7.22 d (^3J 7.9 Hz)	9.62
IVj	8.29	7.24	8.58	7.47, 7.78	2.19	1.88	2.60	5.80	6.89–7.01 m	9.60
IVk	8.32	7.30	8.68	7.50, 7.82	2.21	1.88	2.62	5.94	7.35–7.44 m, 8.00–8.15 m	9.69
IVl	8.56	7.29	8.66	7.49, 7.80	2.20	1.90	2.60	5.83	7.00 C, 7.09–7.19 m	9.64
IVm	8.32	7.38	8.64	7.51, 7.81	2.25	1.90	2.61	5.71	6.50 d, 7.02 d (^3J 8.4 Hz)	9.59
IVn	8.28	7.28	8.60	7.48, 7.79	2.19	1.88	2.60	5.91	7.05 s, 7.10–7.19 m	9.60
IVo	8.26	7.29	8.61	7.50, 7.79	2.20	1.90	2.62	5.94	7.02 s, 7.11–7.23 m	9.58
IVp	8.24	7.22	8.59	7.47, 7.80	2.24	1.92	2.57	5.80	6.40 d, 6.60 d (^3J 7.2 Hz), 6.98 s, 7.30 m	9.50
IVq	8.31	7.30	8.62	7.49, 7.82	2.22	1.87	2.59	5.89	6.50–6.62 m, 7.02 s	9.67
IVr	8.23	7.32	8.61	7.50, 7.81	2.21	1.88	2.60	5.77	6.98 d, 7.10 d (^3J 7.6 Hz)	9.79
IVs	8.41	7.30	8.67	7.49, 7.81	2.27	1.95	2.60	5.78	6.40 s	9.43
IVt	8.38	7.34	8.62	7.49, 7.80	2.23	1.89	2.60	5.79	6.93–7.20 m	9.74
IVu	8.32	7.29	8.61	7.47, 7.81	2.20	1.88	2.58	5.72	6.95–7.09 m, 8.46 d (^3J 7.4 Hz)	9.70
IVv	8.31	7.32	8.57	7.50, 7.79	2.22	1.91	2.61	5.75	6.54 s, 6.72 s, 7.04 s	9.63
IVw	8.30	7.28	8.59	7.52, 7.84	2.20	1.90	2.62	5.78	6.53 d, 6.95 d (^3J 7.6 Hz)	9.71
IVx	8.36	7.37	8.69	7.50, 7.82	2.21	1.92	2.60	5.42	–	9.60

[a] Chemical shifts, δ, ppm: 2.14 s (Me) (**a**); 3.93 s (OMe) (**b**); 3.12 s, 3.22 s [$(OMe)_2$] (**c**); 1.24 t, 4.08 q (OEt) (**d**); 0.98 t, 1.40 q, 3.76 t (OCH_2CH_2Me) (**e**); 3.83 s (OMe) (l); 3.60 s [$N(CH_2CH_2Cl)_2$] (**m**); 3.70 s (OMe), 3.84 s (CO_2Me) (**n**); 1.28 t, 4.10 q (OEt), 3.88 s (CO_2Me) (**o**); 3.78 s (OMe), 4.88 s (OCH_2Ph) (**p**); 1.18 t, 4.13 q (OEt), 8.08 s (OH) (**q**); 3.28 s (SMe) (**t**); 3.60 s [$(OMe)_2$], 8.01 s (OH) (**w**); 2.45 s (Me) (**w**); 1.18–1.82 m (7H cycloaliph.), 4.88 s (CH=CH) (**x**).

Correlation peaks in HMBC spectrum of compound **IVs**[a]

	H^{1}	H^{2}	H^{3}	H^{5}	H^{6}	H^{8}	H^{9}	H^{10}	H^{12}	$H^{14,18}$	$H^{19,20}$	NH	OH
C^{1}			w										
C^{2}			m										
C^{3}	s												
C^{4a}	s		m	s									
C^{6}												m	
C^{6a}				s					s			w	
C^{7a}						w							
C^{8}							w	m	s			m	
C^{9}								m					
C^{11}								m	m				
C^{11a}									s			s	
C^{12}										s			
C^{12a}	s				s				s			s	
C^{12b}		m		s					m				
C^{13}									s	m			
$C^{14,18}$									s	s			
$C^{15,17}$										m	s		s
C^{16}										s			w

[a] Intensity of correlation peaks marked as follows: s, strong; *m*, medium; *w*, weak.

In reaction with aldehydes **IIId, p, q** alongside 4,7-phenanthrolines **IVd, p, q** arise arylmethylenebisdiketones **Vd, p, q**. On heating with 6-quinolylamine (**II**) bisdikenones **Vd, p, q** form the target benzo[*b*]-[4,7]phenanthrolinones **IVd, p, q** and not products of Hantzsch pyridines type **E** evidencing again the thermodynamic control over the process and high CH-acidity of the proton H^{5} in 6-quinolylamine. Apparently intermediate **F** eliminates a molecule of 1,3-cyclohexanedione (**I**) and converts into aminoketone **D** that furnishes on dehydration phenanthroline **IV**.

