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1-Amino-2-hydrazinobenzimidazole and Its Reactions with Some Carbonyl Compounds

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Abstract—1-Amino-2-hydrazinobenzimidazole was obtained for the first time by treating 1-aminobenzimidazole-2-sulfonic acid with hydrazine hydrate. This compound readily condensed with aromatic aldehydes involving both amino groups. The condensation with 2,4-pentanedione affords 1-amino-2-(3,5-dimethylpyrazol-1-yl)benzimidazole, and with α-ketoacids in glacial acetic acid yields mixtures of 10-acetylamino-3-*R*-1,2,4-triazino[4,3-*a*]benzimidazol-4(10*H*)-ones and 4-amino-2-*R*-1,2,4-triazino[2,3-*a*]benzimidazol-3(4*H*)-ones.

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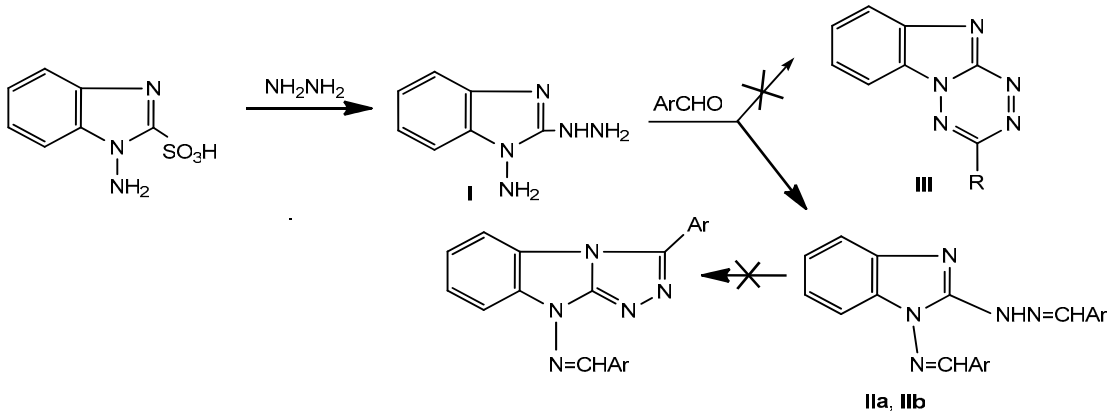
The synthetic importance of 2-hydrazinobenzimidazoles is well known: they underlie the preparation of new heterocyclic systems [1–3], formazans [4], coordination compounds [5]. The synthetic opportunities of *N*-amino-benzimidazoles are no less versatile [6, 7]. We describe in this report 1-amino-2-hydrazinobenzimidazole **I** with both functionnal groups participating in condensations and the features of its reactions with aldehydes, 2,4-pentanedione, and α-ketoacids.

The main method of the preparation of 2-hydrazinobenzimidazoles as known is based on the exchange of a chlorine atom or a sulfo group in the corresponding benzimidazoles [8]. Hydrazine derivative **I** we have obtained in a high yield from 1-aminobenzimidazole-2-sulfonic acid [9] by boiling in excess of hydrazine hydrate. This compound proved to be sufficiently stable and gradually turned darker only at the long storage.

Unlike the 1,2-diaminobenzimidazole which underwent condensation with aromatic aldehydes only at the N-amino group [10], hydrazine **I** reacted at once with 2 mol of aldehyde forming hydrazones **II**. Analogously, e.g., to 4-amino-3-hydrazino-1,2,4-tria-

Scheme 1.

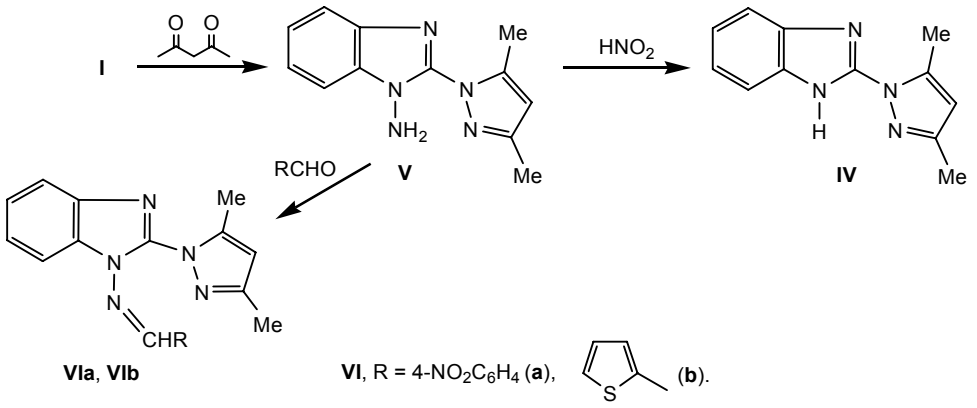


I **III** **IIa**, **IIb**

Ar = Ph (**a**), 2-OHC_6H_4 (**b**).

† Deceased.

Scheme 2.



oline-5-thione the product of this reaction may be tetrazinobenzimidazole **III** [11], yet in this case the results of the elemental analysis and the ^{1}H NMR spectrum of the compound unambiguously prove the composition and the structure of heterocycle **II** (Scheme 1).

Hydrazones **II** do not undergo cyclization either in the melt at a temperature exceeding the melting point by 20°C or at prolonged boiling in glacial acetic acid whereas their *N*-unsubstituted analogs under these conditions transform into 3-aryl-1,2,4-triazolo[4,3-*a*]benzimidazoles [3].

