Synthesis of phthalimidines linked to quinoline derivatives by an amide bridge

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The reactions of 3-acetoxy-2-acetyl(cyanoacetyl)aminoisoindolin-1-one (**1**) with *o*-tosylaminobenzaldehyde and *o*-mesylaminobenzaldehyde morpholinals lead to a mixture of 2-(2-aminoquinoline-3-carboxamido)-3-morpholinoisoindolin-1-one (**3**) and 3-cyanoquinolin-2(1*H*)-one (**4**). The reaction of **1** with 5-nitro-2-tosylaminobenzaldehyde morpholinal yields a mixture of 2-(2-amino-6-nitroquinoline-carboxamido)-3-morpholinoisoindolin-1-one and 3-cyano-6-nitroquinolin-2(1*H*)-one. 3-Acetoxy-2-(quinolino[2,3-*d*]-2-methyl-4-oxopyrimidin-3-yl)isoindolin-1-one (**20**) was prepared by the condensation of *o*-formylbenzoic acid and 2-aminoquinoline-3-carbohydrazide in Ac_2O. The structures of compounds **3**, **4**, and **20** were established by X-ray analysis.

Key words: 3-acetoxy-2-acetyl(cyanoacetyl)aminoisoindolin-1-one; morpholinals of *o*-tosylaminobenzaldehyde, *o*-mesylaminobenzaldehyde, 5-nitro-2-tosylaminobenzaldehyde; 2-(2-aminoquinoline-3-carboxamido)-3-morpholinoisoindolin-1-one; 3-cyanoquinolin-2(1*H*)-one; 3-cyano-6-nitroquinolin-2(1*H*)-one; 3-acetoxy-2-(quinolino[2,3-*d*]-2-methyl-4-oxopyrimidin-3-yl)isoindolin-1-one; quantum chemical study, X-ray diffraction analysis.

The term "twin drugs" accepted in modern medicinal chemistry means physiologically active substances comprising two pharmacophoric groups linked by a covalent bridge.[1] The activity of twin drugs can considerable exceed that of their constituents. A typical example of the "symmetrical twin drug" is the drug BDHP consisting of two molecules of the calcium channel agonist nitrendipine linked by a tetramethylene bridge. The hypotensive activity of BDHP is about 10 times as high as that of nitrendipine.[1,2] Twin drugs can also be composed of two different physiologically active substances. The examples of such compounds comprising isoindoline derivatives and 3-piperazino-1,2-benzoisothiazole linked by different bridges with activities of P_2 dopamine and 5-HT_2 serotonin receptor antagonists are documented.[3,4]

Recently,[5] we have described the synthesis of phthalimidines from *o*-formylbenzoic acid acylhydrazides, including 3-acetoxy-2-acetyl(cyanoacetyl)aminoisoindolin-2-one (**1**). On the basis of a new modification of the Friedlander synthesis,[6] we expected that the reaction of compound **1** with *o*-tosylaminobenzaldehyde morpholinal[7] (**2**) would result in 2-aminoquinoline linked to phthalimidine by the amide bridge. Recrystallization of the reaction product from CH_3CN gave a seemingly homogeneous crystalline substance with a sharp melting point.

However, the X-ray diffraction study showed that it was a mixture of two compounds, namely, the expected 2-(2-aminoquinoline-3-carboxamido)-3-morpholinoisoindolin-1-one (**3**) and 3-cyanoquinolin-2(1*H*)-one (**4**). *N*-Tosylmorpholine (**5**) that is formed in this variant of the Friedlander synthesis[6] was also isolated from the reaction mixture (Scheme 1).

Compounds **3** and **4** could easily be separated, because the former is completely insoluble in acetone and the latter is insoluble in $CHCl_3$.

Presumably, the first step of the reaction is the coupling of **1** with **2** with elimination of two molecules of morpholine and the formation of compound **6** (Scheme 2), which may exist as two geometric isomers, *Z* and *E*, which in turn may exist as several conformers.