Substituent R in the aldehyde somewhat affects the yield of target **IVa–x** (Table1). Benzaldehydes **IIIb–h**, **l, n–q, s** containing atoms of halogen, hydroxy-, alkoxy-, alkoxycarbonyl groups that activate aldehyde molecule by *–I*- or *–I*- and *–M*-effect afforded reaction products **IVb–h, l, n–C, s** in a high yield. Fairly good yield of phenanthrolines **IVu**–**w** was obtained with pyridine- and thiophenecarbaldehydes **IIIu–w**. Here the enhanced polarization and reactivity of the C=O bond in the aldehyde molecule is due to the *–I*-effect of nitrogen or sulfur of the heterocycle. The replacement of a phenyl group in the aldehyde molecule by the naphthyl one resulted in lower yield of compound **IVt** due to steric hindrances from the bulky substituent. The considerable decrease in the yield of phenanthroline **IVj** was apparently caused by the steric effect of two *ortho*-substituents, and in the case of cyclohexenyl derivative **IVx** the isolation was hampered by tarring likely to occur due to polymerization of the initial aldehyde.

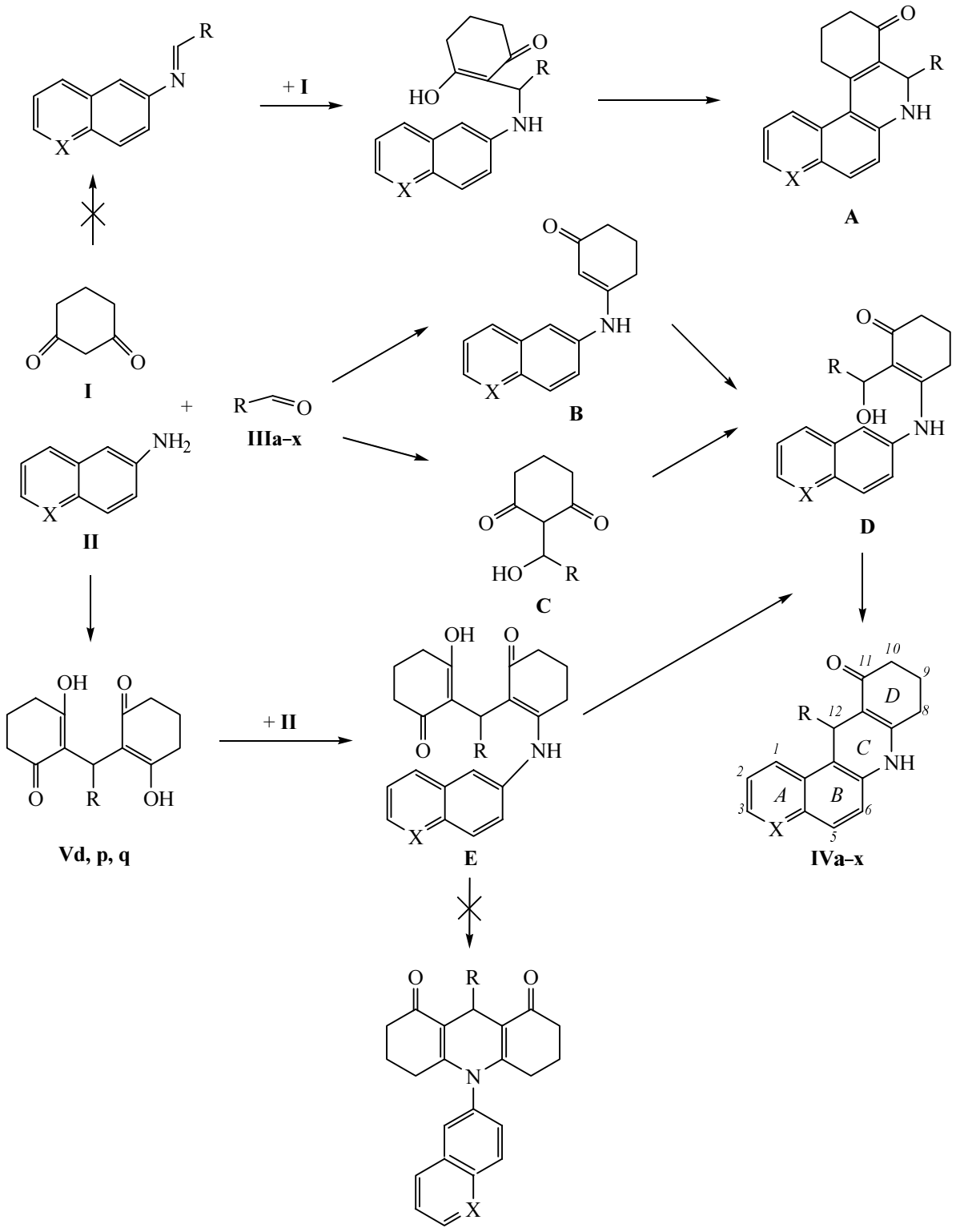
The synthesized fused 4,7-phenanthroline derivatives are high-melting crystalline compounds of white or light-yellow color. Their IR spectra contain characteristic bands of stretching vibrations of NH and CO groups in the regions 3290–3195 and 1625–1580 cm^{-1} respectively. The stretching vibrations of alkyl groups and cycloaliphatic CH bonds give rise to absorption in the region 2960–2870 cm^{-1}, of CH bonds in aromatic rings at 3060–3030 cm^{-1}. In the IR spectra of compounds **IVb–e, l, n–q, s** appear bands corresponding to the C–O–C fragment at 1240–1230 cm^{-1}, in the spectrum of compound **IVt** a strong band is observed at1125 cm^{-1} belonging to the stretching vibrations of C–S bond, and in the spectra of phenanthrolines **IVn, o** a band ν(C=O) of an ester group is present at 1725–1720 cm^{-1}.

