Synthesis of 1-hydroxybenzotriazoles angularly annulated by furazan or furoxan rings

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Synthesis of 6-hydroxy-6*H*-[1,2,3]triazolo[4,5-*e*][2,1,3]benzoxadiazole and a mixture of isomeric 6-hydroxy-6*H*-[1,2,3]triazolo[4,5-*e*][2,1,3]benzoxadiazole-1(3)-oxides is carried out starting from 2,4-dinitrosoresorcinol. Total assignment of the signals in the ^{13}C NMR spectra of *O*-methylated products of these compounds is performed.

Key words: nitrosophenols, 1-hydroxybenzotriazoles, 2,1,3-benzoxadiazoles, 2,1,3-benzoxadiazole *N*-oxides, 2*H*-benzotriazole *N*-oxides, ^{1}H, ^{13}C, ^{15}N NMR spectroscopy.

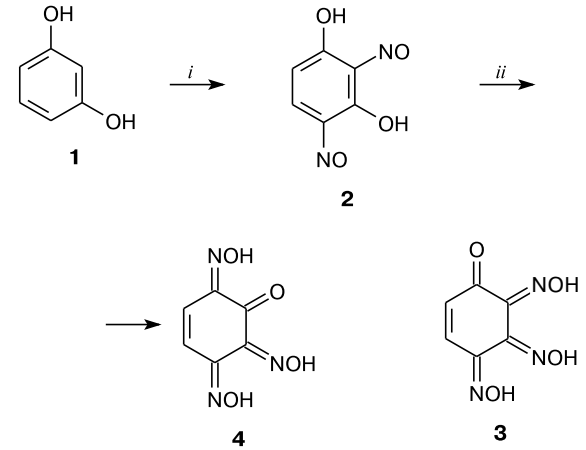
1-Hydroxybenzotriazole is widely used as a promoter in carbodiimide-based[1—3] and other methods for the synthesis of peptides,[4] nucleotides,[5—7] and also in organic synthesis.[8,9] The use of this compound significantly increases the yield and decreases racemization of the reaction products. 1-Hydroxybenzotriazole derivatives containing electron-withdrawing groups in the ring (trifluoromethyl, one or two nitro groups) are highly efficient and are also successfully used in organic synthesis, in the synthesis of peptides and nucleotides.[10,11]

We synthesized 1-hydroxybenzotriazoles annulated by electron-withdrawing heterocycles, namely, furazan and furoxan, in the search for efficient promoters that can be used in the synthesis of peptides, nucleotides and in organic synthesis. Resorcinol (**1**) was used as the starting compound, its nitrosation leads to 2,4-dinitrosoresorcinol (**2**).[12]

Taking into consideration that *o*- and *p*-nitrosohydroxyarenes exist in tautomeric equilibrium with quinone monooximes[13] (nitroso compounds of this type are obtained in both forms), the nitrosation products of hydroxyarenes hereinafter will be referred to as the corresponding nitroso compounds for the simplification of data presentation.

The reaction of compound **2** with hydroxylamine hydrochloride can result in two isomeric trioximes **3** and **4**. It was claimed[14] that isomer **3** was the main product of this reaction, and compound **4** was presented as an admixture. This conclusion was inferred from the presumed formation of 7-hydroxy-4-nitrosobenzofurazan and small amount of 5-hydroxy-4-nitrosobenzofurazan upon reaction of the trioxime with acetic anhydride. Later,[15,16] these conclusions were shown to be erroneous, it was found that only 5-hydroxy-4-nitrosobenzofurazan is formed in the reaction of the trioxime with acetic anhydride. It thus follows that trioxime **4** is the main oximation product of compound **2**. In fact, only one trioxime was obtained by us upon treatment of compound **2** with hydroxylamine hydrochloride in methanol (Scheme 1). No other isomer was detected in the reaction mixture judging by ^{1}H NMR data.

Scheme 1



Reagents and conditions: *i.* $NaNO_2$, H_2SO_4; *ii.* $NH_2OH \cdot HCl$, MeOH, reflux.