Klyuev et al. [12] studied the reaction of 2-hydrazinobenzimidazole with 2,4-pentanedione and found that in this case not a seven-membered ring was closed involving the hydrazino group and the endocyclic nitrogen atom, but a pyrazole ring with the formation of 2-(pyrazol-1-yl)benzimidazole (**IV**). This compound is characterized by a relatively low melting point and a high chromatographic mobility (R_f 0.75), uncommon as a rule for *N*-unsubstituted benzimidazoles. The structure of pyrazolyl derivative **IV** was sufficiently compellingly proved by ^{1}H spectra and X-ray diffraction (XRD) analysis. Later in publications [3, 13] without reference to [12] melting points were indicated differing for each other by nearly 130°C.

We established that 1-amino-2-hydrazinobenzimidazole **I** also underwent cyclization with 2,4-pentanedione involving only the hydrazino group giving 1-amino-2-pyrazolylbenzimidazole **V**, which also was significantly distinguished from the known *N*-aminobenzimidazoles by the high chromatographic mobility, relatively low melting point, and a good solubility in nonpolar solvents (Scheme 2).

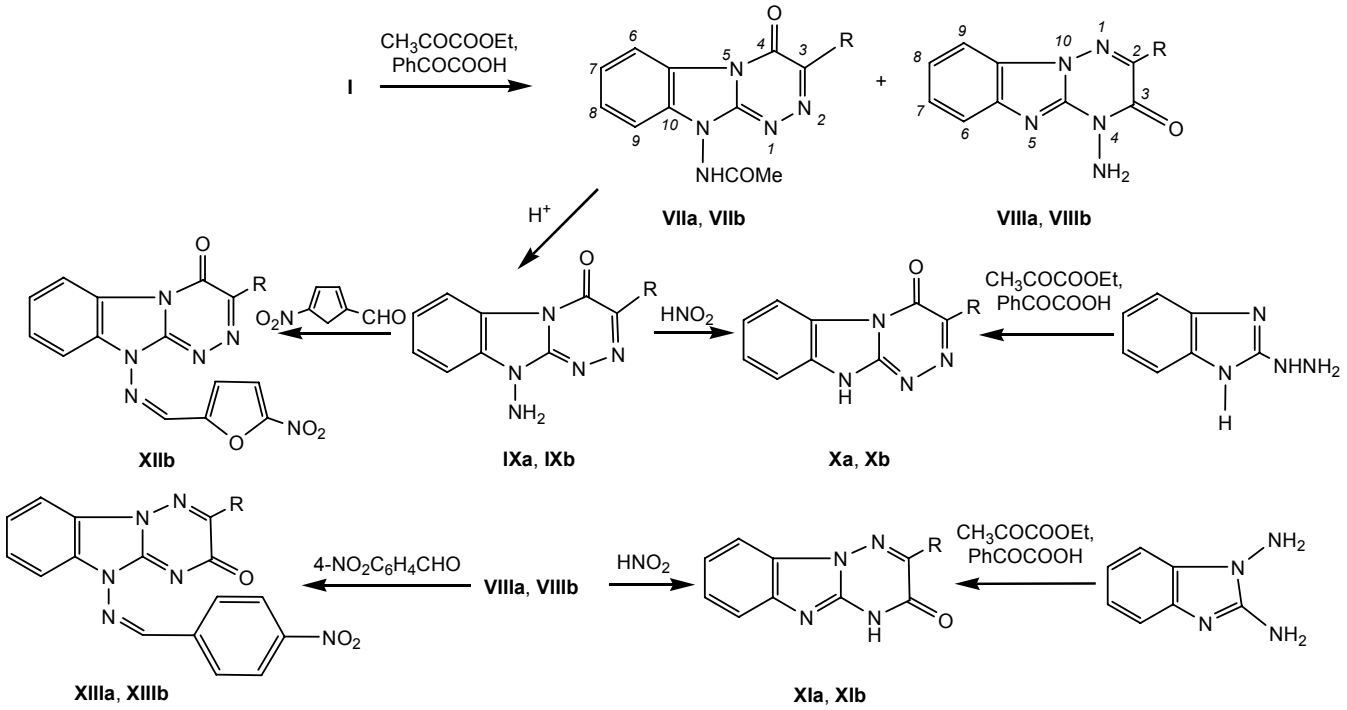
Yet like the most *N*-aminoazoles [6], *N*-amino derivative **V** easily suffered deamination when treated with nitrous acid giving rise to NH-unsubstituted compound **IV** whose physicochemical characteristics coincided with those described in [12]. *N*-Amine **V** readily formed azomethine **VIa** with 4-nitrobenzaldehyde at heating in 2-propanol, but with less reactive 2-formylthiophene the reaction under these conditions did not occur, and the corresponding azomethine **VIb** was obtained in a moderate yield in boiling toluene at the azeotropic removal of water. Initial amine **V** and azomethines **VIa** and **VIb** possess virtually the same chromatographic mobility.

In the mass spectrum of compound **V** the molecular ion peak is the most abundant. Its fragmentation occurs analogously to the other *N*-aminoazoles.

We believe that the unusual physical properties of 2-pyrazolylbenzimidazoles **IV** and **V** are due to the location in the same plane of both heterocyclic scaffolds in these bihetaryls. This configuration proved for pyrazolylbenzimidazole **IV** by XRD analysis [12] is stabilized mainly by the attractive electrostatic interaction of the sp^2-nitrogen atom of the pyrazole ring with the hydrogen atoms of the NH or NNH_2 moieties of the benzimidazole thus sterically impeding the intermolecular association through hydrogen bonds.