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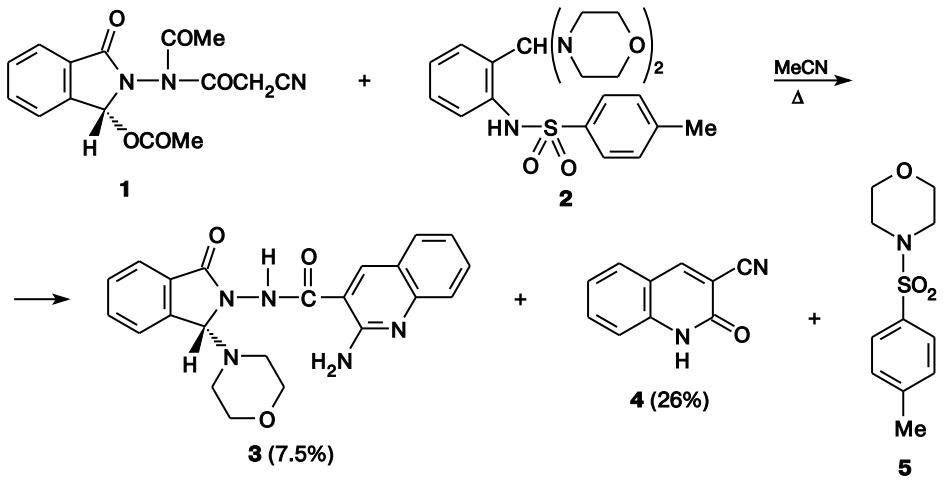
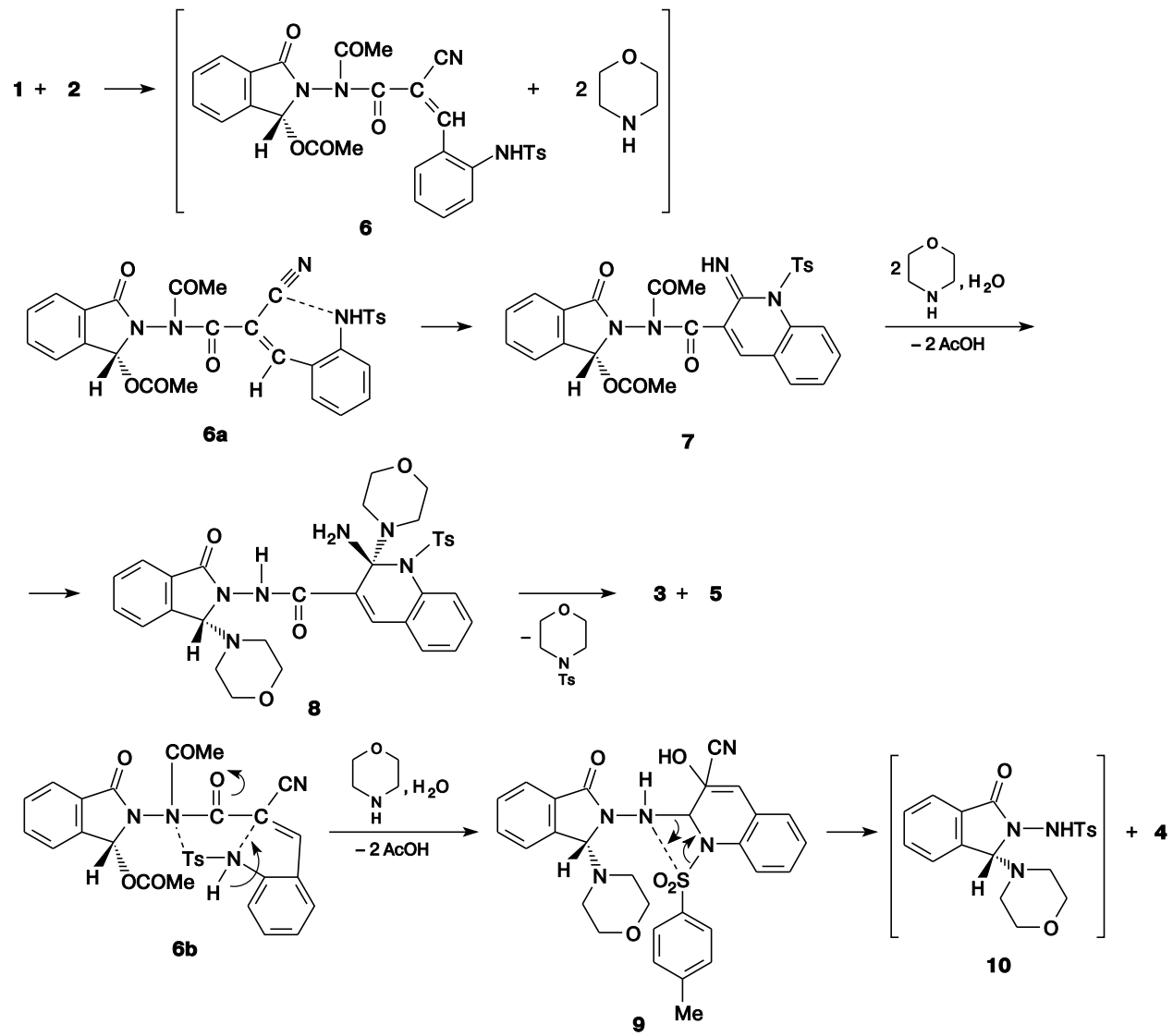
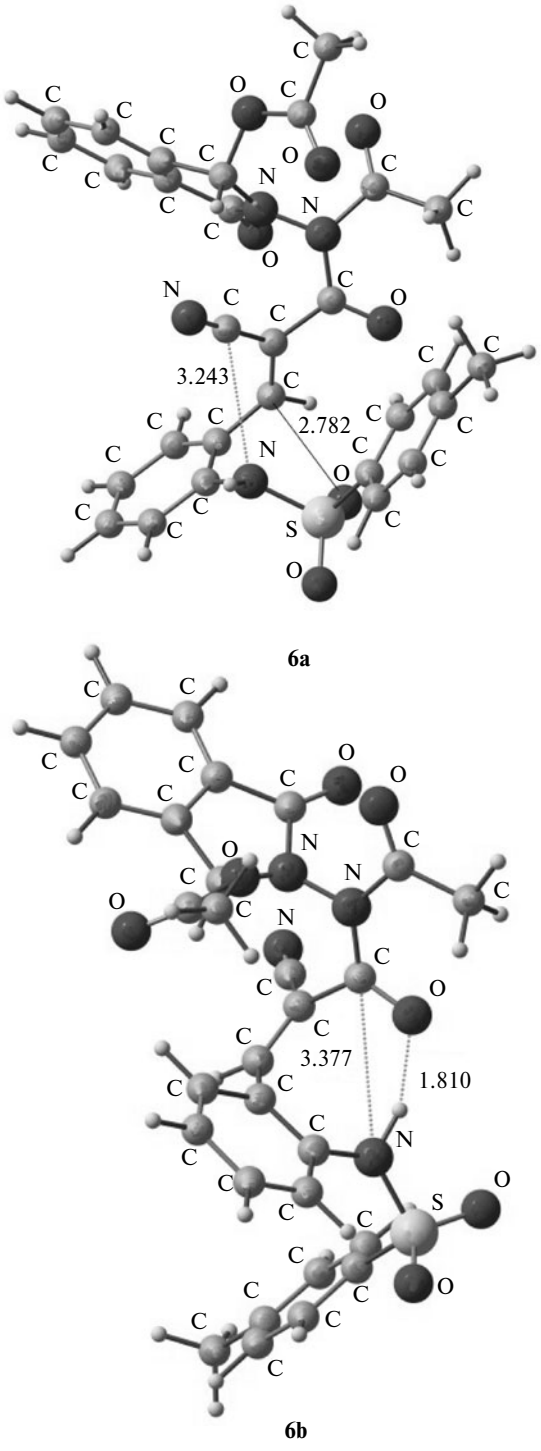
Scheme 1