Electronic spectra of compounds **IVa–x** contain bands in the UV region with a pronounced vibronic structure. The molecules of benzo[*b*]phenanthrolinones **IVa–x** contain three independent chromophore fragments: aryl substituent, carbonyl group, and quinoline ring that makes the main contribution into the system of π-π^{*}-electron transitions. Therefore the bands with λ_{max} 212–220, 240–255, 292–296 nm may be assigned to the 6-quinolylamine system [UV spectrum, λ_{max} nm (log ε): 206 (4.08), 247 (4.35), 279 (3.59)]. A considerable red shoft and increased intensity of the first and the third bands in phenanthrolinones **IVa–x** spectra are likely to be caused by superposition of the absorption bands of phenyl, heteroaromatic, naphthyl, or cyclohexenyl R substituent. The appearance of absorption bands in the longwave part of the spectrum (331–340, 370–388 nm) is due, according to [11], to the presence of a carbonyl group. The substituents in the phenyl ring of compounds **IVa–s** virtually do not affect the position and intensity of the absorption bands.

In the mass spectra of benzophenanthrolinones **IVa–x** are present molecular ion peaks $[M]^{+}$ (I_{rel} 14–48%). The most abundant peak (100%) in the spectra is that of ion $[M - R]^{+}$ (*m/z* 249). In the spectra of all phenanthrolines a peak of ion with *m/z* 193 (8–28%) is present corresponding to elimination of CH_2CH_2CO fragment from ion $[M - R]^{+}$.

EXPERIMENTAL

Mass spectra were measured on FINNIGAN MAT. INCOS-50 instrument at ionizing electrons energy



II, IV, X = N; **III, IV, V**, R = 2-MeC_6H_4 (**a**), 2-$MeOC_6H_4$ (**b**), 2,5-$(MeO)_2C_6H_3$ (**c**), 4-$EtOC_6H_4$ (**d**), 4-$PrOC_6H_4$ (**e**), 2-ClC_6H_4 (**f**), 2-BrC_6H_4 (**g**), 2-IC_6H_4 (**h**), 2,3-$Cl_2C_6H_3$ (**i**), 2,5-$Cl_2C_6H_3$ (**j**), 2-$CF_3C_6H_4$ (**k**), 2-MeO, 5-BrC_6H_3 (**l**), 4-$N(CH_2CH_2Cl)_2C_6H_4$ (**m**), 3-MeO, 4-$MeOCOC_6H_3$ (**n**), 3-EtO, 4-$MeOCOC_6H_3$ (**o**), 3-MeO, 4-$PhCH_2OC_6H_3$ (**p**), 3-EtO, 4-HOC_6H_3 (**q**), 4-$MeSC_6H_4$ (**r**), 4-HO, 3,5-$(MeO)_2C_6H_2$ (**s**), 1-naphthyl (**t**), 2-pyridyl (**u**), 2-thienyl (**v**), 2-(3-methyl)thienyl (**w**), cyclohexen-4-yl (**x**).

70 eV. IR spectra were recorded on a Fourier spectrometer Nicolet Protege-460. NMR spectra were registered on spectrometers Bruker AC-500 (500 MHz) and Tesla BS-567 (100 MHz) in DMSO-d_6; internal reference TMS. UV spectra from solutions of compounds in ethanol (C 10^{-4} mol l^{-1}) were recorded on spectrophotometer Specord UV-Vis. Melting points were measured on a Koeffler heating block.

