Chemistry of Heterocyclic Compounds, Vol. 41, No. 7, 2005

4-HYDROXY-2-QUINOLONES. 84*. SYNTHESIS OF 5-R-5H-5,7a,12-TRIAZA-BENZO[*a*]ANTHRACENE-6,7-DIONES

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2-Aminopyridines react under thermolysis conditions with ethyl 1-R-4-chloro-2-oxoquinoline-3-carboxylates exclusively in the imino form to give the corresponding 5-R-5H-5,7a,12-triazabenzo[a]anthracene-6,7-diones and 4-(pyridyl-2-amino)-1-R-quinolin-2-ones.

Keywords: azabenzoanthracene, 2-aminopyridine, 4-(pyridyl-2-amino)quinolin-2-one, 3-carbethoxy-4-chloroquinolin-2-one

The ability of bifunctional alkylating and/or acylating agents to react readily with 2-aminopyridines has been widely used in organic chemistry to prepare different condensed heterocycles [2-4]. Many of these have found use medically as highly active antiallergic [5], antimicrobial [6, 7], hypotensive [8], and other medicinal agents.

We have previously shown that ethyl 1-R-4-chloro-2-oxoquinoline-3-carboxylates **1** (prepared from 4-hydroxy derivatives in one or in two stages [9]) react with pyridine under reflux to give high yields of the corresponding N-(1-R-3-carbethoxy-2-oxoquinolin-4-yl)pyridinium chlorides [1]. When pyridine is exchanged for its 2-amino-substituted analog there arises the possibility of a more profound structural transformation, in fact heterocyclization involving the carbethoxy and amino groups.

The reaction of the chloro-substituted esters **1** with primary and secondary alkylamines gives 4-alkylamino-3-carbethoxyquinolones [10]. When the N-(1-R-3-carbethoxy-2-oxoquinolin-4-yl)pyridinium chlorides are treated with excess of both aromatic or aliphatic amines [1] the ester group is unaffected. It follows from this that the first stage of the reaction of esters **1** with 2-aminopyridines is the nucleophilic substitution of the active chlorine atom while the structure of the final reaction product is dictated by the tautomeric form in which the 2-aminopyridine takes part.

In neutral medium the 2-aminopyridines exist almost exclusively in the aromatic tautomeric form, the nucleophilic center of which is the pyridine nitrogen atom [11]. In this case, the discussed reaction should give the triazabenzophenanthrenediones **3** *via* the corresponding quaternary pyridinium salts **2**.

If the 2-aminopyridine takes part in the reaction in the imino form which can be favored in quite forcing conditions (250°C) the initial electrophilic attack will go through the exocyclic nitrogen atom [11] to give the quinolinaminopyridines **4** and finally to the triazabenzoanthracenes **5** rather than the isomeric triazabenzophenanthrenes **3**.

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* For Communication 83 see [1].

National Pharmaceutical University, Kharkov 61002, Ukraine; e-mail: uiv@kharkov.ua. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, pp. 1060-1070, July, 2005. Original article submitted March 9, 2004.

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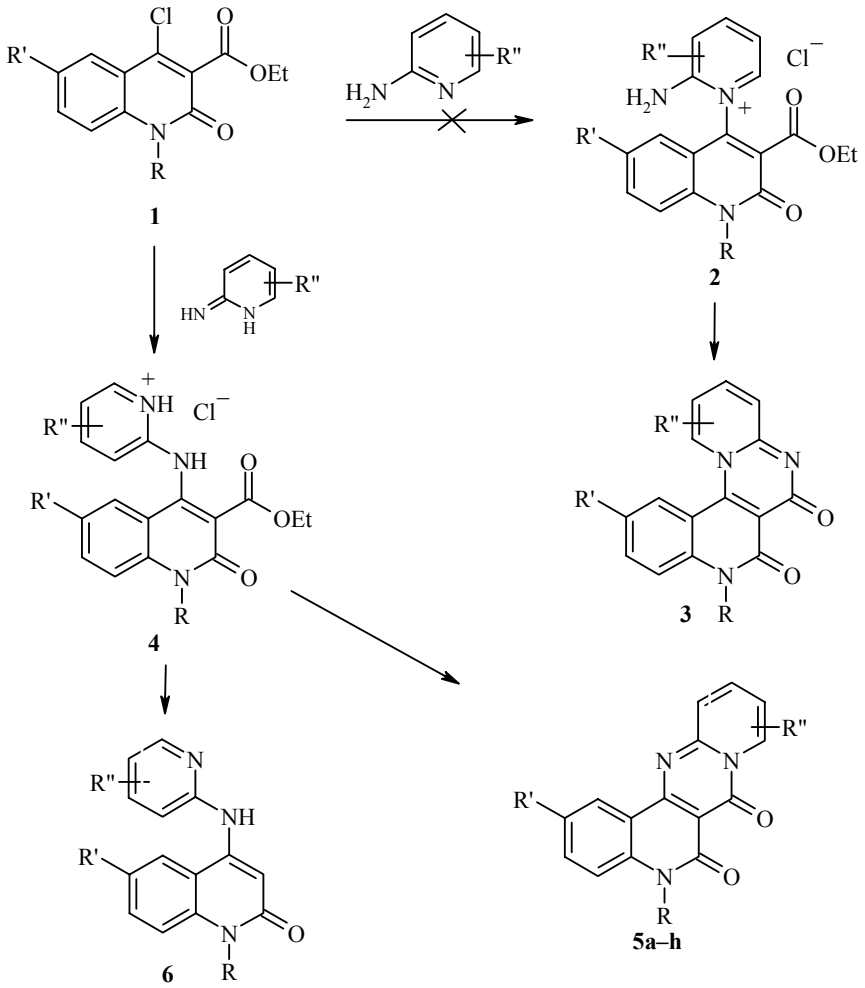