Scheme 2



We performed a quantum chemical study of thermodynamical characteristics of the reaction of compound **1** with **2**. The calculations (B3LYP/3-21G*) suggested[8,9] the possibility of the formation of the respective conformers **6a** (in *Z*-isomer) and **6b** (in *E*-isomer) (Fig. 1), which



6a **6b**

Fig. 1. The structures of conformers **6a** and **6b** as calculated by B3LYP/3-21G* method. The bond lengths are given in Å.

are the most probable intermediates of compounds **3** and **4** whose putative mechanisms are outlined in Scheme 2.

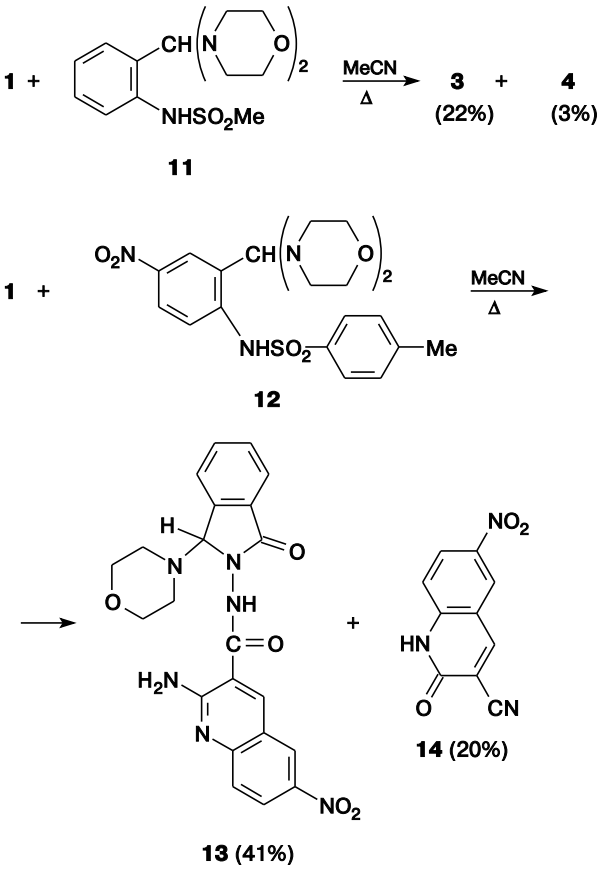
In conformer **6a**, the tosylamino fragment is oriented relative to the C≡N bond in such a manner that the system becomes structurally prepared to further transformation **6a**→**3** (proton transfer to the nitrogen center and the formation of a new NC bond). In conformer **6b**, the tosylamino fragment is oriented relative to the C=O bond in such a manner that the system is structurally prepared to transformation **6b**→**4** (proton transfer to the oxygen center and the formation of a new NC bond). The calculated noncovalent distances N···C in conformers **6a** and **6b** (3.24 and 3.38 Å respectively) are close to the sum of the van der Waals atomic radii of carbon and nitrogen (3.31 Å),[10] therefore the attractive interaction between the oppositely charged atoms is possible. At the same time, the Bader topological analysis of distribution of total electron density (AIM-analysis[11]) in conformer **6a** allows us to conclude the bonding between an oxygen atom of the tosyl group and the sp^2-hybridized carbon atom of the C=C bond bearing two electron-withdrawing substituents (Fig. 1). Thus, the approaching of C and N atoms can be regarded as compulsive. Conformation **6b** is additionally stabilized by the intramolecular hydrogen bond between the amino group and the carbonyl fragment. According to the calculations conformer **6b** is only by 1.8 kcal mol^{-1} energetically more stable then conformer **6a**. Both processes are exothermic: the energetic effect of the reaction resulting in compound **3** is 63.9 kcal mol^{-1}, the energetic effect of the second reaction is almost twice as low (34.5 kcal mol^{-1}). However, the yield of cyanoquinolinone **4** appeared to be considerably higher than the yield of compound **3**, which suggests importance of other factors in addition to the energetic one.

