Synthesis of 12-aryl-1-oxo-1,2,3,4,5,12-hexahydroindolo-[2,1-*b*]quinazoline-6-carbonitriles by recyclization of 11-aryl-1-oxo-2,3,4,5,10b,11-hexahydro-1*H*-indolo[2,3-*b*]quinoline-10b-carbonitriles

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A general and convenient method for the synthesis of 12-aryl-1-oxo-1,2,3,4,5,12-hexahydroindolo[2,1-*b*]quinazoline-6-carbonitriles was proposed. The method is based on the recyclization of 11-aryl-1-oxo-2,3,4,5,10b,11-hexahydro-1*H*-indolo[2,3-*b*]quinoline-10b-carbonitriles. The structure of 12-(3-methoxyphenyl)-8-methyl-1-oxo-1,2,3,4,5,12-hexahydroindolo[2,1-*b*]quinazoline-6-carbonitrile was studied by X-ray diffraction analysis.

Key words: cyclic enehydrazino ketones, arylidenemalononitriles, 11-aryl-1-oxo-2,3,4,5,10b,11-hexahydro-1*H*-indolo[2,3-*b*]quinoline-10b-carbonitriles, recyclization, 12-aryl-1-oxo-1,2,3,4,5,12-hexahydroindolo[2,1-*b*]quinazoline-6-carbonitriles, X-ray diffraction analysis.

Fused heterocyclic systems containing indole and pyrimidine fragments compose some biologically active substances, in particular, antibiotic tryptanthrin.[1—3] We have previously[4,5] found a new stereoselective rearrangement of *N*-arylamino-substituted 1,4-dihydropyridines, which affords 11-aryl-1-oxo-2,3,4,5,10b,11-hexahydro-1*H*-indolo[2,3-*b*]quinoline-10b-carbonitriles (**1**) containing partially hydrogenated indole and pyridine fragments.

In this work we describe the recyclization of heterocyclic system **1** to 12-aryl-1-oxo-1,2,3,4,5,12-hexahydroindolo[2,1-*b*]quinazoline-6-carbonitriles (**2**) in 67—95% yields. The recyclization occurs upon prolonged heating of quinindolines **1** in ethanol in the presence of the strong non-nucleophilic base DBU. Quinazolines **2** that formed are colorless or weakly colored high-melting crystalline compounds, which are virtually insoluble in ethanol to facilitate substantially their isolation.

The structures of compounds **2** were confirmed by the ^{1}H NMR spectroscopic and elemental analysis data (Tables 1 and 2). The structure of 12-(3-methoxy-

Table 1. Yields and elemental analysis data for compounds **2**

Compound	Substituents			Yield (%)	Found / Calculated (%)				Molecular formula
	R	Ar	X		C	H	N	Br	
2a	Me	C_6H_5	Me	87	78.82 78.71	6.15 6.08	11.23 11.01	—	$C_{25}H_{23}N_3O$
2b	H	4-BrC_6H_4	H	85	63.25 63.17	3.74 3.86	10.20 10.05	19.01 19.10	$C_{22}H_{16}BrN_3O$
2c	H	4-BrC_6H_4	Me	95	63.79 63.90	4.32 4.20	9.86 9.72	18.60 18.48	$C_{23}H_{18}BrN_3O$
2d	Me	4-BrC_6H_4	Me	90	65.10 65.22	4.70 4.82	9.20 9.13	17.50 17.36	$C_{25}H_{22}BrN_3O$
2e	H	3-$MeOC_6H_4$	H	80	74.91 74.78	5.07 5.18	11.32 11.37	—	$C_{23}H_{19}N_3O_2$
2f	H	3-$MeOC_6H_4$	Me	78	75.29 75.18	5.64 5.52	11.07 10.96	—	$C_{24}H_{21}N_3O_2$
2g	Me	3-$MeOC_6H_4$	Me	67	75.68 75.89	6.37 6.12	10.01 10.21	—	$C_{26}H_{25}N_3O_2$

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Table 2. ^{1}H NMR spectra (DMSO-d_6, δ, *J*/Hz) of compounds **2**