5 a R = R' = R" = H; **b** R = R' = H, R" = 11-OH; **c** R = R' = H, R" = 11-Me; **d** R = R' = H, R" = 10-Me; **e** R = R' = H, R" = 8-Me; **f** R = R' = H, R" = 9-Cl; **g** R = R' = H, R" = 9-Br; **h** R = Me, R' = R" = H; **i** R = Me, R'= H, R" = 10-Me; **j** R = Et, R' = H, R" = 11-OH; **k** R = Pr, R' = R" = H; **l** R = Pr, R' = H, R" = 11-Me; **m** R = Pr, R' = H, R" = 9-Cl; **n** R = Et, R' = Cl, R" = H

Melting equimolar amounts of the esters **1** and 2-aminopyridines and recrystallization from DMF gave satisfactory yields of light-yellow, crystalline materials which sublime on heating and were not soluble in water or alcohols (Table 1). The only exception is the reaction with 2-amino-6-methylpyridine which evidently reacts with difficulty due to steric hindrance and, as a result, the yield of the final product is only 19%.

A distinctive feature of the ^{1}H NMR spectra of the synthesized compounds is the presence of two proton signals at quite low field (around 8.5 to 9 ppm) (Table 2). A comparative analysis of the spectroscopic parameters of the unsubstituted compound and its analogs with the substituents separately in the aminopyridine and quinoline parts of the molecule shows that they are due to the protons at the position 5 and 6 in the starting esters **1** and the aminopyridines respectively. On the one hand, the marked paramagnetic shift of the resonance signals of the indicated protons (e.g. for the quinolone proton, corresponding to position 1 in structures **3** or **5** it averages 0.5 ppm when contrasted with the model ethyl 4-amino- [1] and 4-alkylamino-1H-2-oxoquinoline-3-carboxylates [10]) can be explained by a van der Waal effect which arises through their strong steric interaction. Of the two proposed structures such an effect is seen only for phenanthrenes [12], hence the products of the reaction of the ethyl 1-R-4-chloro-2-oxoquinoline-3-carboxylates **1** with 2-aminopyridines can be characterized as the 5-R-5,8,12a-triazabenzo[*c*]phenanthrene-6,7-diones **3**. On the other hand, the experimental data obtained

TABLE 1. Characteristics of 5-R-5H-5,7a,12-Triazabenzo[*a*]anthracene-6,7-diones **5a-n**

Compound	Empirical formula	Found, % / Calculated, %			mp, °C	Yield, %
		C	H	N		
5a	$C_{15}H_9N_3O_2$	68.31 / 68.44	3.58 / 3.45	15.85 / 15.96	414-416	77
5b	$C_{15}H_9N_3O_3$	64.67 / 64.52	3.14 / 3.25	15.19 / 15.05	397-399	68
5c	$C_{16}H_{11}N_3O_2$	69.45 / 69.31	4.13 / 4.00	15.02 / 15.15	394-396	70
5d	$C_{16}H_{11}N_3O_2$	69.23 / 69.31	4.17 / 4.00	15.26 / 15.15	445-447	72
5e	$C_{16}H_{11}N_3O_2$	69.21 / 69.31	4.10 / 4.00	15.22 / 15.15	337-339	19
5f	$C_{15}H_8ClN_3O_2$	60.66 / 60.52	2.60 / 2.71	14.01 / 14.11	388-390	74
5g	$C_{15}H_8BrN_3O_2$	52.50 / 52.66	2.49 / 2.36	12.33 / 12.28	430-432	66
5h	$C_{16}H_{11}N_3O_2$	69.22 / 69.31	4.13 / 4.00	15.04 / 15.15	365-367	80
5i	$C_{17}H_{13}N_3O_2$	70.20 / 70.09	4.64 / 4.50	14.30 / 14.42	344-346	72
5j	$C_{17}H_{13}N_3O_3$	66.58 / 66.44	4.23 / 4.26	13.79 / 13.67	375-377	65
5k	$C_{18}H_{15}N_3O_2$	70.70 / 70.81	4.84 / 4.95	13.88 / 13.76	278-280	76
5l	$C_{19}H_{17}N_3O_2$	71.57 / 71.46	5.46 / 5.37	13.03 / 13.16	270-272	63
5m	$C_{18}H_{14}ClN_3O_2$	63.60 / 63.63	4.07 / 4.15	12.45 / 12.37	256-258	67
5n	$C_{17}H_{12}ClN_3O_2$	62.77 / 62.88	3.60 / 3.71	12.84 / 12.90	310-312	71

can be interpreted as a simple consequence of the proximity of the indicated protons to electronegative nitrogen atoms in the triazabenzoanthracenes **5**. Hence, without additional investigation of model compounds, ^{1}H NMR can unfortunately not allow an unambiguous conclusion regarding the structure of the compounds obtained.