We also performed the analogous reaction with *o*-mesylaminobenzaldehyde morpholinal (**11**). Compound **3** was the major product with quinolinone **4** as the minor by-product (Scheme 3). Starting from phthalimidine **1** and 5-nitro-2-tosylaminobenzaldehyde morpholinal **12** (Refs. 12, 13) we obtained 2-(2-amino-6-nitroquinoline-3-carboxamido)-3-morpholinoisoindolin-1-one (**13**) and 3-cyano-6-nitroquinolin-2(1*H*)-one (**14**) (Scheme 3).

The calculations for the reaction with the mesyl derivative also indicate the possibility of the formation of conformers **15a** (in *Z*-isomer) and **15b** (in *E*-isomer) characterized by shortened distance N···C (Fig. 2). In conformer **15a**, the mesylamino fragment is oriented relative to the C≡N bond in such a manner that the system becomes structurally prepared to further transformation **15a**→**3**, while in conformer **15b** the mesylamino fragment is oriented relative to the C=O in such a manner that the system is structurally prepared to transformation **15b**→**4**. The calculated noncovalent distances N···C in conformers **15a** and **15b** (2.847 and 2.940 Å, respectively) are considerably shortened than those in the tosyl derivative and are

considerably smaller than the sum of the van der Waals atomic radii of carbon and nitrogen. Both conformers are additionally stabilized by a hydrogen bond, which determines the direction of the further proton migration. The hydrogen bond is rather strong (1.76 Å) in compound **15b** and considerably weaker (2.24 Å) in compound **15a**. Conformer **15a** is by 15.3 kcal mol^{-1} more energetically favorable than conformer **15b**. According to our calculations, both processes are exothermic. The energetic effect of the reaction resulting in compound **3** is 56.8 kcal mol^{-1}, the energetic effect of the second reaction is 40.1 kcal mol^{-1}.

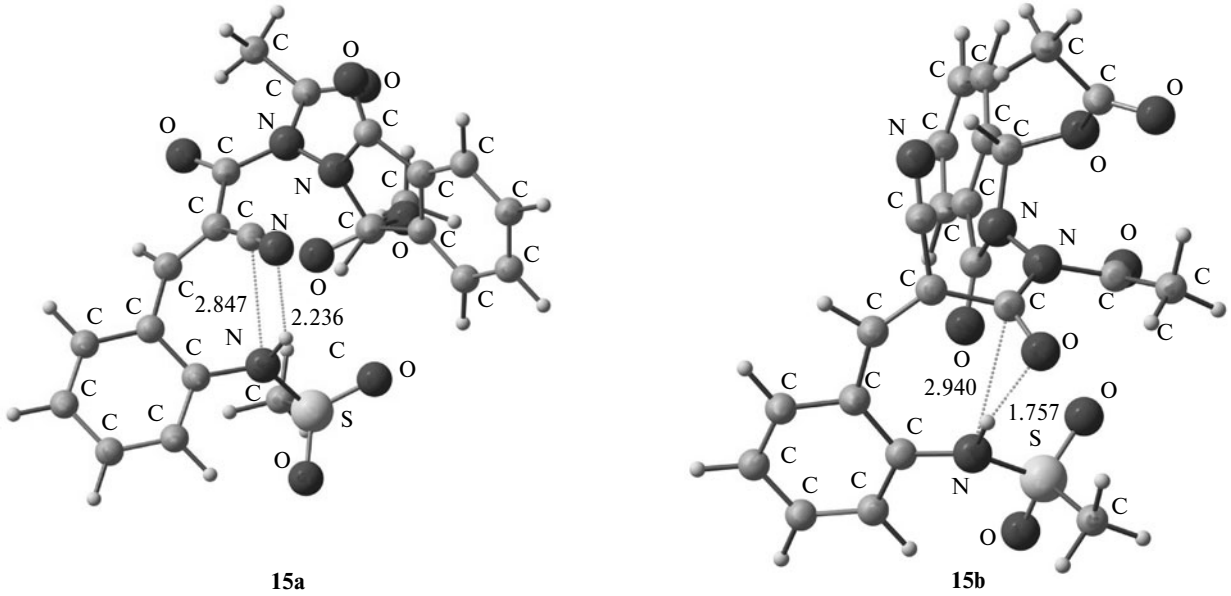
Scheme 3



Theoretically, an alternative synthesis of a derivative of compound **3** was possible, *viz.*, by cyclization of hydrazone **18** prepared from *o*-formylbenzoic acid **16** and 2-aminoquinolin-3-carbohydrazide **17** (see Ref. 6) in acetic anhydride (Scheme 4). However, in this reaction instead of the expected compound **19** the product of further condensation **20** was isolated (Scheme 4), whose structure was established by X-ray analysis.

The general view of molecule **4** is shown in Fig. 3. Molecule **4** is planar (the root-mean-square deviation is 0.015 Å). In the crystal structure, the molecules form the centrosymmetric dimers owing to the rather strong H-bond N(1)—H(1N)...O(1) (H...O 1.92 Å, N...O 2.799(3) Å, N—H...N 165°).