Compound	CMe_2 (s, 3 H)	CH_2	CH (s, 1 H)	NH (br.s, 1 H)	Ar	Me (s, 3 H)
2a	0.85; 1.05	2.05 (d, 1 H, *J* = 18); 2.25 (d, 1 H, *J* = 18); 2.55—2.65 (m, 2 H)	6.40	11.25	6.85 (d, 1 H, *J* = 8); 7.10—7.30 (m, 7 H)	2.30
2b	—	1.80—2.05 (m, 2 H); 2.25—2.35 (m, 2 H); 2.70—2.80 (m, 2 H)	6.48	11.25	7.00—7.15 (m, 2 H); 7.25 (d, 2 H, *J* = 8); 7.30—7.50 (m, 4 H)	—
2c	—	1.80—2.05 (m, 2 H); 2.20—2.30 (m, 2 H); 2.60—2.70 (m, 2 H)	6.42	11.45	6.85 (d, 1 H, *J* = 8); 7.20—7.30 (m, 3 H); 7.45 (d, 2 H, *J* = 8)	2.30
2d	0.90; 1.10	2.05 (d, 1 H, *J* = 18); 2.25 (d, 1 H, *J* = 18); 2.55—2.65 (m, 2 H)	6.40	11.20	6.85 (d, 1 H, *J* = 8); 7.15—7.25 (m, 4 H); 7.45 (d, 2 H, *J* = 8)	2.30
2e	—	1.80—2.05 (m, 2 H); 2.25—2.35 (m, 2 H); 2.65—2.75 (m, 2 H)	6.45	11.25	3.70 (s, 3 H, OMe); 6.72 (m, 2 H); 6.90 (s, 1 H); 7.00—7.15 (m, 3 H); 7.40 (m, 2 H)	—
2f	—	1.80—2.05 (m, 2 H); 2.25—2.35 (m, 2 H); 2.70—2.80 (m, 2 H)	6.40	11.30	3.70 (s, 3 H, OMe); 6.70 (d, 2 H, *J* = 8); 7.25 (d, 2 H, *J* = 8); 7.30—7.50 (m, 4 H)	2.30
2g	0.90; 1.10	2.10 (d, 1 H, *J* = 18); 2.30 (d, 1 H, *J* = 18); 2.55—2.70 (m, 2 H)	6.40	11.20	3.65 (s, 3 H, OMe); 6.70—6.75 (m, 2 H); 6.85—6.90 (m, 2 H); 7.10—7.20 (m, 3 H); 7.30 (d, 1 H, *J* = 8)	2.30