Neither does chromatography-mass spectrometry give a direct answer although it does show that the synthesized materials are pure and form stable molecular ions when ionized. This is evidenced by their high intensity in the majority of cases whereas the fragment ions rarely exceed 30% (Table 3). The molecular ions are typified by the successive elimination of two molecules of CO. Exceptions are the 5-N-ethyl and N-propyl derivatives, the molecular ions of which initially lose the N-alkyl substituents under electron impact conditions. However, they then successively lose the two CO molecules, i.e. their spectra then fully agree with the spectra of the 5-NH derivatives. It was interesting that peaks for $[M\text{-}OH]^+$, $[M\text{-}Me]^+$, $[M\text{-}Cl]^+$, or $[M\text{-}Br]^+$ fragments were virtually absent in the mass spectra of the compounds prepared from the substituted 2-aminopyridines, their intensities not exceeding 9%. Hence such a fragmentation route can be considered as atypical for the class of compounds studied.

Final evidence for the question of the structure of the reaction products from the esters **1** and 2-aminopyridines came from X-ray analytical data which unambiguously showed that they are the 5-R-5H-5,7,12a-triazabenzo[*a*]anthracene-6,7-diones **5a-n**. Moreover, it was found that in the benzanthracene **5n** (Fig. 1) all of the non-hydrogen atoms (with the exception of atom $C_{(17)}$) lie in a single plane to an accuracy of 0.03 Å. Atom $C_{(17)}$ is placed virtually perpendicularly to the molecular plane (torsional angle $C_{(1)}$–$N_{(1)}$–$C_{(16)}$–$C_{(17)}$ 88.5(3)°). The bicyclic fragment $C_{(8)}$–$C_{(7)}$–$N_{(2)}$–$C_{(10)}$···$C_{(14)}$–$N_{(3)}$–$C_{(15)}$ shows a clear alternation of bonds. In the dihydropyridine ring the $C_{(9)}$–$O_{(1)}$ 1.232(3), $N_{(1)}$–$C_{(1)}$ 1.391(4), and $N_{(1)}$–$C_{(9)}$ 1.392(4) Å bond lengths are

TABLE 2. ^{1}H NMR Spectra of Compounds **5a-n**

Compound	Chemical shifts, δ, ppm (*J*, Hz)				
	H arom.			R	R"
	H-8 (1H)	H-1 (1H)	other aromatic proton signals		
5a	9.04 (d, *J* = 6.6)	8.52 (d, *J* = 8.2)	8.08-7.14 (6H, m)	11.40 (1H, s, NH)	—
5b	9.03 (d, *J* = 7.7)	8.51 (d, *J* = 7.2)	7.57-7.16 (5H, m)	11.41 (1H, s, NH)	10.32 (1H, s, OH)
5c	8.91 (d, *J* = 6.8)	8.55 (d, *J* = 7.9)	7.94-7.10 (5H, m)	11.29 (1H, s, NH)	2.62 (3H, s, CH_3)
5d	8.96 (d, *J* = 7.2)	8.50 (d, *J* = 8.0)	7.63-7.17 (5H, m)	11.38 (1H, s, NH)	2.49 (3H, s, CH_3)
5e	—	8.42 (d, *J* = 8.1)	7.75-6.90 (6H, m)	11.32 (1H, s, NH)	2.87 (3H, s, CH_3)
5f	9.00 (s)	8.50 (d, *J* = 8.2)	8.12-7.18 (5H, m)	11.50 (1H, s, NH)	—
5g	9.07 (s)	8.50 (d, *J* = 8.3)	8.17-7.17 (5H, m)	11.47 (1H, s, NH)	—
5h	9.04 (d, *J* = 6.5)	8.59 (d, *J* = 8.1)	8.06-7.20 (6H, m)	3.52 (3H, s, CH_3)	—
5i	8.92 (d, *J* = 6.9)	8.64 (d, *J* = 8.3)	7.73-7.18 (5H, m)	3.53 (3H, s, CH_3)	2.48 (3H, s, CH_3)
5j	9.05 (d, *J* = 7.9)	8.56 (d, *J* = 7.2)	7.59-7.15 (5H, m)	4.28 (2H, q, *J* = 6.9, NCH_2); 1.22 (3H, t, *J* = 7.0, CH_3)	10.30 (1H, s, OH)
5k	9.00 (d, *J* = 6.9)	8.67 (d, *J* = 8.1)	8.08-7.22 (6H, m)	4.16 (2H, t, *J* = 7.3, NCH_2); 1.67 (2H, m, $C\underline{H}_2CH_3$); 0.94 (3H, t, *J* = 7.3, CH_3)	—
5l	8.89 (d, *J* = 6.8)	8.73 (d, *J* = 8.0)	7.97-7.20 (5H, m)	4.18 (2H, t, *J* = 7.4, NCH_2); 1.64 (2H, m, $C\underline{H}_2CH_3$); 0.96 (3H, t, *J* = 7.4, CH_3)	2.64 (3H, s, CH_3)
5m	8.97 (s)	8.61 (d, *J* = 8.1)	8.03-7.17 (5H, m)	4.15 (2H, t, *J* = 7.4, NCH_2); 1.62 (2H, m, $C\underline{H}_2CH_3$); 0.95 (3H, t, *J* = 7.4, CH_3)	—
5n	8.98 (d, *J* = 7.0)	8.47 (s)	8.05-7.23 (5H, m)	4.17 (2H, q, *J* = 6.9, NCH_2); 1.19 (3H, t, *J* = 6.9, CH_3)	—

longer than their mean values of 1.210, 1.353, and 1.339 Å respectively [13]. A similar bond lengthening has been found in related compounds [14-16].