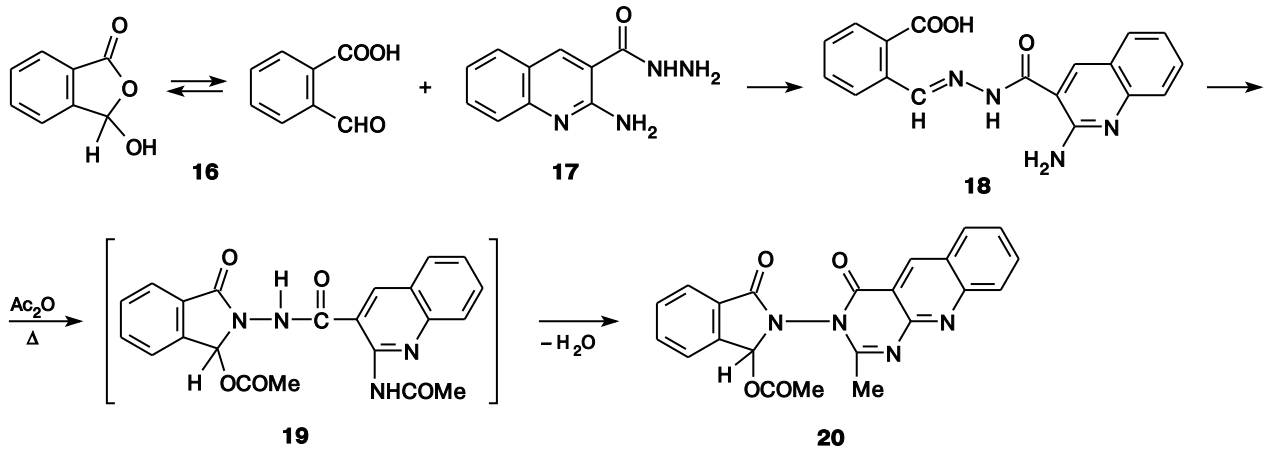
Molecule **3** is outlined in Fig. 4. The quinoline and phthalimidine fragments are planar (the root-mean-square deviations are 0.037 and 0.023 Å, respectively). The central amide fragment NHCO is rotated relative to both the quinoline (40.57(9)°) and the phthalimidine (77.5(2)°) rings. In the former case, it is connected with the steric repulsion of the hydrogen atoms at N(3) and N(15) along with the presence of a weak intramolecular hydrogen bond between the carbonyl group C(13)=O(3) and the amino group N(5)—H(5)N(2)...O(3) (H...O 2.12 Å, N...O



15a 15b

Fig. 2. The structures of conformers **15a** and **15b** as calculated by B3LYP/3-21G* method. The bond lengths are given in Å.

Scheme 4



2.808(4) Å, N—H...N 132°). The structure of the fragment phthalimidine—NHCO can be explained by the steric repulsion of the substituents at N(1) and N(8) from the nearest atoms of the central fragment NHCO and, probably, by the anomeric interaction between of the lone-electron pair of the N(2) atom and the N(3)—C(13) bond antibonding orbital.

In the crystal, the carbonyl group C(8)=O(2) takes part in the intermolecular hydrogen bonding with the hydrogen atom of the amide group N(3)—H(3)N...O(2) (H...O 1.97 Å, N...O 2.869(3) Å, N—H...N 174°) along with the formation of the centrosymmetric dimers that link in the ribbons by a weaker H-bond N(5)—H(5)N(1)...N(4) (H...N 2.15 Å, N...N 3.052(4) Å, N—H...N 177°), located along the crystallographic axis *c* (Fig. 2, *b*).

The general view of molecule **20** is shown in Fig. 5. The tricyclic quinoline-oxopyrimidine fragment has a planar structure (the root-mean-square is 0.061 Å), while the five-membered ring of the phthalimidine fragment is characterized by the flattened envelope conformation, the nitrogen atom N(4) deviates from the ring plane (including the benzene ring atoms) by 0.148(2) Å. The mutual orientation of the cyclic fragments is close to perpendicular (the interplanar angle is 79.48(2)°), it is caused, as in molecule **4**, by the steric repulsion of the *ortho*-substitu-

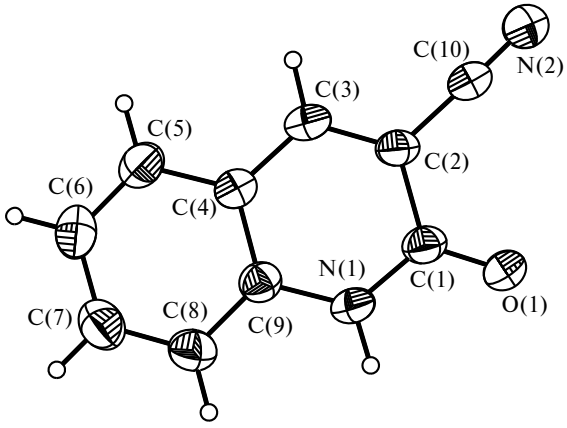


Fig. 3. The general view of molecule **4** with displacement of atoms by ellipsoids drawn at the 50% probability level.