2-Hydrazinobenzimidazole and its 1-alkyl derivatives are known to undergo cyclization with α-ketoacids through the intermediate formation of relatively stable hydrazones giving finally 1,2,4-triazino[4,3-*a*]-benzimidazol-4-ones [2] capable of efficient blocking adenosine receptors [14]. 1,2-Diaminobenzimidazole and its 2-alkylamino derivatives also easily underwent cyclization with α-ketoacids furnishing isomeric 1,2,4-triazino-[2,3-*a*]-benzimidazol-3-ones [15, 16]. Therefore both these

Scheme 3.



R = Me (**a**), Ph (**b**).

cyclization versions are theoretically probable for 1-amino-2-hydrazinobenzimidazole **I**.

We established that the heating of compound **I** with ethyl pyruvate or phenylglyoxalic acid in glacial acetic acid afforded a mixture of 10-acetylamino-1,2,4-triazino[4,3-*a*]benzimidazol-4-ones **VIIa** and **VIIb** and 4-amino-1,2,4-triazino[2,3-*a*]benzimidazol-3-ones **VIIIa** and **VIIIb** in a nearly quantitative overall yield. Therewith in the reaction with ethyl pyruvate as shows the ^{1}H NMR spectrum of the reaction mixture the ratio of triazinones **VIIIa** and **VIIa** equals 1.2 : 1, and with phenylglyoxalic acid, on the contrary, acetylamino derivative **VIIb** is the main reaction product (yield 70%) (Scheme 3).

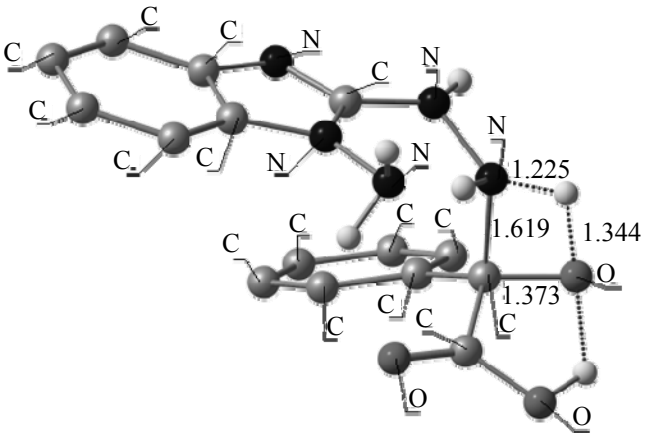
Acetylamino derivatives **VII** are readily hydrolyzed with conc. HCl into amines **IX**; therewith in their IR spectra the absorption bands in the region ν 1700 cm^{-1} belonging to the vibration of the C=O bond of the acetyl group disappear.

In the ^{1}H NMR spectra of triazinones **VII** and **IX** the proton signals of H^6 under the effect of the CO group shift downfield and appear as a doublet in the region 8.4–8.5 ppm. In the spectra of isomeric triazinones **VIII** where this interaction with the remote CO group is very weak the proton signals of H^6 and H^9 are observed at 7.8 and 7.7 ppm providing a possibility to reliably identify the structures **VIII** and **IX**. The chemical shifts of the protons of the *N*-amino group in compounds **VIII** and **IX** are virtually identical (6.21 and 6.20 ppm).

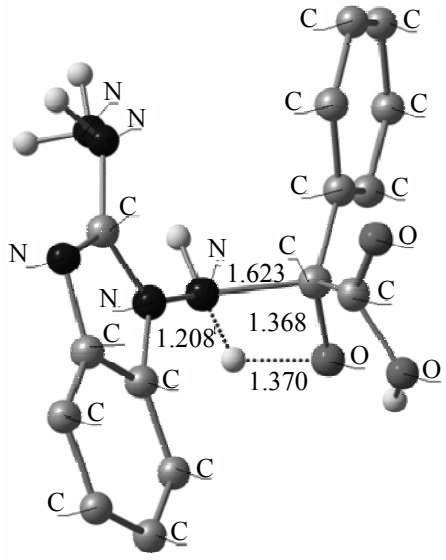
N-Amines **VIII** and **IX** were deaminated in the presence of nitrous acid giving NH-unsubstituted compounds **X** and **XI** identical to the known cyclization products of 2-hydrazino- and 1,2-diaminobenzimidazole with the corresponding α-ketoacids; this fact proved the structure of products obtained.

At heating with aldehydes in glacial acetic acid amines **VIII** and **IX** provided azomethines **XII** and **XIII**.

In the course of the cyclocondensation of hydrazine **I** with α-ketoacids the primary nucleophilic addition to the keto group may occur involving two competing centers, hydrazine and *N*-amino groups. According to the quantum-chemical calculations by the DFT method (B3LYP/6-31G**) in the absence of solvation and of the effect of the proton catalysis the reaction involving the hydrazino group through the transition state



TS1



TS2

Transition states at the phenylglyoxalic acid addition to hydrazine **I** [hydrogen atoms of the phenyl group and benzimidazole fragment are not shown; the figures correspond to bond lengths (Å) in four-membered reaction nodes of transition states].

TS1 (see the figure) is by 6–7 kcal mol^{-1} more favorable than with the participation of the *N*-amino group through TS2. However since TS2 is far more polar than TS1 ($\mu_{calc.}$ 7.0 and 2.5 D respectively), in the solution the preference of the first reaction route becomes less considerable.