The benzoanthracene molecule **5n** shows a shortening of intramolecular contacts between the benzene ring $C_{(1)}\cdots C_{(6)}$, the carbonyl $C_{(9)}=O_{(1)}$ group, and the ethyl substituent $C_{(2)}\cdots H_{(16a)}$ 2.54, $C_{(16)}\cdots H_{(2)}$ 2.53 (sum of van der Waal radii 2.87 [17]), $H_{(16a)}\cdots H_{(2)}$ 2.02(2.34), $O_{(1)}\cdots H_{(16b)}$ 2.29 Å (2.46 Å). This does not lead to lengthening of the $N_{(1)}$–$C_{(16)}$ bond. Shortened contacts are also observed between the $N_{(2)}$ and $N_{(5)}$ atoms (2.43, sum of van der Waal radii 2.67 Å) and between the $O_{(2)}$ and $H_{(14)}$ atoms (2.31, 2.46 Å). Intermolecular contacts found in the crystal of the benzanthracene **5n** are $Cl_{(1)}\cdots C_{(17')}$ (1 - *x*, 0.5 + *y*, 1.5 - *z*) 3.55 (3.61) and $Cl_{(1)}\cdots H_{(17b')}$ (1 - *x*, 0.5 + *y*, 1.5 - *z*) 2.93 Å (3.06 Å).

In addition, a more detailed study shows that the reaction discussed does not proceed by a single route. The ^{1}H NMR spectra of the substances precipitated by water from the filtrate after removal of the benzoanthracene **5** showed both residues of the benzoanthracene and also other compounds. In one instance it was actually possible to isolate a crystalline ethanol solvate material (1:1 composition) in a pure state suitable

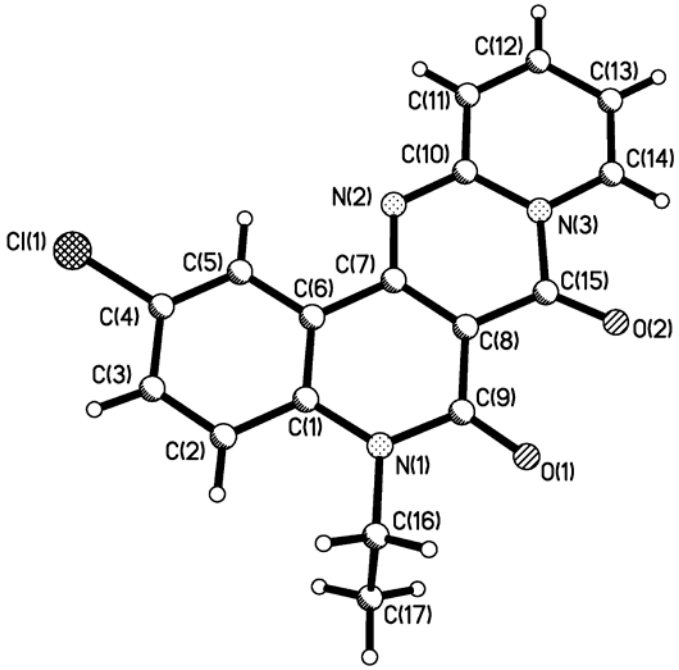

Fig. 1. Structure of the benzoanthracene molecule **5n** with atomic numbering.

for X-ray analysis (Fig. 2). This compound was shown to be 4-(6-methylpyridyl-2-amino)-1H-quinolin-2-one (**6e**) (R = R' = H, R" = 6-Me) which had been formed as a result of the thermolysis of the carbethoxy group of the corresponding quinolinaminopyridine **4** (a feature typical of this class of substances as a whole [18]).

The dihydropyridine ring of the pyridylaminoquinolin-2-one **6e** exists in a "strongly flattened *boat*" conformation (folding parameters: $S = 0.09$, $\theta = 81.1°$, $\psi = 1.2°$ [19]). The deviations of the $N_{(1)}$ and $C_{(7)}$ atoms from the mean plane of the remaining ring atoms are -0.04 and -0.06 Å respectively. Some twist is observed for

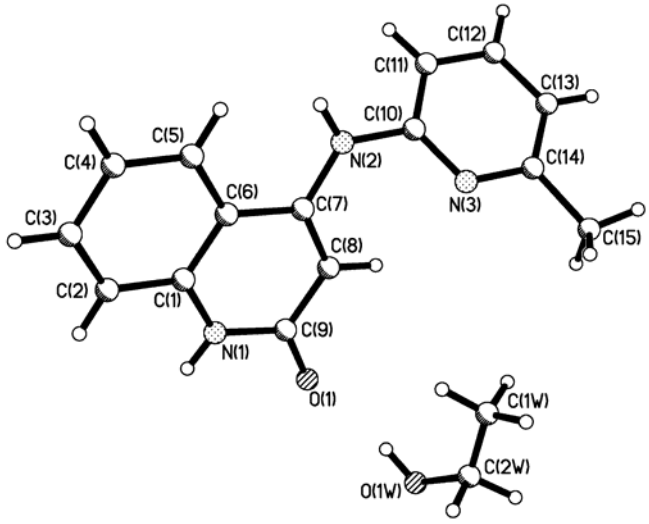

Fig. 2. Structure and atomic numbering for the ethanol solvate of the pyridylaminoquinolin-2-one **6e**.