Synthesis of 1-hydroxybenzotriazole fused with the furazan ring was carried out according to Scheme 2. Treatment of compound **4** with acetic anhydride leads to

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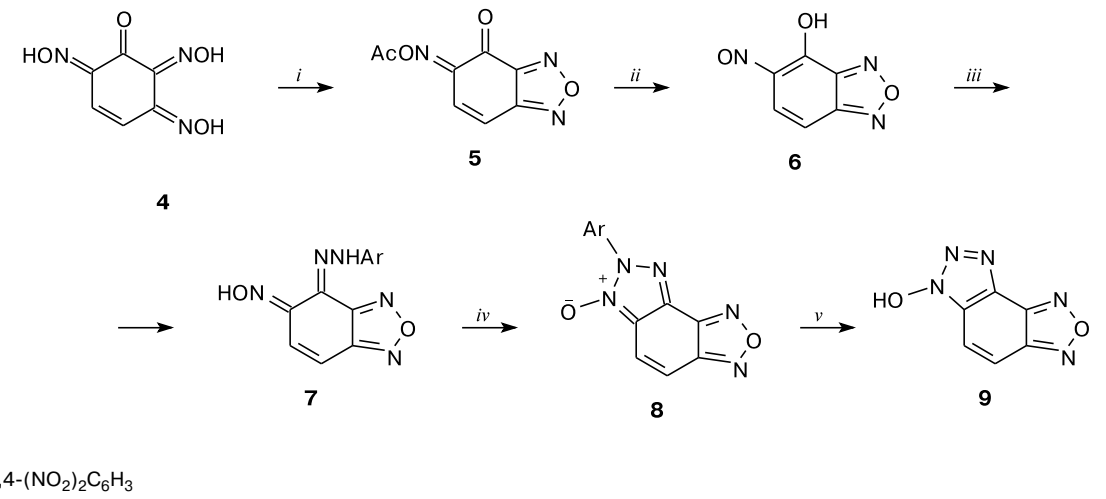
Scheme 2



Ar = 2,4-$(NO_2)_2C_6H_3$

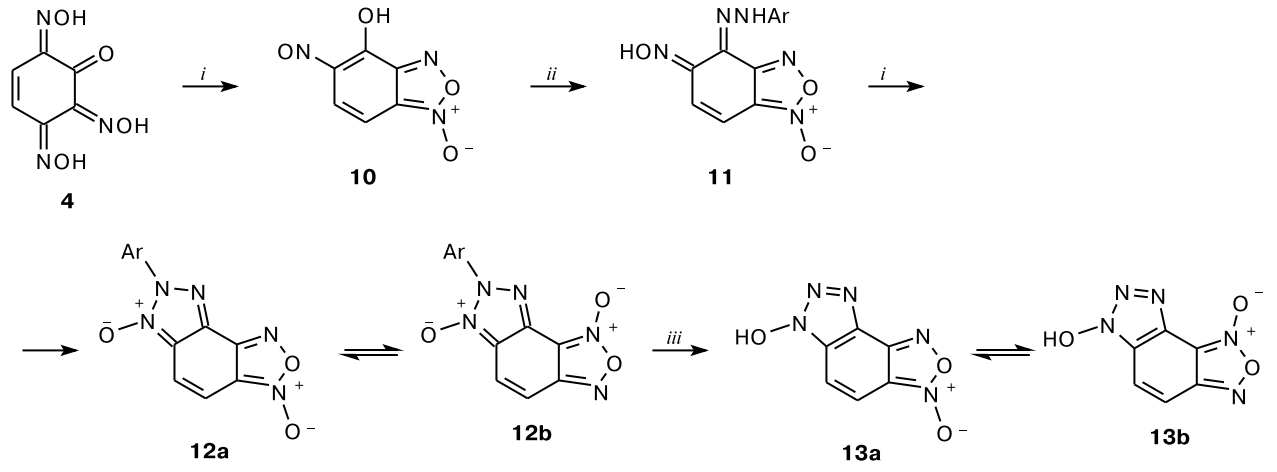
Reagents and conditions: *i*. Ac_2O, 80—90 °C; *ii*. H^+, MeOH, reflux; *iii*. 2,4-DNPH, MeOH, HCl (gas), 20 °C; *iv*. MnO_2, $CHCl_3$, 50—55 °C; *v*. MeONa, MeOH, 40 °C.

5-acetoxyiminodihydrobenzofurazan-4-one (**5**), hydrolysis of which results in 4-hydroxy-5-nitrosobenzofurazan **6**, which has been obtained earlier[17] from 5-nitrobenzofurazan. Hydrazono oxime **7** is formed upon reaction of compound **6** with 2,4-dinitrophenylhydrazine (2,4-DNPH). It is known[18] that oxidation of hydrazono oximes leads to triazole *N*-oxides. Triazolobenzofurazan **8** was obtained by the oxidation of compound **7** with MnO_2 in chloroform in 80.4% yield. As has been shown earlier,[19—23] 2,4-dinitrophenyl group in 2*H*-benzotriazoles is readily eliminated under the action of nucleophilic reagents. Treatment of compound **8** with sodium methoxide leads to hydroxytriazolobenzofurazan **9**. The structure of this compound was established by analytical and spectral data.