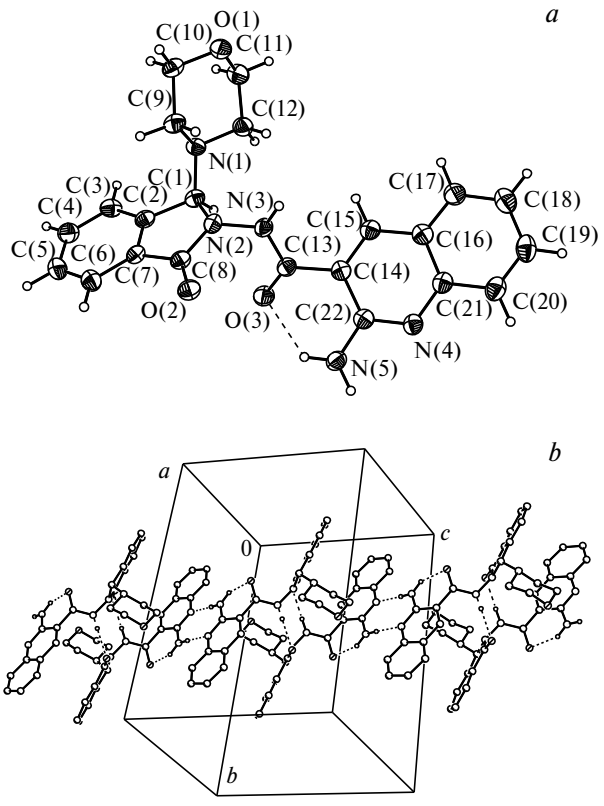


Fig. 4. The molecular (*a*) and crystal (*b*) structure of compound **3** with displacement of atoms by ellipsoids drawn at the 50% probability level.

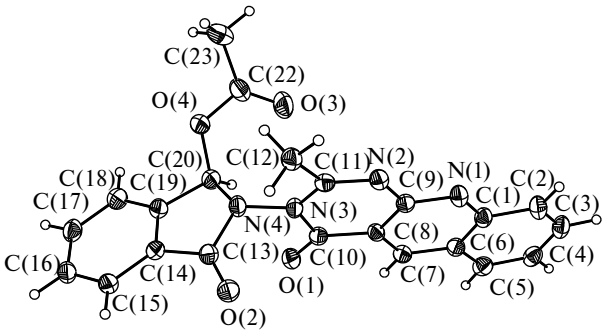


Fig. 5. The general view of molecule **20** with displacement of atoms by ellipsoids drawn at the 50% probability level.

ents of the rings. It should be mentioned that the structure of the fragment phthalimidine—NRCO appeared to be almost the same in molecules **3**, **20**, and in **1**, which was described by us earlier.[5] The N—N bonds lengths are also identical (in **3**, N(2)—N(3) 1.387(3) Å; in **20**, N(3)—N(4) 1.389(2) Å; in **1** (see. Ref. 5), N(1)—N(2) 1.390(3) Å) and close to the average value of the single N—N bond 1.401 Å (see Ref. 14). A slight difference in the structure of the five-member ring and the rotation of the NRCO group could be influenced by the crystal packing effect.

The crystal structure of compound **20** is stabilized by the van der Waals and the weak C—H...O interactions, and also by the weak stacking interaction between the tricyclic fragments (the interplanar spacing is 3.325(2) Å, the shortest interaction N(1)...N(5) is 3.406(2) Å), which leads to formation of centrosymmetric dimers.

Experimental

The IR spectra were recorded on a Varian Excalibur 3100 FT-IR spectrometer using an attenuated total internal reflectance. The ^{1}H NMR spectra were recorded on a Varian UNITY-300 spectrometer. The mass spectra were obtained on an Agilrut 1200 Bruker Daltonic NicrOTOF-Q instrument with the direct inlet in the negative/positive ions mode that permits detecting of the molecular weight from the peak with *m/z* of the quasi-molecular ion $[M - H]^-/[M + H]^+$.

2-(2-Aminoquinoline-3-carboxamido)-3-morpholino-isoindolin-1-one (3) and 3-cyanoquinolin-2(1*H*)-one (4). ***A.*** A mixture of 3-acetoxy-2-acetyl(cyanoacetyl)aminoisoindolin-1-one (**1**) (Ref. 5) (0.32 g, 1 mmol) and *o*-tosylaminobenzaldehyde morpholinal **2** (Ref. 7) (0.43 g, 1 mmol) in 6 mL of MeCN was refluxed for 1 h, cooled with ice, the precipitate that formed was filtered off, washed with a small amount of cold MeCN and dried. The obtained crystalline product (90 mg) represented a mixture of compounds **3** and **4**. It was refluxed with 2 mL of $CHCl_3$, cooled, the precipitate was filtered off, washed with 1 mL of $CHCl_3$, and petroleum ether and dried to obtain 44 mg (26 %) of quinolone **4** as a colorless substance, m.p. 305 °C (Ref. 15: m.p. >300 °C). The chloroform filtrate was concentrated, the residue was triturated with acetone, filtered off, washed with acetone and dried to obtain 30 mg (7.5%) of compound **3** as a yellow substance, m.p. 245—247 °C. Found: N, 17.62%. $C_{22}H_{21}N_5O_3$. Calculated: N, 17.36%.

The acetonitrile filtrate was concentrated, the residue was extracted with boiling isooctane to give *N*-tosylmorpholine (**5**) (Ref. 6) as a colorless substance, m.p. 147—148 °C (Ref. 6: m.p. 147—150 °C).

IR of compound **4**, ν/cm^{-1}: 3456 (NH), 2229 (C≡N), 1662 (CO), 1620, 1564, 1490 (arom.).