TABLE 3. Mass Spectra of Compounds **5a-n**

Compound	*m/z* (I_{rel}, %)				
	$[M]^+$	$[M–(R–H)]^+$	$[M–(R–H)–CO]^+$	$[M–(R–H)–2CO]^+$	$[M–R"]^+$
5a	263 (100)	—	235 (27)	207 (12)	—
5b	279 (100)	—	251 (16)	223 (8)	262 (9)
5c	277 (100)	—	249 (23)	221 (14)	262 (7)
5d	277 (100)	—	249 (30)	221 (11)	262 (4)
5e	277 (100)	—	249 (27)	221 (8)	262 (2)
5f	297 (100)	—	269 (23)	241 (6)	262 (5)
5g	341 (100)	—	313 (28)	285 (17)	262 (3)
5h	277 (100)	—	249 (24)	221 (15)	—
5i	291 (100)	—	263 (24)	235 (10)	276 (2)
5j	307 (11)	279 (100)	251 (16)	223 (12)	290 (2)
5k	305 (43)	263 (100)	235 (26)	207 (10)	—
5l	319 (37)	277 (100)	249 (21)	221 (12)	304 (5)
5m	339 (29)	297 (100)	269 (30)	241 (9)	304 (7)
5n	325 (34)	297 (100)	269 (21)	241 (14)	290 (8)

the $C_{(7)}$=$C_{(8)}$ double bond (torsional angle $C_{(6)}$–$C_{(7)}$–$C_{(8)}$–$C_{(9)}$ 5.5(4)°). The formation of an intermolecular bond between the carbonyl oxygen and the solvent molecule ($O_{(1w)}$–$H_{(10w)}$···$O_{(1)}$ H···O 1.85 Å, O–H···O 170°) and the intermolecular hydrogen bond $N_{(1)}$–$H_{(1N)}$···$O_{(1y)}$ (*-x*, *-y*, *-z*) (H···O' 1.95 Å, N–H···O' 172°) leads to a marked redistribution of the electron density in the ring. The $O_{(1)}$–$C_{(9)}$ 1.257(3) Å (mean value 1.210 [13]),

TABLE 4. Bond Lengths (*l*) in the Structure of Compounds **5n** and **6e**

Benzoanthracene **5n**		Pyridylaminoquinolin-2-one **6e**	
Bond	*l*, Å	Bond	*l*, Å
$Cl_{(1)}$–$C_{(4)}$	1.734(3)	$O_{(1)}$–$C_{(9)}$	1.257(3)
$N_{(1)}$–$C_{(9)}$	1.392(4)	$N_{(1)}$–$C_{(1)}$	1.380(3)
$N_{(2)}$–$C_{(10)}$	1.322(4)	$N_{(2)}$–$C_{(10)}$	1.406(4)
$N_{(3)}$–$C_{(14)}$	1.375(4)	$N_{(3)}$–$C_{(14)}$	1.357(4)
$N_{(3)}$–$C_{(15)}$	1.455(4)	$C_{(1)}$–$C_{(2)}$	1.395(4)
$O_{(2)}$–$C_{(15)}$	1.212(4)	$C_{(3)}$–$C_{(4)}$	1.392(4)
$C_{(1)}$–$C_{(2)}$	1.407(4)	$C_{(5)}$–$C_{(6)}$	1.415(4)
$C_{(3)}$–$C_{(4)}$	1.379(5)	$C_{(7)}$–$C_{(8)}$	1.371(4)
$C_{(5)}$–$C_{(6)}$	1.390(4)	$C_{(10)}$–$C_{(11)}$	1.371(4)
$C_{(7)}$–$C_{(8)}$	1.393(4)	$C_{(12)}$–$C_{(13)}$	1.367(5)
$C_{(8)}$–$C_{(9)}$	1.451(4)	$C_{(14)}$–$C_{(15)}$	1.487(5)
$C_{(11)}$–$C_{(12)}$	1.357(5)	$C_{(1W)}$–$C_{(2W)}$	1.508(1)
$C_{(13)}$–$C_{(14)}$	1.343(5)	$N_{(1)}$–$C_{(9)}$	1.359(3)
$N_{(1)}$–$C_{(1)}$	1.391(4)	$N_{(2)}$–$C_{(7)}$	1.372(3)
$N_{(1)}$–$C_{(16)}$	1.471(4)	$N_{(3)}$–$C_{(10)}$	1.321(4)
$N_{(2)}$–$C_{(7)}$	1.347(4)	$C_{(1)}$–$C_{(6)}$	1.395(4)
$N_{(3)}$–$C_{(10)}$	1.386(4)	$C_{(2)}$–$C_{(3)}$	1.362(4)
$O_{(1)}$–$C_{(9)}$	1.232(3)	$C_{(4)}$–$C_{(5)}$	1.366(4)
$C_{(1)}$–$C_{(6)}$	1.390(4)	$C_{(6)}$–$C_{(7)}$	1.445(4)
$C_{(2)}$–$C_{(3)}$	1.376(4)	$C_{(8)}$–$C_{(9)}$	1.416(4)
$C_{(4)}$–$C_{(5)}$	1.370(4)	$C_{(11)}$–$C_{(12)}$	1.370(5)
$C_{(6)}$–$C_{(7)}$	1.450(4)	$C_{(13)}$–$C_{(14)}$	1.370(5)
$C_{(8)}$–$C_{(15)}$	1.431(4)	$O_{(1W)}$–$C_{(2W)}$	1.407(7)
$C_{(10)}$–$C_{(11)}$	1.413(4)		
$C_{(12)}$–$C_{(13)}$	1.389(5)		
$C_{(16)}$–$C_{(17)}$	1.518(5)		