Therewith the higher regioselectivity of the cyclization with phenylglyoxalic acid as compared with ethyl pyruvate is obviously due to the lower electrophilicity of the carbon atom in its keto group in agreement with the general trend of increased selectivity of the reaction at the decrease in the substrate reactivity (http://goldbook.iupac.org/R05186.html).

EXPERIMENTAL

IR spectra were recorded on a spectrophotometer Varian Excalibur 3100 FT-IR from samples in solid phase. ^{1}H NMR spectra were registered on a spectrometer Varian Unity-300 (300 MHz), solvent DMSO-d_6, $CDCl_3$ for compounds **II**, **V**, and **VI**. Chemical shifts of protons are given with respect to the residual protons of deuterated solvents. Mass spectrum of electron impact (70 eV) was obtained on an instrument Finnigan MAT INCOS 50 with the direct admission of the sample into the ion source.

The reaction progress was monitored and the homogeneity of compounds was checked by TLC on plates with Al_2O_3 of III activity grade, eluent $CHCl_3$, development in iodine vapor. Eluent for compounds **VII–IX** was a mixture $CHCl_3$–EtOH, 20 : 1.

The optimization of geometry of hydrazine **I**, phenylglyoxalic acid, and transition states TS1 and TS2 was carried out using the program Firefly 8.0 [17], partially based on the code of the program GAMESS [18]. The calculation of the energy of the found structures was performed with accounting for the correction for the oscillation energy of the zero level applying the scaling factor 0.961 [19].

1-Aminobenzimidazole-2-sulfonic acid was synthesized by procedure [9], hydrazine hydrate, aldehydes, 2,4-pentanedione, phenylglyoxalic acid, and ethyl pyruvate were purchased from Aldrich.

1-Amino-2-hydrazinobenzimidazole (I). A solution of 2.13 g (0.01 mol) of 1-aminobenzimidazole-2-sulfonic acid in 15 mL of hydrazine hydrate was boiled for 2.5 h. The precipitate separated on cooling was filtered off, washed with 30 mL of cold water. Yield 1.50 g (93%), colorless crystals, mp 216–218°C (H_2O), gradually darkening when exposed to air. ^{1}H NMR spectrum, δ, ppm: 4.23 s (2H, NH$\underline{NH_2}$), 5.49 s (2H, NNH_2), 6.92–6.96 m (2H, $H^{5,6}$), 7.10–7.13 m (1H, H^7), 7.17–7.21 m (1H, H^4), 7.33 br.s (1H, NH). Found, %: C 51.32; H 5.67; N 42.70. $C_7H_9N_5$. Calculated, %: C 51.52; H 5.56; N 42.92.

1-Benzylideneamino-2-benzylidenehydrazinobenzimidazole (IIa). A solution of 0.33 g (2 mmol) of hydrazine **I** and 0.4 mL (4 mmol) of benzaldehyde in 5 mL of 2-propanol was boiled for 1.5 h. The light-yellow precipitate separated on cooling was filtered off and washed with ether. Yield 0.50 g (73%), mp 82–83°C

(*i*-PrOH), R_f 0.9. IR spectrum, ν, cm^{-1}: 3300–3100 (NH), 1615 (C=N), 1584. ^1H NMR spectrum, δ, ppm:* 7.04–7.12 m (3H, $H^{3'-5'}$), 7.33–7.52 m (7H, $H^{4-7,3''-5''}$), 7.77 d (2H, $H^{2',6'}$, *J* 7.2 Hz), 7.87 d (2H, $H^{2'',6''}$, *J* 7.2 Hz), 8.47 s (1H, NH), 8.86 s (1H, =CH′), 10.12 s (1H, =CH"). Found, %: C 74.52; H 5.20; N 20.81. $C_{21}H_{17}N_5$. Calculated, %: C 74.32; H 5.05; N 20.63.

1-(2-Hydroxybenzylidene)amino-2-(2-hydroxybenzylidene)hydrazinobenzimidazole (IIb) was obtained similarly to compound **IIa**. Yield 70%, light-yellow needle crystals, mp 111–112°C (*i*-PrOH), R_f 0.75. ^1H NMR spectrum, δ, ppm: 6.93–7.42 m ($12H_{arom}$), 8.44 s (1H, NH), 8.53 s (1H, =CH'), 10.15 s (1H, =CH"), 10.95 s (1H, OH), 11.55 s (1H, OH). Found, %: C 68.12; H 4.47; N 19.04. $C_{21}H_{17}N_5O_2$. Calculated, %: C 67.91; H 4.61; N 18.86.

1-Amino-2-(3,5-dimethylpyrazol-1-yl)benzimidazole V. A slurry of 0.50 g (3 mmol) of hydrazine **I** and 0.3 mL (3 mmol) of 2,4-pentanedione in 7 mL of 2-propanol was boiled for 1 h till complete dissolution of the precipitate, and then for 2 h more. The solution was evaporated to dryness, the residue was chromatographed on a column packed with Al_2O_3 (60 × 20 mm), eluent chloroform. The fraction with R_f 0.8 was separated. Yield 0.52 g (76%), mp 124–125°C (isooctane). IR spectrum, ν, cm^{-1}: 3310, 3169 (NH_2), 1592, 1573, 1548, 1479. ^1H NMR spectrum, δ, ppm: 2.32 s (3H, CH_3), 2.62 s (3H, CH_3), 5.51 s (2H, NH_2), 6.06 s (1H, $H^{4'}$), 7.24–7.36 m (2H, $H^{5,6}$), 7,56 d (1H, H^7, *J* 7.5 Hz), 7.68 d (1H, H^4, *J* 8.1 Hz). Mass spectrum, *m/z* (I_{rel}, %): 227 (100) $[M]^+$, 212 (10), 198 (42.9), 118 (17.1), 96 (17.1), 81 (21.4), 75 (17.1), 43 (32.1). Found, %: C 63.52; H 5.60; N 30.94. $C_{12}H_{13}N_5$. Calculated, %: C 63.42; H 5.77; N 30.81.