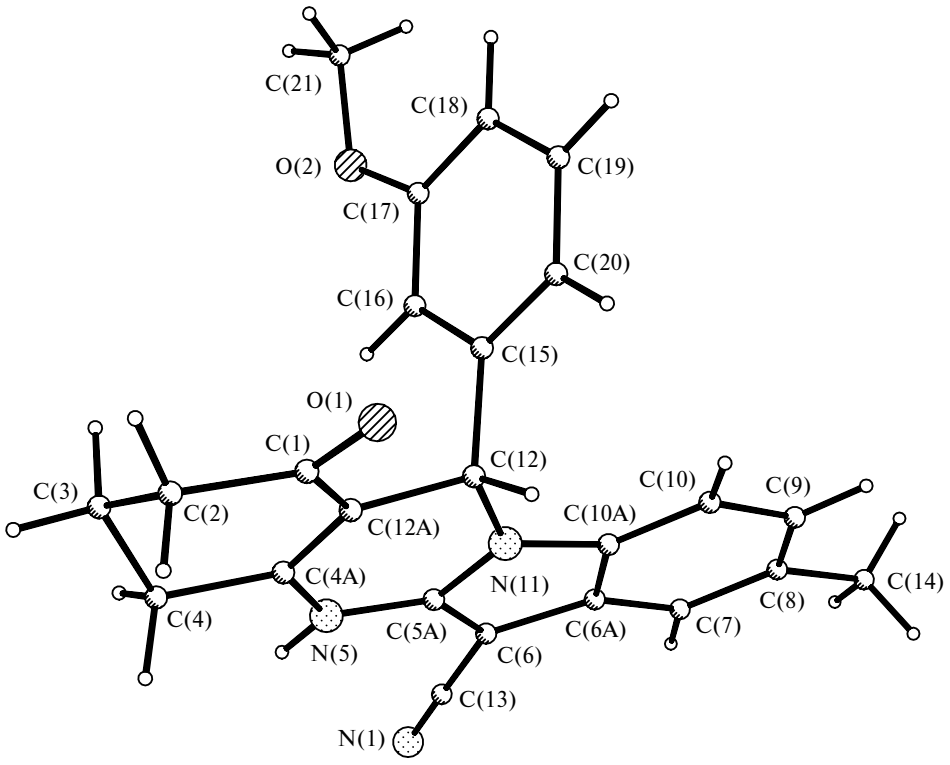


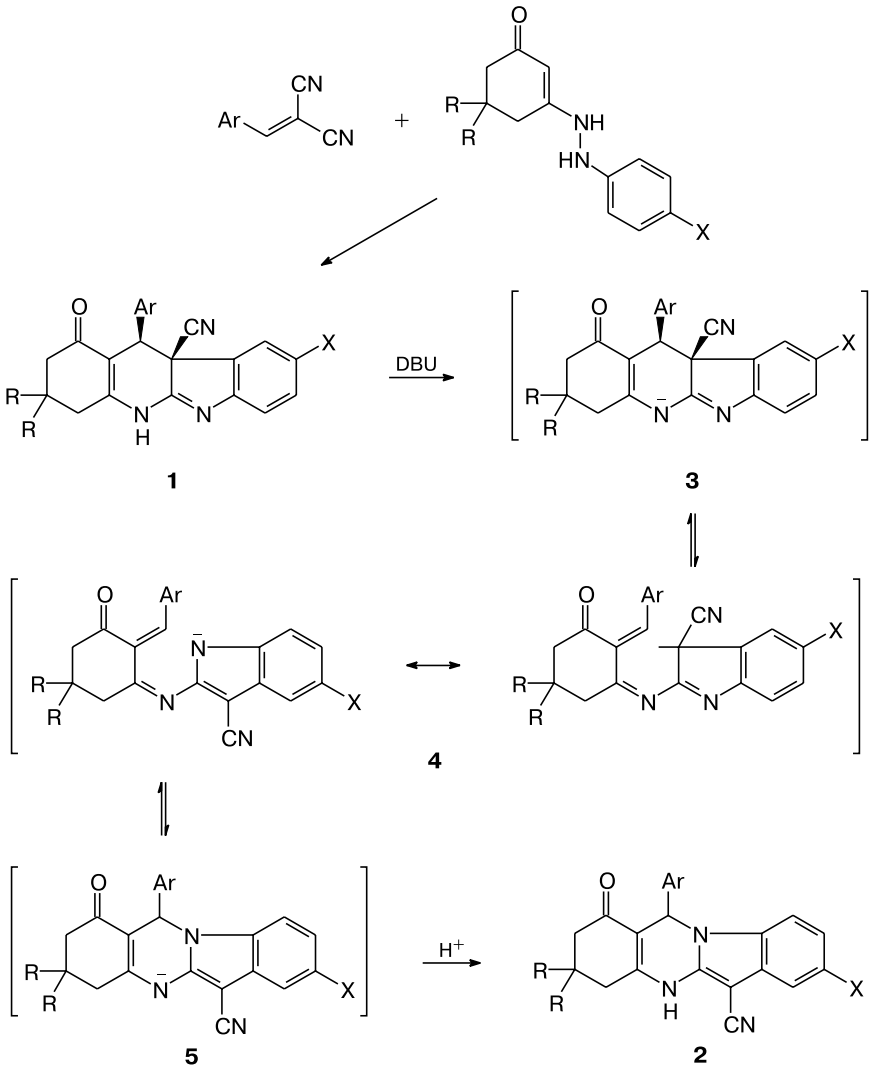
Fig. 1. Structure of compound **2f**.

phenyl)-8-methyl-1-oxo-1,2,3,4,5,12-hexahydroindolo[2,1-*b*]quinazoline-6-carbonitrile (**2f**) was established by X-ray diffraction analysis (Fig. 1).

The following scheme of formation of quinazolines **2** can be proposed. In the first stage, anion **3** is rapidly generated, which is indicated by the fast dissolution of initial compounds **1** in ethanol after the addition of an equimolar amount of DBU. Then the anion undergoes the tetrahydropyridine cycle opening to form anion **4**, which is recyclized to anion **5**. The subsequent acidification of the reaction mixture with acetic acid affords product **2** in high yield (Scheme 1). The high rate of recyclization of **4** to **5** is confirmed by the isolation of a mixture of initial compound **1** and product **2**. The mixture contains no protonated forms of intermediate **4** if the reaction mixture is acidified with an equivalent amount of acetic acid after a time interval insufficient for the completion of the reaction (TLC monitoring). The higher stability of anion **5** over that of the anion of initial heterocycle **3** seems to be the driving force of the rearrangement.

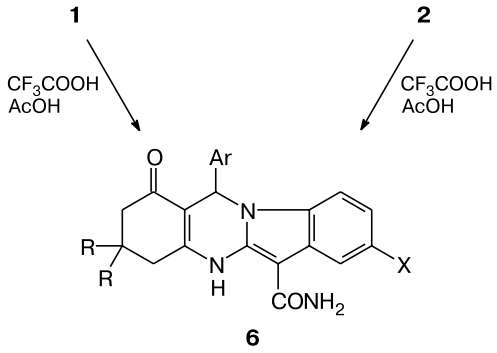
This recyclization also occurs in an acidic medium. For example, refluxing of initial indoloquinolines **1** in a mixture of acetic and trifluoroacetic acid affords amides **6**. The structures of compounds **6** were confirmed by the transformation of the products of base-catalyzed recyclization of **2** into amides **6** on heating in a mixture of acetic and trifluoroacetic acids (Scheme 2). The nitrile function is transformed into the amide function, most likely, under the action of a minor amount of water, which is contained in the mixture of acids used.