TABLE 5. Valence Angles (ω) in the Structure of Compounds **5n** and **6e**

Benzoanthracene **5n**		Pyridylaminoquinolin-2-one **6e**	
Angle	ω, deg.	Angle	ω, deg.
$C_{(1)}–N_{(1)}–C_{(9)}$	122.7(3)	$C_{(9)}–N_{(1)}–C_{(1)}$	123.5(2)
$C_{(9)}–N_{(1)}–C_{(16)}$	116.3(2)	$C_{(10)}–N_{(3)}C_{(14)}$	117.9(3)
$C_{(14)}–N_{(3)}C_{(10)}$	121.1(3)	$N_{(1)}–C_{(1)}–C_{(2)}$	119.4(2)
$C_{(10)}–N_{(3)}C_{(15)}$	122.1(3)	$C_{(3)}–C_{(2)}–C_{(1)}$	120.4(3)
$C_{(6)}–C_{(1)}–C_{(2)}$	119.3(3)	$C_{(5)}–C_{(4)}–C_{(3)}$	120.9(3)
$C_{(3)}–C_{(2)}–C_{(1)}$	119.6(3)	$C_{(1)}–C_{(6)}–C_{(5)}$	117.8(2)
$C_{(5)}–C_{(4)}–C_{(3)}$	120.2(3)	$C_{(5)}–C_{(6)}–C_{(7)}$	124.1(2)
$C_{(3)}–C_{(4)}–Cl_{(1)}$	118.9(3)	$C_{(8)}–C_{(7)}–C_{(6)}$	118.9(2)
$C_{(1)}–C_{(6)}–C_{(5)}$	119.7(3)	$C_{(7)}–C_{(8)}–C_{(9)}$	122.1(2)
$C_{(5)}–C_{(6)}–C_{(7)}$	120.0(3)	$O_{(1)}–C_{(9)}–C_{(8)}$	123.5(2)
$N_{(2)}–C_{(7)}–C_{(6)}$	117.0(3)	$N_{(3)}–C_{(10)}–C_{(11)}$	123.3(3)
$C_{(7)}–C_{(8)}–C_{(15)}$	119.6(3)	$C_{(11)}–C_{(10)}–N_{(2)}$	119.4(3)
$C_{(15)}–C_{(8)}–C_{(9)}$	118.8(3)	$C_{(13)}–C_{(12)}–C_{(11)}$	118.8(3)
$O_{(1)}–C_{(9)}–C_{(8)}$	123.5(3)	$N_{(3)}–C_{(14)}–C_{(13)}$	121.4(3)
$N_{(2)}–C_{(10)}–N_{(3)}$	122.4(3)	$C_{(13)}–C_{(14)}–C_{(15)}$	122.4(3)
$N_{(3)}–C_{(10)}–C_{(11)}$	117.4(3)	$C_{(7)}–N_{(2)}–C_{(10)}$	126.2(2)
$C_{(11)}–C_{(12)}–C_{(13)}$	119.7(3)	$N_{(1)}–C_{(1)}–C_{(6)}$	119.9(2)
$C_{(13)}–C_{(14)}–N_{(3)}$	120.3(3)	$C_{(6)}–C_{(1)}–C_{(2)}$	120.8(2)
$O_{(2)}–C_{(15)}–N_{(3)}$	117.1(3)	$C_{(2)}–C_{(3)}–C_{(4)}$	119.7(3)
$N_{(1)}–C_{(16)}–C_{(17)}$	111.5(3)	$C_{(4)}–C_{(5)}–C_{(6)}$	120.5(3)
$C_{(1)}–N_{(1)}–C_{(16)}$	121.0(2)	$C_{(1)}–C_{(6)}–C_{(7)}$	118.2(2)
$C_{(10)}–N_{(2)}–C_{(7)}$	117.9(3)	$C_{(8)}–C_{(7)}–N_{(2)}$	123.0(2)
$C_{(14)}–N_{(3)}–C_{(15)}$	116.8(3)	$N_{(2)}–C_{(7)}–C_{(6)}$	118.1(2)
$C_{(6)}–C_{(1)}–N_{(1)}$	120.0(3)	$O_{(1)}–C_{(9)}–N_{(1)}$	119.4(2)
$N_{(1)}–C_{(1)}–C_{(2)}$	120.7(3)	$N_{(1)}–C_{(9)}–C_{(8)}$	117.1(2)
$C_{(2)}–C_{(3)}–C_{(4)}$	120.6(3)	$N_{(3)}–C_{(10)}–N_{(2)}$	117.3(2)
$C_{(5)}–C_{(4)}–Cl_{(1)}$	120.9(3)	$C_{(12)}–C_{(11)}–C_{(10)}$	118.8(3)
$C_{(4)}–C_{(5)}–C_{(6)}$	120.5(3)	$C_{(12)}–C_{(13)}–C_{(14)}$	119.9(3)
$C_{(1)}–C_{(6)}–C_{(7)}$	120.2(3)	$N_{(3)}–C_{(14)}–C_{(15)}$	116.3(3)
$N_{(2)}–C_{(7)}–C_{(8)}$	124.7(3)	$C_{(2W)}–O_{(1W)}–H_{(1OW)}$	113(3)
$C_{(8)}–C_{(7)}–C_{(6)}$	118.3(3)	$O_{(1W)}–C_{(2W)}–C_{(1W)}$	119.4(6)
$C_{(7)}–C_{(8)}–C_{(9)}$	121.6(3)		
$O_{(1)}–C_{(9)}–N_{(1)}$	119.3(3)		
$N_{(1)}–C_{(9)}–C_{(8)}$	117.2(3)		
$N_{(2)}–C_{(10)}–C_{(11)}$	120.2(3)		
$C_{(12)}–C_{(11)}–C_{(10)}$	120.8(3)		
$C_{(14)}–C_{(13)}–C_{(12)}$	120.6(3)		
$O_{(2)}–C_{(15)}–C_{(8)}$	129.6(3)		
$C_{(8)}–C_{(15)}–N_{(3)}$	113.2(3)		