2-(3,5-Dimethylpyrazol-1-yl)benzimidazole (IV). To a solution of 0.23 g (1 mmol) of amino derivative **V** in 2 mL of glacial acetic acid cooled with an ice bath was added a solution of 0.07 g (1 mmol) of $NaNO_2$ in 1 mL of water, 0.5 h later the mixture was doubly diluted with water, a precipitate separated and was filtered off and washed with water. Yield 0.18 g (85%), mp 134–135°C (134–136 [12], 175 [3], >300°C [13]). ^1H NMR spectrum, δ, ppm: 2.29 s (3H, CH_3), 2.74 s (3H, CH_3), 6.05 s (1H, $H^{4'}$), 7.07–7.12 m (2H, $H^{5,6}$), 7.45 d.d (2H, $H^{4,7}$, *J* 2.7 Hz), 12.51 s (1H, NH).

2-(3,5-Dimethylpyrazol-1-yl)-1-(4-nitrobenzylidene)aminobenzimidazole (VIa). A solution of 0.23 g (1 mmol) of amine **V** and 0.15 g (1 mmol) of 4-nitrobenzaldehyde in 3 mL of 2-propanol was boiled for 1 h in the presence of catalytic amount of piperidine. On cooling the formed yellow precipitate was filtered off and washed with ether. Yield 0.26 g (71%), mp 216–217°C (*i*-PrOH), R_f 0.8. IR spectrum, ν, cm^{-1}: 1598, 1575, 1541, 1518. ^1H NMR spectrum, δ, ppm: 2.32 s (3H, CH_3), 2.36 s (3H, CH_3), 6.11 s (1H, $H^{4'}$), 7.41–7.46 m (2H, $H^{5,6}$), 7.75 d (2H, $H^{2'',6''}$, *J* 7.8 Hz), 7.83–7.91 m (2H, $H^{4,7}$), 8.30–8.33 m (3H, $H^{3'',5''}$, =CH). Found, %: C 63.52; H 4.28; N 23.18. $C_{19}H_{16}N_6O_2$. Calculated, %: C 63.33; H 4.48; N 23.32.

2-(3,5-Dimethylpyrazol-1-yl)-1-(thenylidene-2)-aminobenzimidazole (VIb). A solution of 0.23 g (1 mmol) of amine **V** and 0.1 mL (1 mmol) of 2-formylthiophene in 5 mL of toluene was boiled for 3 h with azeotropic distilling off water, the solution was evaporated to dryness, the residue was recrystallized from 2-propanol. Yield 0.19 g (58%), colorless crystals, mp 131–132°C. IR spectrum, ν, cm^{-1}: 1612, 1557, 1521, 1448. ^1H NMR spectrum, δ, ppm: 2.22 s (3H, CH_3), 2.48 s (3H, CH_3), 6.09 s (1H, $H^{4'}$), 7.17 t (1H, $H^{4''}$, *J* 5.0, 3.7 Hz), 7.31–7.41 m (2H, $H^{5,6}$), 7.59–7.61 d.d (1H, $H^{5''}$, *J* 3.7, 1.1 Hz), 7.69–7.72 m (2H, $H^{3'',7}$), 7.77–7.80 m (1H, H^4), 8.80 s (1H, =CH). Found, %: C 63.40; H 4.52; N 21.74; S 9.83. $C_{17}H_{15}N_5S$. Calculated, %: C 63.53; H 4.70; N 21.79; S 9.98.

Reaction of hydrazine I with ethyl pyruvate. A solution of 0.50 g (3 mmol) of hydrazine **I** and 0.33 mL (3 mmol) of ethyl pyruvate in 5 mL of glacial acetic acid was boiled for 2 h. The precipitate formed on cooling (0.34 g) was separated and recrystallized from MeCOOH. We obtained 0.22 g of colorless crystals of **4-amino-2-methyl-1,2,4-triazino[2,3-*a*]benzimidazol-3(4*H*)-one (VIIIa)**, mp 262–264°C, R_f 0.2. IR spectrum, ν, cm^{-1}: 3287, 3178 (NH_2), 1682 (C=O), 1638, 1604, 1554. ^1H NMR spectrum, δ, ppm: 2.45 s (3H, CH_3), 6.10 s (2H, NH_2), 7.28–7.38 m (2H, $H^{7,8}$), 7.64 d (1H, H^6, *J* 8.7 Hz), 7.74 d (1H, H^9, *J* 8.4 Hz). Found, %: C 55.60; H 4.16; N 32.35. $C_{10}H_9N_5O$. Calculated, %: C 55.81; H 4.22; N 32.54.