Scheme 1



2a	**2b**	**2c**	**2d**	**2e**	**2f**	**2g**	
Ar	Ph	4-BrC_6H_4	4-BrC_6H_4	4-BrC_6H_4	3-$MeOC_6H_4$	3-$MeOC_6H_4$	3-$MeOC_6H_4$
R	Me	H	H	Me	H	H	Me
X	Me	H	Me	Me	H	Me	Me

Scheme 2



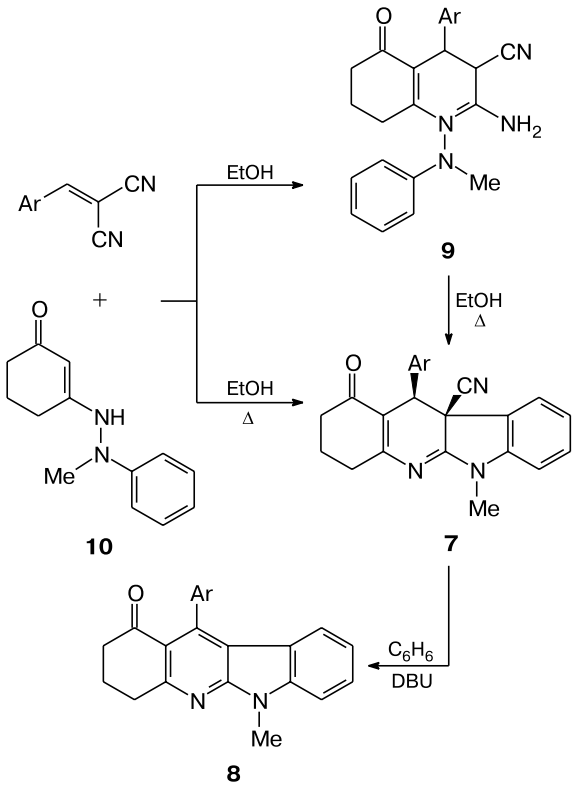
6

The rearrangement becomes impossible in the case of compounds **7** bearing the methyl group at the nitrogen atom. The reaction of **7** with DBU affords tetrahydroindoloquinoline **8** due to the elimination of hydrogen cyanide. Indoloquinolines **7** were synthesized according to the scheme including the reaction of arylidene derivatives of malononitrile with enamino ketone **10** and prolonged refluxing of dihydropyridines **9** that formed in ethanol (Scheme 3). Products **7** can also be obtained directly from arylidinemalononitriles and enamino ketone **10** without isolation of intermediate compounds **9**.

The ^{1}H NMR spectra show that compounds **9** exist as a mixture of two rotamers (**A** and **B**), like their analogs containing no methyl group at the nitrogen atom.[6] Rotamers **A** and **B** exhibit different chemical shifts for the signals of protons in position 4 of the dihydropyridine ring and protons of the amino group. Two rotamers can be observed, probably, due to the hindered rotation about the N—N bond because the molecule is sterically overcrowded. It is noteworthy that 1,4-dihydropyridines bearing an aryl substituent in position 4 are characterized by the sterically hindered boat conformation.[7]

The structure of 12-(3-methoxyphenyl)-8-methyl-1-oxo-1,2,3,4,5,12-hexahydroindolo[2,1-*b*]quinazoline-6-carbonitrile (**2f**) was studied by X-ray diffraction analysis (Fig. 1, Tables 3 and 4). The basis of the molecule is a tetracyclic framework consisting of three consequently fused fragments, namely, cyclohexenone, pyrimidine, and indole joint along the C(4a)—C(12a) and N(11)—C(5a) bonds. The cyclohexenone fragment (***A***) has a sofa conformation: the C(1), C(2), C(4), C(4a), and C(12a) atoms lie in the same plane (with an accuracy of ±0.03 Å), and the C(3) atom deviates from this plane by 0.650 Å. The pyrimidine fragment (***B***) also takes the sofa conformation, but much more flattened: the C(12) atom deviates from the plane of other five atoms, *viz.*, C(12a), C(4a), N(5), C(5a), and N(11) (the plane holds with an accuracy of ±0.01 Å), by 0.177 Å. The indole fragment (***C***) is planar within ±0.008 Å. The angles between the ***A***, ***B***, and ***C*** fragments do not exceed 2—5°. Thus, except for the C(3) and C(12) atoms, the tetracyclic fragment of the

Scheme 3



8

molecule is planar (the root-mean-square deviation is ±0.04 Å). The C(3) and C(12) atoms deviate from this plane by 0.563 and 0.332 Å, respectively. The methoxyphenyl substituent is pseudo-axially oriented with respect to cycle ***B***. The benzene ring is turned out about the C(12)—C(15) bond with respect to the framework of the molecule by 88.40°. The methoxyl group is turned out by 8.38° with respect to the benzene ring.