$N_{(1)}–C_{(9)}$ 1.359(3) (1.339), $N_{(1)}–C_{(1)}$ 1.380(3) (1.353), $C_{(7)}–C_{(8)}$ 1.371(4) Å (1.326 Å) bonds are lengthened and the $C_{(6)}–C_{(7)}$ 1.445(4) (1.470) and $C_{(8)}–C_{(9)}$ 1.416(4) Å (1.455 Å) are shortened. Similar effects have been seen in the 4-(4-ethoxyphenylamino)-1H-quinolin-2-one previously studied by us [16].

The steric repulsion between the aromatic ring $C_{(1)}\cdots C_{(6)}$ and the NH group (shortened contacts $C_{(5)}\cdots H_{(2N)}$ 2.56 Å (sum of van der Waal radii 2.87 [17]), $H_{(5)}\cdots N_{(2)}$ 2.60 (2.67), and $H_{(5)}\cdots H_{(2N)}$ 2.08 Å (2.34 Å)) determine the pyramidal configuration of the $N_{(2)}$ atom (sum of valence angles 358°). This also probably explains the lengthening of the $N_{(2)}–C_{(7)}$ 1.372(3) and $N_{(2)}–C_{(10)}$ 1.406(3) Å bonds when compared with the mean values of 1.339 and 1.353 Å respectively.

The pyridine ring is virtually coplanar with the $C_{(7)}–C_{(8)}$ bond (torsional angle $C_{(10)}–N_{(2)}–C_{(7)}–C_{(8)}$ -2.5(4)°) and is turned relative to the $C_{(7)}–N_{(2)}$ bond by -44.5(4)° (torsional angle $C_{(7)}–N_{(2)}–C_{(10)}–N_{(3)}$) despite the formation of the weak intramolecular hydrogen bond $C_{(8)}–H_{(8)}\cdots N_{(3)}$ H···N 2.35 Å, C–H···N 121°. The presence

of various substituents at atoms $C_{(10)}$ and $C_{(14)}$ in the pyridine ring is the reason for the lengthening of the $N_{(3)}$–$C_{(14)}$ 1.357(4) Å and shortening of the $N_{(3)}$–$C_{(10)}$ bond 1.321(4) Å when compared with the mean value of 1.337 Å in pyridine. A weak intermolecular hydrogen bond $N_{(2)}$–$H_{(2N)}$···$O_{(1w")}$ (*x*, *y* - 1, *z*) (H···O" 2.23 Å, N–H···O" 160°) is also formed in the crystal of the **6e** molecule.

It should be mentioned that there is a significant difference in the ^{1}H NMR spectrum of the pyridylaminoquinolin-2-one **6e** which hinders its simple interpretation from the spectra of the structural analogs 4-amino- [1] and 4-(4-ethoxyphenylamino)-1H-quinolin-2-ones [18]. This characteristic feature is an unusually large low field shift of the signals for the proton at position 3 of the quinoline ring (by 2 ppm) and the 4-NH group proton (by about 1 ppm). The reason for this effect is likely the participation of the $C_{(3)}$–H proton in the intramolecular hydrogen bond already mentioned with the pyridine nitrogen atom and also the proximity of the latter to the 4-NH group.