12-Aryl(heteryl-, cyclohexenyl)-8,9,10,12-tetrahydro-7*H*-benzo[*b*][4,7]phenanthrolin-11-ones (IVa–x). A solution of 5 mmol of 1,3-cyclohexanedione (**I**), 5 mmol of 6-quinolylamine (**II**), and 5 mmol of an appropriate aldehyde **IIIa–x** in 20 ml of 1-butanol was heated at reflux for 3–4 h. The separated precipitate was filtered off and recrystallized from a mixture ethanol–benzene, 2 : 1 .

^{13}C NMR spectrum of compound **IVs**, δ, ppm: 20.95 (C^{9}), 26.82 (C^{8}), 35.02 (C^{12}), 36.80 (C^{10}), 55.95 ($2OCH_3$), 105.58 ($C^{14,18}$), 108.46 (C^{11a}), 116.71 (C^{12a}), 120.34 (C^{6}), 121.64 (C^{2}), 126.65 (C^{12b}), 128.83 (C^{5}), 130.99 (C^{1}), 133.92 (C^{16}), 134.40 (C^{6a}), 137.62 (C^{13}), 145.48 (C^{4a}), 147.53 ($C^{3,15,17}$), 152.24 (C^{7a}), 193.86 (C^{11}).

2-Arylmethylenebis(1,3-cyclohexanediones) (Vd, p, q) were obtained by procedure described for preparation of compounds **IVa–x**. Bisdiketones **Vd, p, q** were isolated by evaporating the mother liquor after separation of the precipitate of phenanthroline **IVd, p, q**; compounds **Vd, q** were recrystallized from ethanol, bisdione **Vp** from 2-propanol. Yield of compound **Vd** 11%, mp 218–219°C. IR spectrum, ν, cm^{-1}: 1655 (C=O), 1235 (COC), 2940–2855 (CH_2). ^{1}H NMR spectrum, δ, ppm: 1.40 t, 4.00 q (OEt), 1.98 m, 2.28 m, 2.59 m (14H, CH_2, CH), 4.43 s (1H, RCH), 6.45 d, 6.93 d (4H, H arom). Found, %: C 70.63; H 6.59. $C_{21}H_{24}O_5$. Calculated, %: C 70.79; H 6.74.

Yield of compound **Vp** 8%, mp 221–222°C. IR spectrum, ν, cm^{-1}: 1645 (C=O), 1240 (COC), 2950–2855 (CH_2). ^{1}H NMR spectrum, δ, ppm: 1.39 t, 4.02 q (OEt), 1.92–2.80 m (14H, CH_2, CH), 4.41 s (1H, RCH), 6.41 d.d, 6.56 d, 6.78 d (3H, H arom), 8.04 (OH). Found, %: C 67.52; H 6.31. $C_{21}H_{24}O_6$. Calculated, %: C 67.52; H 6.31.

Yield of compound **Vq** 9%, mp 234–235°C. IR spectrum, ν, cm^{-1}: 1645 (C=O), 1240 (COC), 2950–2855 (CH_2). ^{1}H NMR spectrum, δ, ppm: 1.39 t, 4.02 q (OEt), 1.92–2.80 m (14H, CH_2, CH), 4.41 s (1H, RCH), 6.41 d.d, 6.56 d, 6.78 d (3H, H arom), 8.04 (OH). Found, %: C 67.52; H 6.31. $C_{21}H_{24}O_6$. Calculated, %: C 67.52; H 6.31.

Yield of compound **Vq** 9%, mp 234–235°C. IR spectrum, ν, Cm^{-1}: 1650 (C=O), 1240 (COC), 2935–2860 (CH_2). ^{1}H NMR spectrum, δ, ppm: 1.80–2.70 m (14H, CH_2, CH), 3.71 s (OMe), 4.52 s (1H, RCH), 5.00 m (OCH_2), 6.56–6.90 m, 7.30–7.50 m (8H, H arom). Found, %: C 71.80; H 6.24. $C_{26}H_{27}O_6$. Calculated, %: C 71.72; H 6.21.

Bisdiketones **Vd, p, q** were also obtained by heating at reflux 10 mmol of 1,3-cyclohexanedione (**I**) and 5 mmol of the corresponding aldehyde **IIId, p, q** in 20 ml of ethanol for 20 min. Yield of compounds **Vd, p, q** 78–95%.

Condensation of 2-arylmethylenbis(1,3-cyclohexanediones) (Vd, p, q) with 6-quinolylamine (II). A solution of 5 mmol of bisdiketone **Vd, p, q**, and 5 mmol of amine **II** in 20 ml of butanol was refluxed for 3 h. The separated precipitate of the reaction product was filtered off and recrystallized from a mixture ethanol–benzene, 2:1. Yield of phenanthrolines **IVd, p, q** 52–76%.

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