The tetracyclic framework in molecule **2f** is, in essence, a structural isomer with respect to the tetracyclic framework in the earlier studied molecules of 9-methyl-1-oxo-11-(4-bromophenyl)-2,3,4,5,10b,11-hexahydro-1*H*-indolo[2,3-*b*]quinoline-10b-carbonitrile and 9-methyl-1-oxo-11-(3,4,5-trimethoxyphenyl)-2,3,4,5,10b,11-hexahydro-1*H*-indolo[2,3-*b*]quinoline-10b-carbonitrile[2] but, compared to the latter, it is considerably flattened. All bond lengths in the structure are close to the average statistical values.[8]

Thus, the recyclization of quinindolines **1** affords 12-aryl-1-oxo-1,2,3,4,5,12-hexahydroindolo[2,1-*b*]quinazoline-6-carbonitriles (**2**). Nitriles **2** can be transformed by acids into amides **6**. The method was proposed for the synthesis of 11-aryl-6-methyl-4-oxo-2,3,4,6,10b,11-hexahydroindolo[2,3-*b*]quinoline-10b-carbonitriles (**7**), which were transformed into 11-aryl-6-methyl-2,3,4,6-1*H*-1-tetrahydroindolo[2,3-*b*]quinolinones (**8**) under the action of DBU.

Experimental

^{1}H NMR spectra were recorded on Bruker AM-300 (300 MHz) and Bruker WM-250 (250 MHz) instruments in DMSO-d_6. Melting points were measured on a Boetius heating stage and were not corrected. All reaction mixtures were analyzed and purity of isolated products was monitored by TLC on Silufol UV 254 plates using a AcOEt—hexane mixture as the eluent.

X-ray diffraction study. Colorless triclinic crystals of $C_{24}H_{21}N_3O_2$ were grown from a solution in an acetonitrile—DMF mixture. Unit cell parameters: a = 6.373(4), b = 11.377(8), c = 13.689(9) Å, α = 84.058(12), β = 83.115(13), γ = 76.826(12)°, V = 956.4(11) Å^3. The space group was $P\bar{1}$, Z = 2, d_{calc} = 1.332 g cm^{-3}, m.p. ~200 °C, M = 383.44. Cell parameters and intensities of 5344 independent reflections were measured on a Bruker SMART four-circle automated diffractometer at 110 K (a graphite monochromator, Mo-Kα radiation, φ/ω scan mode). Intensities of reflections were measured in the interval of angles $1.84 \geq \theta \leq 30.22°$. In calculations 3712 reflections with $I > 2\sigma(I)$ were used. The structure was solved by the direct method, during which all nonhydrogen atoms of the molecule were revealed. The parameters of the structure were refined by the F^2 values using the least-squares method in the anisotropic approximation for nonhydrogen atoms. Hydrogen atoms were localized in the difference electron density syntheses and then refined isotropically by the least-squares method. The final divergence factor was R_1 = 0.069 (wR_2 = 0.168), and for all reflections R_1 = 0.093 (wR_2 = 0.184). The Bruker SHELXTL program packages were used in calculations. The coordinates of atoms, temperature parameters, and geometric parameters of the molecule were deposited at the Cambridge Bank of Structural Data. The main geometric parameters are presented in Tables 3 and 4.

Synthesis of 12-aryl-1-oxo-1,2,3,4,5,12-hexahydroindolo[2,1-*b*]quinazoline-6-carbonitriles (2) (general procedure). A solution of compound **1** (1.0 mmol) and DBU (0.18 g, 1.2 mmol) in ethanol (5 mL) was refluxed for 6 h. The reaction mixture was cooled, and AcOH (0.1 mL) was added. The precipitate of product **2** that formed was filtered off and washed on the filter with ethanol (5 mL). The melting points of compounds **2** are >330 °C. The yields, elemental analysis results, and ^{1}H NMR spectroscopic data of compounds **2** are presented in Tables 1 and 2.

Synthesis of 12-aryl-1-oxo-1,2,3,4,5,12-hexahydroindolo[2,1-*b*]quinazoline-6-carboxamides (6a—c) (general procedure). A solution of compound **1** or **2** (0.3 mmol) was refluxed for 3 h in a mixture of acetic (1 mL) and trifluoroacetic (1 mL) acids. The solvent was evaporated, and ethanol (2 mL) was added to the residue. Precipitated product **6** was filtered off and washed with ethanol (5 mL).