EXPERIMENTAL

^{1}H NMR spectra for the synthesized compounds were recorded on a Varian Mercury VX-200 (200 MHz) instrument using DMSO-d_6 solvent and TMS internal standard. Mass spectra were recorded on a Finnigan MAT Incos 50 quadrupole spectrometer in total scanning mode within the range 33-700 *m/z*, electron impact ionization 70 eV with direct introduction of the sample and heating velocity of about 5°C/s.

8-Methyl-5H-5,7,12a-triazabenzo[*a*]anthracene-6,7-dione (5e). A mixture of ethyl 1-H-4-chloro-2-oxoquinoline-3-carboxylate (**1**) (2.51 g, 0.01 mol) and 2-amino-6-methylpyridine (1.08 g, 0.01 mol) was thoroughly stirred and held for 20-30 min in a metal bath at 250°C. After cooling, the residue was dissolved in refluxing DMF, purified through carbon, and filtered. The crystals formed of the benzanthracene **5e** were filtered off, washed on the funnel with alcohol and then water and dried.

All of the benzoanthracenes **5** (Table 1) were prepared by the same method.

4-(6-Methylpyridyl-2-amino)-1H-quinolin-2-one (6e, R = R' = H, R'' = 6-Me). After removal of the benzoanthracene **5e** in the preceding method the filtrate was treated with water. The precipitate was filtered off, washed with water, and dried. Yield 1.58 g (63%). Double recrystallization from aqueous ethanol gave translucent solvate crystals; mp 225-227°C (sealed capillary). The pure material with mp 271-273°C was prepared by holding the finely ground solvate in a desiccator cabinet at 100-110°C for 3 days. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 11.20 (1H, s, CONH); 8.92 (1H, s, NH); 8.18 (1H, d, *J* = 8.1, H-5); 7.63 (1H, t, *J* = 7.3, H-4'); 7.49 (1H, t, *J* = 7.2, H-7); 7.43 (1H, s, H-3); 7.29 (1H, d, *J* = 8.6, H-8); 7.23-7.10 (2H, m, H-6 and H-3'); 6.84 (1H, d, *J* = 7.4, H-5'); 2.43 (3H, s, CH_3). Found, %: C 71.55; H 5.17; N 16.77. $C_{15}H_{13}N_3O$. Calculated, %: C 71.69; H 5.21; N 16.72.

X-ray Analysis. Crystals of the benzoanthracene **5n** are monoclinic, at 20°C *a* = 8.730(2), *b* = 15.672(5), *c* = 11.484(4) Å, β = 111.05(2)°; *V* = 1466.4(8) Å^3; M_r = 325.75; *Z* = 4; space group $P2_1/c$, d_{calc} = 1.475 g/cm^3, μ(MoKα) = 0.274 mm^{-1}, *F*(000) = 672. Crystals of the ethanol solvate of the pyridylaminoquinolin-2-one **6e** are monoclinic, at 20°C *a* = 11.131(4), *b* = 9.477(3), *c* = 15.332(5) Å; β = 107.98(3)°; *V* = 1538.4(9) Å^3; M_r = 297.35; *Z* = 4; space group $P2_1/c$; d_{calc} = 1.284 g/cm^3; μ(MoKα) = 0.086 mm^{-1}; *F*(000) = 632. Unit cell parameters and intensities for 2614 reflections (2427 independent with R_{int} = 0.042) for benzoanthracene **5n** and 2799 reflections (2578 independent with R_{int} = 0.04) for the pyridylaminoquinolin-2-one **6e** were measured on a Siemens P3/PC, automatic four circle diffractometer (MoKα, graphite monochromator, θ/2θ scanning, $2\theta_{max}$ = 50°).

The structure was solved by a direct method using the SHELXTL program package [20]. The position of the hydrogen atoms was revealed in electron density difference synthesis. Refinement of the hydrogen atom positions was carried out using the "riding" method with $U_{iso} = nU_{eq}$ for the non-hydrogen atom bonded to the given hydrogen (*n* = 1.5 for methyl groups and *n* = 1.2 for remaining hydrogen atoms). The atoms $H_{(1N)}$, $H_{(2N)}$,

and $H_{(10w)}$ in the structure of the pyridylaminoquinolin-2-one **6e** were refined isotropically. All of the remaining hydrogen atoms in this compound were refined using the riding method with nonfixed U_{iso}. Limits were set for the bond lengths in the solvent molecule ($C(sp^3)$–$C(sp^3)$ 1.51(1) Å) in the refinement. The structures were refined for F_2 by a full matrix, least squares analysis in the anisotropic approximation for non hydrogen atoms to wR_2 = 0.091 for 2427 reflections (R_1 = 0.045 for 1190 reflections with $F > 4\sigma$ (F), S = 0.858) for the benzoanthracene **5n** and to wR_2 = 0.155 for 2578 reflections (R_1 = 0.059 for 1597 reflections with $F > 4\sigma$ (F), S = 0.972) for the pyridylaminoquinolin-2-one **6e**. The full crystallographic information is deposited in the Cambridge data base (benzoanthracene **5n** No. CCDC 240007 and the pyridylaminoquinolin-2-one **6e** No. CCDC 240006). The interatomic distances and valence angles are given in Tables 4 and 5.

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