The combined filtrates were evaporated to dryness, the residue (0.44 g) was treated with 10 mL of boiling chloroform. The insoluble 0.1 g of compound **VIIIa** was separated. The overall yield of amine **VIIIa** 0.32 g (50%). The residue after evaporation of the chloroform extract was twice recrystallized from CH_3CN to obtain 0.23 g (29%) of **10-acetylamino-3-methyl-1,2,4-triazino[4,3-*a*]benzimidazol-4(10*H*)-one (VIIa)**, colorless crystals, mp 235–237°C, R_f 0.05. The spots of

* Here and hereinafter one stroke designates the position of substituents at the hydrazino group, two strokes, at the *N*-amino group.

compound **VIIa** were not visualized on chromatograms in iodine vapor, but were seen under UV irradiation. IR spectrum, ν, cm^{-1}: 3360–3170 (NH), 1716 (C=O), 1697 (C=O), 1582. ^1H NMR spectrum, δ, ppm: 2.20 s (3H, CH_3), 2.45 s (3H, CH_3), 7.37–7.42 m (2H, $H^{7,8}$), 7.54 d (1H, H^9, *J* 8.1 Hz), 8.43 d (1H, H^6, *J* 8.1 Hz), 11.45 s (1H, NH). Found, %: C 56.17; H 4.35; N 27.09. $C_{12}H_{11}N_5O_2$. Calculated, %: C 56.03; H 4.31; N 27.22.

Reaction of hydrazine I with phenylglyoxalic acid. A solution of 0.50 g (3 mmol) of hydrazine **I** and 0.45 g (3 mmol) of phenylglyoxalic acid in 5 mL of glacial acetic acid was boiled for 2 h. The light-yellow precipitate formed on cooling of **10-acetylamino-3-phenyl-1,2,4-triazino[4,3-*a*]-benzimidazol-4(10*H*)-one (VIIb)** was filtered off and washed with ether. Yield 0.67 g (70%), mp 254–255°C (MeCOOH). IR spectrum, ν, cm^{-1}: 3300–3100 (NH), 1722 (C=O), 1698 (C=O), 1578, 1466. ^1H NMR spectrum, δ, ppm: 2.48 s (3H, CH_3), 7.39–7.48 m (5H, $H^{7,8,3'-5'}$), 7.59–7.68 m (1H, H^9), 8.11–8.21 m (2H, $H^{2',6'}$), 8.55 d (1H, H^6, *J* 7.8 Hz), 11.63 s (1H, NH). Found, %: C 64.10; H 4.22; N 22.03. $C_{17}H_{13}N_5O_2$. Calculated, %: C 63.94; H 4.10; N 21.93.

The filtrates was evaporated to dryness, the residue (0.27 g) was chromatographed on a column (15 × 20 mm) packed with Al_2O_3, eluent a mixture $CHCl_3$–EtOH, 20 : 1, collecting the fraction with R_f 0.2 of **4-amino-2-phenyl-1,2,4-triazino[2,3-*a*]benzi-midazol-3(4*H*)-one (VIIIb)**. Yield 0.18 g (21%), light-yellow crystals, mp 236–237°C (BuOH). IR spectrum, ν, cm^{-1}: 3310, 3192 (NH_2), 1678, 1654, 1638, 1610, 1436. ^1H NMR spectrum, δ, ppm: 6.21 s (2H, NH_2), 7.34–7.39 m (2H, $H^{7,8}$), 7.54–7.56 m (3H, $H^{3'-5'}$), 7.68 d (1H, H^6, *J* 7.5 Hz), 7.84 d (1H, H^9, *J* 7.0 Hz), 8.05–8.08 m (2H, $H^{2',6'}$). Found, %: C 65.13; H 4.08; N 25.41. $C_{15}H_{11}N_5O$. Calculated, %: C 64.97; H 4.00; N 25.26.

10-Amino-3-methyl-1,2,4-triazino[4,3-*a*]benzimidazol-4(10*H*)-one (IXa). A solution of 0.26 g (1 mmol) of 10-acetylamine **VIIa** in 3 mL of conc. HCl was boiled for 10 min, neutralized with 22% NH_4OH and on cooling the separated precipitate was filtered off. Yield 0.17 g (81%), colorless crystals, mp 225–226°C (BuOH), R_f 0.1. IR spectrum, ν, cm^{-1}: 3333–3280 (NH_2), 1688, 1676, 1605, 1570, 1467. ^1H NMR spectrum, δ, ppm: 2.48 s (3H, CH_3), 6.05 s (2H, NH_2), 7.36–7.42 m (1H, H^8), 7.62–7.63 m (2H, $H^{7,9}$), 8.37 d (1H, H^6, *J* 8.1 Hz). Found, %: C 56.03; H 4.32; N 32.47. $C_{15}H_{11}N_5O$. Calculated, %: C 55.81; H 4.22; N 32.54.

10-Amino-3-phenyl-1,2,4-triazino[4,3-*a*]benzimidazol-4(10*H*)-one (IXb) was obtained similarly. Yield 83%, light-yellow crystals, mp 219–221°C (BuOH), R_f 0.1. IR spectrum, ν, cm^{-1}: 3316, 3216 (NH_2), 1671, 1633, 1602, 1557, 1454. ^1H NMR spectrum, δ, ppm: 6.20 s (2H, NH_2), 7.34–7.56 m (5H, $H^{7,8,3'-5'}$), 7.63–7.68 m (1H, H^9), 8.18–8.20 m (2H, $H^{2',6'}$), 8.48 d (1H, H^6, *J* 8.1 Hz). Found, %: C 64.78; H 3.85; N 25.12. $C_{15}H_{11}N_5O$. Calculated, %: C 64.97; H 4.00; N 25.26.