12-(4-Bromophenyl)-8-methyl-1-oxo-1,2,3,4,5,12-hexahydroindolo[2,1-*b*]quinazoline-6-carboxamide (6a). The yield was 35% (from **1c**) and 53% (from **2c**). M.p. 254—255 °C. ^{1}H NMR, δ: 10.12 (s, 1 H, NH); 7.70 (s, 1 H, CONHH); 7.42 (d, 2 H, H_{Ar}, J = 8 Hz); 7.21—7.10 (m, 4 H, H_{Ar} and CONHH); 6.80 (d, 1 H, H_{Ar}, J = 8 Hz); 6.43 (s, 1 H, CH); 2.90—2.65 (m, 2 H, CH_2); 2.40—2.20 (m, 2 H, CH_2); 0.35 (s, 3 H, CH_3); 2.05—1.75 (m, 2 H, CH_2). Found (%): C, 61.70; H, 4.27; N, 9.56; Br, 17.45. $C_{23}H_{20}BrN_3O_2$. Calculated (%): C, 61.34; H, 4.48; N, 9.33; Br, 17.74.

Table 3. Bond lengths (d) in molecule **2f**

Bond	d/Å	Bond	d/Å	Bond	d/Å	Bond	d/Å
O(1)—C(1)	1.230(2)	N(11)—C(10A)	1.409(2)	C(4A)—C(12A)	1.357(3)	C(8)—C(9)	1.409(3)
O(2)—C(17)	1.375(2)	N(11)—C(12)	1.471(2)	C(5A)—C(6)	1.402(2)	C(8)—C(14)	1.511(3)
O(2)—C(21)	1.425(2)	C(1)—C(12A)	1.463(2)	C(6)—C(13)	1.410(2)	C(9)—C(10)	1.400(3)
N(1)—C(13)	1.150(2)	C(1)—C(2)	1.522(3)	C(6)—C(6A)	1.450(2)	C(10)—C(10A)	1.384(3)
N(5)—C(5A)	1.371(2)	C(2)—C(3)	1.521(3)	C(6A)—C(7)	1.405(2)	C(12)—C(12A)	1.522(3)
N(5)—C(4A)	1.375(2)	C(3)—C(4)	1.528(3)	C(6A)—C(10A)	1.416(2)	C(12)—C(15)	1.539(2)
N(11)—C(5A)	1.359(2)	C(4)—C(4A)	1.514(3)	C(7)—C(8)	1.392(3)		

Table 4. Bond angles (ω) in molecule **2f**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
C(17)—O(2)—C(21)	117.62(16)	N(11)—C(5A)—N(5)	120.39(15)	C(10)—C(9)—C(8)	121.74(17)
C(5A)—N(5)—C(4A)	120.30(15)	N(11)—C(5A)—C(6)	110.17(15)	C(10A)—C(10)—C(9)	117.71(16)
C(5A)—N(11)—C(10A)	108.96(13)	N(5)—C(5A)—C(6)	129.43(16)	C(10)—C(10A)—N(11)	130.15(15)
C(5A)—N(11)—C(12)	124.84(14)	C(5A)—C(6)—C(13)	125.47(16)	C(10)—C(10A)—C(6A)	122.11(15)
C(10A)—N(11)—C(12)	125.71(14)	C(5A)—C(6)—C(6A)	106.35(15)	N(11)—C(10A)—C(6A)	107.72(15)
O(1)—C(1)—C(12A)	120.86(17)	C(13)—C(6)—C(6A)	127.93(15)	N(11)—C(12)—C(12A)	108.57(13)
O(1)—C(1)—C(2)	121.63(15)	C(7)—C(6A)—C(10A)	118.92(16)	N(11)—C(12)—C(15)	111.23(13)
C(12A)—C(1)—C(2)	117.50(16)	C(7)—C(6A)—C(6)	134.30(15)	C(12A)—C(12)—C(15)	111.20(14)
C(3)—C(2)—C(1)	113.48(15)	C(10A)—C(6A)—C(6)	106.77(14)	C(4A)—C(12A)—C(1)	120.92(16)
C(2)—C(3)—C(4)	110.84(16)	C(8)—C(7)—C(6A)	119.93(16)	C(4A)—C(12A)—C(12)	122.73(14)
C(4A)—C(4)—C(3)	110.56(15)	C(7)—C(8)—C(9)	119.57(16)	C(1)—C(12A)—C(12)	116.33(15)
C(12A)—C(4A)—N(5)	121.38(16)	C(7)—C(8)—C(14)	120.71(16)	N(1)—C(13)—C(6)	179.3(2)
C(12A)—C(4A)—C(4)	123.28(15)	C(9)—C(8)—C(14)	119.72(17)	C(16)—C(15)—C(20)	120.03(15)
N(5)—C(4A)—C(4)	115.34(16)				