IR of compound **3**, ν/cm^{-1}: 3489, 3375, 3166 (NH), 1722, 1666 (NH), 1615, 1584, 1565 (arom.). ^{1}H NMR (DMSO-d_6) of compound **3**, δ: 2.69 (m, 2 H, NCH_2); 2.83 (m, 2 H, NCH_2); 3.59 (m, 4 H, OCH_2); 5.61 (s, 1 H, NH); 6.92 (s, 2 H, NH_2); 7.20 (t, 1 H, NH_{arom}, J = 7.2 Hz); 7.40—7.80 (m, 7 H, NH_{arom}); 8.59 (s, 1 H, $N(4)H_{quinoline}$).

A. A mixture of compound **1** (0.32 g, 1 mmol) and *o*-mesylaminobenzaldehyde morpholinal (**11**) (see Ref. 16) (0.36 g, 1 mmol) in 5 mL of MeCN was refluxed for 25 min. During this time the red solution became almost colorless and a precipitate formed. The reaction mixture was cooled with ice, the precipitate was filtered off, washed with cold MeCN, and dried. The precipitate (132 mg) was refluxed with 5 mL of acetone, cooled with ice, filtered off, washed with acetone, and dried to obtain 90 mg (22 %) of compound **3**, which was identified based on the IR-specrtum, melting point and the absence of a decrease in the melting point when mixed with the authentic sample.

The acetone filtrate was concentrated, the residue was triturated with 3 mL of $CHCl_3$, filtered off, washed with $CHCl_3$, and dried to obtain 5 mg (3%) of compound **4**, which was identified based on the IR-specrtum, melting point and the absence of a decrease in the melting point when mixed with the authentic sample.

2-(2-Amino-6-nitroquinoline-3-carboxamido)-3-morpholino-isoindolin-1-one (13) and 3-cyano-6-nitroquinolin-2(1*H*)-one (14). A mixture of compound **1** (0.32 g, 1 mmol) and the complex of 5-nitro-2-tosylaminobenzaldehyde morpholinal (**12**) (see Refs 12, 13) with CCl_4 (0.65 g, 1.03 mmol) in 6 mL of MeCN was refluxed for 1 hour, cooled with ice, with trituration by a glass rod. The precipitate was filtered off, washed with cold MeCN, and dried to obtain 0.185 g (41%) of almost pure compound **13** as colorless crystals, m.p. 235—240 °C (from MeCN).

Compound 13. Found (%): C, 58.72; H, 4.65; N, 18.87. $C_{22}H_{20}N_6O_5$. Calculated (%): C, 58.93; H, 4.50; N, 18.74. IR, ν/cm^{-1}: 3414, 3294, 3152 (NH), 1718, 1672 (CO), 1645, 1615, 1573 (arom.), 1521, 1334 (NO_2). ^{1}H NMR (DMSO-d_6), δ: 2.70 (m, 2 H, NCH_2); 2.84 (m, 2 H, NCH_2); 3.60 (m, 4 H, OCH_2); 5.60 (s, 1 H, CH); 7.40—7.62 (m, 5 H, NH_2, NH_{arom}); 7.69 (t, 1 H, NH_{arom}, J = 7.5 Hz); 7.77 (d, 1 H, NH_{arom}, J = 7.5 Hz); 8.28 (dd, 1 H, C(7)H, ^3J = 9.3, ^4J = 2.4 Hz); 8.75 (d, 1 H, C(5')H, J = 2.4 Hz); 8.78 (s, 1 H, C(4')H); 11.27 (s, 1 H, NH). MS, *m/z*: found 447.1103 $[M - H]^-$; $C_{22}H_{20}N_6O_5$; calculated: $[M - H]^-$ = 447.429.

The acetonitrile filtrate of compound **13** was concentrated, the residue was triturated with $CHCl_3$, the precipitate was filtered off, washed with $CHCl_3$ and petroleum ether, and dried to obtain 44 mg (20%) of quinolone **14** as a colorless substance, sublimation temperature was >270 °C.

Compound 14. Found (%): C, 56.52; H, 2.49; N, 19.78. $C_{10}H_5N_3O_3$. Calculated (%): C, 56.61; H, 2.38; N, 19.81. IR, ν/cm^{-1}: 2235 (CN), 1660 (CO), 1625, 1568 (arom.), 1531,

1343 (NO_2). ^{1}H NMR (DMSO-d_6), δ: 7.48 (d, 1 H, N(8)H, J = 9.3 Hz); 8.35 (br d, 1 H, N(7)H); 8.78 (s, 1 H, N(5)H); 8.89 (s, 1 H, N(4)H); 12.97 (s, 1 H, NH). MS, *m/z*: found 214.0163 $[M - H]^-$; $C_{10}H_5N_3O_3$; calculated: $[M - H]^-$ = 214.159.

o*-Formylbenzoic acid 2-aminoquinoline-3-carbonylhydrazone (18) and 3-acetoxy-2-(quinolino[2,3-*d*]-2-methyl-4-oxopyrimidin-3-yl)isoindolin-1-one (20).** ***A. Hydrazone **18** was prepared according to the general method described earlier,[5] *viz.,* by mixing hot solutions of *o*-formylbenzoic acid **16** (0.3 g, 2 mmol) in 5 mL of Pr^{i}OH and hydrazide **17** (see Ref. 6) (0.404 g, 2 mmol) in 12 mL of Pr^{i}OH. The yellow precipitate of compound **18** separated after a short induction period was cooled to room temperature, filtered off, washed with Pr^{i}OH and petroleum ether, dried, and used in the synthesis of compound **20** without further purification. The yield of compound **20** was 0.66 g (quantitative), m.p. >240 °C (decomp.). Found: N, 16.41%. $C_{18}H_{14}N_4O_3$. Calculated: N, 16.76%. IR, ν/cm^{-1}: 3230 br (NH, OH), 1697, 1659 (CO), 1563, 1535, 1504 (arom.).