3-Methyl-1,2,4-triazino[4,3-*a*]benzimidazol-4(10*H*)-one (Xa). At cooling with an ice bath to a solution of 0.11 g (0.5 mmol) of amine **IXa** in 2 mL of glacial acetic acid was added a solution of 0.04 g (0.6 mmol) of $NaNO_2$ in 1 mL of water. After 0.5 h the formed precipitate was filtered off and washed with water. Yield 0.1 g (100%), mp 317–318°C (DMF), (320°C [2]). IR spectrum, ν, cm^{-1}: 3160–2432, 1698, 1639, 1604, 1557, 1451, 1285, 1174, 897, 843, 808. IR spectrum was identical to the spectrum of an authentic sample obtained by the cyclization of 2-hydrazinobenzimidazole with ethyl pyruvate by procedure [2].

Compounds **Xb**, **XIa** and **XIb** were similarly obtained.

3-Phenyl-1,2,4-triazino[4,3-*a*]benzimidazol-4-(10*H*)-one (Xb) was obtained from amine **VIIb**. Yield 98%, mp >320°C (DMΦA), (322–323°C [2]). IR spectrum, ν, cm^{-1}: 3148–2400 (NH), 1697, 1640, 1605, 1526, 1444, 1288, 1256, 1196, 891, 796, 757, 688, 664. IR spectrum was identical to the spectrum of an authentic sample obtained by the cyclization of 2-hydrazinobenzimidazole with phenylglyoxalic acid by procedure [2].

2-Methyl-1,2,4-triazino[2,3-*a*]benzimidazol-3-(4*H*)-one (XIa) was obtained from 4-amino derivative **VIIIa**. Yield 100%. Colorless crystals, mp 350–352°C (DMF) (350–355°C [15]). IR spectrum, ν, cm^{-1}: 3074–2557 (NH), 1618, 1596, 1579, 1552, 1513, 1498, 1400, 1187. IR spectrum was identical to the spectrum of an authentic sample obtained from 1,2-diamino-benzimidazole and ethyl pyruvate by procedure [15].

2-Phenyl-1,2,4-triazino[2,3-*a*]benzimidazol-3-(4*H*)-one (XIb) was obtained from 4-amino derivative **VIIIb**. Yield 100%, mp 352–355°C (DMF–H_2O) (355–358°C [15]). IR spectrum, ν, cm^{-1}: 3054–2640 (NH), 1629, 1611, 1528, 1441, 1214, 1014, 779, 747. IR spectrum was identical to the spectrum of an authentic sample obtained by the cyclization of 1,2-diaminobenzimidazole with phenylglyoxalic acid [15].

10-(5-Nitrofurfurylidene)amino-3-phenyl-1,2,4-triazino[4,3-*a*]benzimidazol-4(10*H*)-one (XIIb). A solution of 0.14 g (0.5 mmol) of amine **IXb** and 0.07 g (0.5 mmol) of 5-nitrofurfural in 2 mL of glacial acetic acid was boiled for 15 min. The formed yellow precipitate was separated after cooling. Yield 0.2 g (100%), mp 248–250°C (BuOH), R_f 0.7. ^{1}H NMR spectrum, δ, ppm: 7.52–759 m (4H, H$^{8\text{ or }7,3'-5'}$), 7.70–7.75 m (2H, H$^{7\text{ or }8,3''}$), 7.86–7.91 m (2H, H$^{9,4''}$), 8.22–8.25 m (2H, H$^{2',6'}$), 8.51 d (1H, H^6, *J* 7.8 Hz), 10.34 s (1H, =CH). Found, %: C 59.83; H 3.17; N 21.15. $C_{20}H_{12}N_6O_4$. Calculated, %: C 60.00; H 3.02; N 20.99.

2-Methyl-4-(4-nitrobenzylidene)amino-1,2,4-triazino[2,3-*a*]benzimidazol-3(4*H*)-one (XIIIa). A solution of 0.11 g (0.5 mmol) of amine **VIIIa** and 0.08 g (0.5 mmol) of 4-nitrobenzaldehyde in 2 mL of glacial acetic acid was boiled for 1 h. The formed after cooling yellow precipitate was filtered off and washed with ether. Yield 0.15 g (85%), mp 273–275°C (MeCOOH), R_f 0.8. ^{1}H NMR spectrum, δ, ppm: 2.43 s (3H, CH_3), 7.35–7.38 m (2H, H^{7,8}), 7.67–7.70 m (1H, H^6), 7.78–7.80 m (1H, H^9), 8.27 d (2H, H$^{2'',6''}$, *J* 8.7 Hz), 8.43 d (2H, H$^{3'',5''}$, *J* 8.4 Hz), 9.67 s (1H, =CH). Found, %: C 58.40; H 3.26; N 23.89. $C_{17}H_{12}N_6O_3$. Calculated, %: C 58.62; H 3.47; N 24.13.

4-(4-Nitrobenzylideneamino)-2-phenyl-1,2,4-triazino[2,3-*a*]benzimidazol-3(4*H*)-one (XIIIb) was similarly obtained from amine **VIIIb**. Yield 89%. Yellow crystals, mp 241–242°C (MeCOOH), R_f 0.8. ^{1}H NMR spectrum, δ, ppm: 7.36–7.39 m (2H, H^{7,8}), 7.51–7.55 m (3H, H$^{3'-5'}$), 7.64–7.66 m (1H, H^6), 7.81–7.84 m (1H, H^9), 8.07–8.10 m (2H, H$^{2',6'}$), 8.33 d (2H, H$^{2'',6''}$, *J* 9.0 Hz), 8.41 d (2H, H$^{3'',5''}$, *J* 8.7 Hz), 9.73 s (1H, =CH). Found, %: C 64.32; H 3.57; N 20.30. $C_{22}H_{14}N_6O_3$. Calculated, %: C 64.39; H 3.44; N 20.48.