3,3,8-Trimethyl-1-oxo-12-phenyl-1,2,3,4,5,12-hexahydroindolo[2,1-*b*]quinazoline-6-carboxamide (6b). The yield was 43% (from **1a**) and 84% (from **2a**). M.p. 195—197 °C. ^{1}H NMR, δ: 10.08 (s, 1 H, NH); 7.67 (s, 1 H, CONHH); 7.30—7.05 (m, 7 H, H_{Ar} and CONHH); 6.80 (d, 1 H, H_{Ar}, J = 8 Hz); 6.40 (s, 1 H, CH); 2.80—2.7 (m, 2 H, CH_2); 2.35 (s, 3 H, CH_3); 2.25 (s, 1 H, CHH); 2.10 (s, 1 H, CHH); 1.05 and 0.90 (both s, 6 H, 2 CH_3). Found (%): C, 75.40; H, 6.21; N, 10.78. $C_{25}H_{25}N_3O_2$. Calculated (%): C, 75.16; H, 6.31; N, 10.52.

12-(3-Methoxyphenyl)-1-oxo-1,2,3,4,5,12-hexahydroindolo[2,1-*b*]quinazoline-6-carboxamide (6c). The yield was 38% (from **1e**) and 62% (from **2e**). M.p. 251—252 °C. ^{1}H NMR, δ: 10.15 (s, 1 H, NH); 7.85 (d, 1 H, H_{Ar}, J = 8 Hz), 7.35 (d, 1 H, H_{Ar}, J = 8 Hz); 7.20—6.95 (m, 5 H, H_{Ar} and CONHH); 6.87 (s, 1 H, H_{Ar}); 6.75—6.70 (m, 2 H, H_{Ar}); 6.45 (s, 1 H, CH); 2.95—2.60 (m, 2 H, CH_2); 2.35—2.25 (m, 2 H, CH_2); 2.00—1.75 (m, 2 H, CH_2). Found (%): C, 71.42; H, 5.59; N, 10.71. $C_{23}H_{21}N_3O_3$. Calculated (%): C, 71.30; H, 5.46; N, 10.85.

Synthesis of 11-aryl-6-methyl-4-oxo-2,3,4,6,10b,11-hexahydro-1*H*-indolo[2,3-*b*]quinoline-10b-carbonitriles (7a,b) (general procedure). ***A***. A mixture of enaminone **10** (0.22 g, 1 mmol) and benzylidenemalononitrile (0.23 g, 1 mmol) in ethanol (4 mL) was refluxed for 6 h. The solution was cooled down, and the precipitate that formed was filtered off and washed with cold ethanol (5 mL).

B. A solution of compound **9** (0.5 mmol) was refluxed for 6 h in ethanol (2 mL). The precipitate that formed was filtered off and washed with ethanol.

11-(4-Bromophenyl)-6-methyl-4-oxo-2,3,4,6,10b,11-hexahydro-1*H*-indolo[2,3-*b*]quinoline-10b-carbonitrile (7a). The yield was 48% (method *A*) and 63% (method *B*). M.p. 205—206 °C. ^{1}H NMR, δ: 7.65—7.30 (m, 5 H); 7.15—7.00 (m, 2 H); 6.32 (d, 1 H, J = 8 Hz); 4.20 (s, 1 H, CH); 3.45 (s, 3 H, NMe); 2.80—2.70 (m, 2 H); 2.40—2.20 (m, 2 H); 2.05—1.95 (m, 2 H). Found (%): C, 63.70; H, 4.26; N, 9.79; Br, 18.29. $C_{23}H_{18}BrN_3O$. Calculated (%): C, 63.90; H, 4.20; N, 9.72; Br, 18.48.

6-Methyl-4-oxo-11-phenyl-2,3,4,6,10b,11-hexahydro-1*H*-indolo[2,3-*b*]quinoline-10b-carbonitrile (7b). The yield was 45% (method *A*) and 53% (method *B*). M.p. 181—182 °C. ^{1}H NMR, δ: 7.50—7.30 (m, 6 H); 7.15—7.10 (m, 1 H); 6.20 (d, 1 H, J = 8 Hz); 4.12 (s, 1 H, CH); 3.45 (s, 3 H, NMe); 2.80—2.70 (m, 2 H); 2.40—2.20 (m, 2 H); 2.05—1.95 (m, 2 H). Found (%): C, 78.30; H, 5.30; N, 11.67. $C_{23}H_{19}N_3O$. Calculated (%): C, 78.16; H, 5.42; N, 11.89.