A. Compound **18** (0.33 g, 1 mmol) was heated with Ac_2O (2 mL) until dissolution and the solution was refluxed for 3 min, and cooled. Then MeOH (3 mL) and H_2O (20 mL) were added. The aqueous layer was decanted from the sedimented oil, the latter was dissolved in a small amount of MeOH and added to the ice-cooled supernatant liquid with trituration by a glass rod. When the solidification was complete, the solid was filtered off, washed with 50% EtOH, and dried to obtain 0.26 g (65%) of compound **20** as a colorless substance, m.p. 202—205 °C (from a mixture of toluene—isooctane). The analytically pure product was prepared by recrystallization from a mixture of toluene (7.5 mL) and isooctane (2.5 mL). The structure of the product was established by X-ray diffraction analysis. Found: N, 14.28%. $C_{22}H_{16}N_4O_4$. Calculated: N, 13.99%. IR, ν/cm^{-1}: 1739, 1689 (NH), 1605, 1597, 1562, 1492 (arom.). ^{1}H NMR ($CDCl_3$), δ: 2.19 (s, 3 H, NHMe); 2.70 (s, 3 H, Me); 7.40 (s, 1 H, NH); 7.45—8.10 (m, 7 H, NH_{arom}); 8.24 (d, 1 H, N(7)H, J = 8.6 Hz); 9.17 (s, 1 H, C(5')H).

X-Ray diffraction study of compounds 4, 3 and 20. The single crystals of compounds **4**, **3**, and **20** suitable for X-ray diffraction study were grown by slow concentration of their solutions in MeCN. The experimental intensities of reflections were measured using a SMART 1000 CCD and a SMART APEX2 CCD diffractometers (λ(Mo-Kα) = 0.71073 Å, graphite monochromator, ω-scanning technique). The initial arrays of measured intensities were processed using the SAINT Plus,[17] SADABS,[18]

Table 1. The crystal data and the parameters X-ray study for compounds **4**, **3** and **20**

Parameter	**4**	**3**	**20**
Molecular formula	$C_{10}H_6N_2O$	$C_{22}H_{21}N_5O_3$	$C_{22}H_{16}N_4O_4$
Molecular weight	170.17	403.44	400.39
Crystal color	Light yellow		Yellow
Crystal shape	Plates		Prisms
Crystal dimensions, mm	0.25×0.10×0.02	0.20×0.10×0.02	0.20×0.15×0.15
T/K	296(2)	120(2)	120(2)
Crystal system	Monoclinic		Triclinic
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a/Å	3.900(2)	8.969(2)	6.8709(7)
b/Å	11.553(6)	19.817(4)	8.4846(9)
c/Å	17.841(10)	12.015(3)	16.157(2)
α/deg	90	90	94.491(2)
β/deg	91.036(13)	109.804(4)	94.512(2)
γ/deg	90	90	99.064(2)
V/Å^3	803.8(8)	2009.3(8)	923.3(2)
Z	4	4	2
d_{calc}/g cm^{-3}	1.406	1.334	1.440
Absorption coefficient μ/mm^{-1}	0.095	0.092	0.102
F(000)	352	848	416
Scaning interval by θ/deg	2.10—29.00	2.06—27.00	2.44—28.00
Number of measured reflections	9548	18464	9563
Number of independent reflections	2129	4342	4427
R_{int}	0.0973	0.0986	0.0218
Number of refined parameters	118	271	273
Number of reflections with $I \geq 2\sigma(I)$	993	2219	3426
Fullness of reflections array (%)	99.3	98.9	99.4
GOOF	0.978	1.029	1.012
Convergence of refinement($R_1(F)$)[a] of reflections with $I \geq 2\sigma(I)$	0.0529	0.0586	0.0555
Convergence of refinement of all reflections ($wR_2(F^2)$[b]	0.1196	0.1819	0.1127
Residual electron density (min/max), e/Å^3	0.154/−0.174	0.282/−0.283	0.362/−0.252

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma(F_o)$; [b] $wR_2 = (\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

APEX2[19] programs. The structures was solved by the direct method and refined by the full-matrix least-squares method with anisotropic displacement parameters for nonhydrogen atoms based on F^2_{hkl}. The hydrogen atoms were positioned at geometrically calculated positions, except for the hydrogen atoms at the nitrogen atoms, whose position was located in the difference electron density synthesis and then normalized to the distance of 0.90 Å. All hydrogen atoms were refined using a riding model ($U_{iso}(H) = nU_{eq}(C,N)$, where $n = 1.5$ for the carbon atoms of the methyl groups, $n = 1.2$ for the other C and N atoms). The processing and the refinement of the structures was performed using the SHELXTL program.[20] The crystallographic data and parameters of X-ray diffraction study are given in Table 1.

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