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REFERENCES

1. Povstyanoi, M.V., Logachev, E.V., and Kochergin, P.M., *Chem. Heterocycl. Comp.*, 1976, vol. 12, p. 603.
2. Povstyanoi, M.V., Logachev, E.V., and Kochergin, P.M., *Ukr. Khim. Zh.*, 1977, vol. 43, p. 746.
3. Badr, M.Z.A., Mahmoud, A.M., Mahgoub, S.A., and Hozien, Z.A., *Bull. Chem. Soc. Jpn.,* 1988, vol. 61, p. 1339.
4. Bednyagina, N.P., Postovskii, I.Ya., Garnovskii, A.D., and Osipov, O.A., *Russ. Chem. Rev.*, 1975, vol. 44, p. 493.
5. Abramenko, V.L., Garnovskii, A.D., Sergienko, V.S., Porai-Koshits, M.A., and Minaeva, N.A., *Koord. Khim.*, 1990, vol. 16, p. 1500; Lukov, V.V., Bogatureva, E.V., Kogan, V.A., Starikov, A.G., and Lokshin, V.A., *Zh. Neorg. Khim.*, 1991, vol. 36, p. 2310.
6. Kuz'menko, V.V., and Pozharskii, A.F., *Adv. Heterocyclic Chem.*, 1992, vol. 53, p. 89.
7. Vasil'chenko, I.S., Kuz'menko, T.A., Shestakova, T.E., Borisenko, R.N., Divaeva, L.N., Burlov, A.S., Borisenko, N.I., Uflyand, I.E., and Garnovskii, A.D., *Russ. J. Coord. Chem.*, 2005, vol. 31, p. 747; Kuz'menko, T.A., Divaeva, L.N., and Morkovnik, A.S., *Russ. Chem. Bull.*, 2011, vol. 60, p. 548.
8. Bednyagina, N.P., and Postovskii, I.Ya., *Zh. Obshc. Khim.*, 1960, vol. 30, p. 1431; Mokrushina, G.A., and Bednyagina, N.P., *Chem. Heterocycl. Comp.*, 1970, vol. 6, p. 1304.
9. Kuz'menko, T.A., Kuz'menko, V.V., Pozharskii, A.F., and Simonov, A.M., *Chem. Heterocycl. Comp.*, 1988, vol. 24, p. 880.
10. Zeiger, A.V., and Joullie, M.M., *J. Org. Chem.*, 1977, vol. 42, p. 542; Kumar, A., Parshad, M., Gupta, R.K., and Kumar, D., *Synthesis*, 2009, p. 1663.
11. Dickinson, H.G., and Jacobson, N.W., *J. Chem. Soc., Chem. Commun.*, 1970, p. 1719.
12. Klyuev, N.A., Povstyanoi, N.V., Aleksandrov, G.G., and Gumennyi, V.P., *Chem. Heterocycl. Comp.*, 1983, vol. 19, p. 79.
13. Joshi, K.C., Jain, R., Dandia, A., and Sharma, K., *J. Heterocyclic. Chem.*, 1988, vol. 25, p. 1641.
14. Da Settimo, F., Primofiore, G., Taliani, S., Marini, A.M., La Motta, C., Novellino, E., Greco, G., Lavecchia, A., Trincavelli, L., and Martini, C., *J. Med. Chem.*, 2001, vol. 44, p. 316; Scatena, A., Fornai, F., Trincavelli, M.L., Taliani, S., Daniele, S., Pugliesi, I., Cosconati, S., Martini, C., and Da Settimo, F., *ACS Chem. Neurosci.*, 2011, vol. 2, p. 526; Taliani, S., Pugliesi, I., Barresi, E., Simorini, F., Salerno, S., La Motta, C., Marini, A.M., Cosimelli, B., Cosconati, S., Di Maro, S., Marinelli, L., Daniele, S., Trincavelli, M.L., Greco, G., Novellino, E., Martini, C., and Da Settimo, F., *J. Med. Chem.*, 2012, vol. 55, p. 1490.
15. I-fu, Ho R., and Day, A.R., *J. Org. Chem.*, 1973, vol. 38, p. 3084.
16. Kuz'menko, T.A., Kuz'menko, V.V., Pozharskii, A.F., and Simonov, A.M., *Chem. Heterocycl. Comp.*, 1988, vol. 24, p. 880; Kuz'menko, T.A., Kuz'menko, V.V., Morkovnik, A.S., and Divaeva, L.N., *Chem. Heterocycl. Comp.*, 2006, vol. 42, p. 648.
17. Granovsky, A.A. www: http://classic.chem.msu.su/gran/firefly/index.html.
18. Schmidt, M.W., Baldridge, K.K., Boatz, J.A., Elbert, S.T., Gordon, M.S., Jensen, J.H., Koseki, S., Matsunaga, N., Nguyen, K.A., Su, S., Windus, T.L., Dupuis, M., and Montgomery, J.A., *J. Comput. Chem.*, 1993, vol. 14, p. 1347.
19. Irikura, K.K., Johnson, R.D. III, and Kacker, R.N., *J. Phys. Chem. A.*, 2005, vol. 109, p. 8430.