11-(4-Bromophenyl)-6-methyl-2,3,4,6-tetrahydro-1*H*-1-indolo[2,3-*b*]quinolinone (8). A solution of compound **7** (0.15 g, 0.35 mmol) and DBU (0.15 g, 1 mmol) in benzene (4 mL) was refluxed for 6 h. The solvent was evaporated, and ethanol (2 mL) was added to the residue. The precipitate that formed was filtered off and washed with ethanol (5 mL). Compound **5** was obtained in 53% yield (0.08 g). M.p. 280—281 °C. ^{1}H NMR, δ: 7.75—7.65 (m, 3 H); 7.50 (t, 1 H); 7.05 (t, 1 H); 6.40 (d, 1 H, J = 8 Hz); 3.93 (s, 3 H, NMe); 3.35—3.25 (m, 2 H); 2.50—2.60 (m, 2 H); 2.05—2.15 (m, 2 H). Found (%): C, 65.45; H, 4.16; N, 6.79; Br, 19.49. $C_{22}H_{17}BrN_2O$. Calculated (%): C, 65.20; H, 4.23; N, 6.91; Br, 19.71.

Synthesis of 2-amino-4-aryl-1-methylanilino-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitriles (9a,b) (general procedure). A mixture of benzylidenemalononitrile (1 mmol) and enamino ketone **6** (1 mmol) was boiled for 5—10 min in ethanol (3 mL). The resulting solution was left for 12 h at ~20 °C. The precipitate that formed was filtered off and washed with ethanol.

2-Amino-4-(4-bromophenyl)-1-methylanilino-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (9a). The yield was 65%. M.p. 170—172 °C. ^{1}H NMR, δ: 7.55 (***A***) and 7.45 (***B***) (both s, 2 H, CH_{Ar}); 7.35—7.10 (m, 4 H, CH_{Ar}); 6.85 (m, 1 H, CH_{Ar}); 6.60 (m, 2 H, CH_{Ar}); 6.93 (***A***) and 6.80 (***B***) (both s, 2 H, NH_2); 4.48 (***A***) and 4.40 (***B***) (both s, 1 H, CH); 3.30 (***B***) and 3.27 (***A***) (both s, 3 H, NCH_3); 2.70—2.50 (m, 2 H, CH_2); 2.25—2.05 (m, 2 H, CH_2); 1.90—1.50 (m, 2 H, CH_2). Found (%): C, 61.65; H, 4.53; N, 12.25; Br, 17.94. $C_{23}H_{21}BrN_4O$. Calculated (%): C, 61.48; H, 4.71; N, 12.47; Br, 17.78.

2-Amino-1-methylanilino-5-oxo-4-phenyl-1,4,5,6,7,8-hexahydroquinoline-3-carbonitrile (9b). The yield was 70%. M.p. 187—189 °C. ^{1}H NMR, δ: 7.40—7.15 (m, 7 H, CH_{Ar}); 6.85 (m, 1 H, CH_{Ar}); 6.62 (m, 2 H, CH_{Ar}); 6.47 (***A***) and 6.25 (***B***) (both s, 2 H, NH_2); 4.48 (***A***) and 4.40 (***B***) (both s, 1 H, CH); 3.30 (***B***) and 3.27 (***A***) (both s, 3 H, NCH_3); 2.70—2.50 (m, 2 H, CH_2); 2.25—2.05 (m, 2 H, CH_2); 1.90—1.50 (m, 2 H, CH_2). Found (%): C, 74.71; H, 6.12; N, 15.19. $C_{23}H_{22}N_4O$. Calculated (%): C, 74.57; H, 5.99; N, 15.12.

3-(2-Methyl-2-phenylhydrazino)cyclohex-2-en-1-one (10). A solution of cyclohexane-1,3-dione (2.24 g, 0.02 mol), *N*-methyl-*N*-phenylhydrazine (2.32 g, 0.02 mol), and *para*-toluenesulfonic acid (0.1 g) in benzene (30 mL) was refluxed for 3 h with azeotropic distillation of water. The solvent was evaporated, and the residue was recrystallized from ethyl acetate. The product was obtained in 60% yield (2.70 g). M.p. 139—141 °C. ^{1}H NMR, δ: 8.90 (s, 1 H, NH); 7.25 (m, 2 H); 6.85—6.75 (m, 3 H); 4.98 (s, 1 H, CH); 3.05 (s, 3 H, CH_3); 2.30—2.40 (m, 2 H); 2.10—2.15 (m, 2 H); 1.85—1.95 (m, 2 H).

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