Annulation of 1-hydroxybenzotriazole by the furoxan ring was carried out according to Scheme 3. Compound **10** is formed upon oxidation of compound **4** with MnO_2 in acetonitrile in 70% yield.

Mass spectrum of this compound and the results of elemental analysis corresponded to molecular formula $C_6H_3N_3O_2$. The signals for two hydrogen atoms in the form of doublets are observed in the ^1H NMR spectrum at δ 6.97 and 7.38 with SSCC 10.4 Hz, and a broadened signal for one proton is observed at δ 5.56. The signals for

Scheme 3



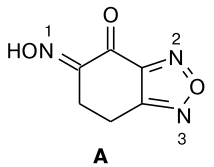
Reagents and conditions: *i*. MnO_2, acetonitrile, 20 °C; *ii*. 2,4-DNPH, MeOH, HCl (gas), 20 °C; *iii*. MeONa, MeOH, 40 °C.

Table 1. Calculated and experimental (in DMSO-d_6) chemical shifts of the carbon atoms of compounds **14**, **15a**, and **15b**

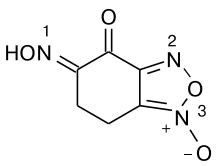
Compound	Method	δ							
		C(3a)	C(4)	C(5)	C(5a)	C(8a)	C(8b)	OMe	r^2 *
14	Experiment	149.6	117.4	118.3	128.7	141.8	129.6	69.6	—
	B3LYP/6G-31*	154.7	123.4	118.9	133.5	145.0	135.2	71.5	0.995 (0.75)
	riB3LYP/L1	151.8	121.3	117.9	132.0	143.4	134.4	70.4	0.996 (0.76)
	PBE/L2	154.5	122.5	119.1	133.4	145.9	136.8	71.2	0.995 (0.75)
15a	Experiment	113.2	114.6	114.5	129.5	145.0	130.6	69.3	—
	B3LYP/6G-31*	119.9	119.8	113.5	134.9	146.2	136.2	71.4	0.986 (0.78, 0.38, 0.61)
	riB3LYP/L1	114.8	117.3	112.7	133.1	143.8	135.8	70.3	0.989 (0.77, 0.35, 0.58)
	PBE/L2	114.1	117.9	114.8	134.5	143.7	138.5	71.1	0.984 (0.76, 0.34, 0.56)
15b	Experiment	152.3	119.0	118.5	127.2	104.9	127.6	69.3	—
	B3LYP/6G-31*	156.7	126.0	118.4	131.8	108.1	133.1	71.5	0.993 (0.49, 0.32, 0.60)
	riB3LYP/L1	151.6	124.4	116.7	130.5	102.8	131.5	70.2	0.987 (0.48, 0.31, 0.57)
	PBE/L2	150.8	126.4	116.8	132.6	100.7	132.1	71.0	0.973 (0.48, 0.28, 0.54)

* r is coefficient of correlation between calculated and experimental chemical shifts. Coefficient for the alternative signal assigment, and also (in the case of compounds **15a** and **15b**) coefficients obtained with an assumption that signal sets corresponding to these compounds are mixed up are given in the brackets.

six carbon atoms are observed in the ^{13}C NMR spectrum (Table 1), two of them are connected with hydrogen atoms. The signals at δ 169.44, 153.36 and 150.45, apparently, correspond to the carbon atoms that are connected with the nitrogen and oxygen atoms. The remaining signal at δ 109.02 was assigned to the carbon atom that is connected with the *N*-oxide group. The presence of the signal in the high field of the ^{13}C NMR spectrum, which corresponds to the carbon atom connected with the *N*-oxide group, is typical of benzofuroxans.[24] These data allow us to assign the structure of 4-hydroxy-5-nitrosobenzofuroxan to compound **10**. In order to find out in which form — quinonoid or nitrosophenol — compounds **6** and **10** exist, we recorded ^{15}N NMR spectra. It is known that chemical shifts of nitrogen atoms of the oxime and the nitroso groups differ very much.[25] 5-Hydroxyimino-4-oxo-4,5,6,7-tetrahydrobenzofurazan **A** and 5-hydroxyimino-4-oxo-4,5,6,7-tetrahydrobenzofuroxan **B**, which have been synthesized by us earlier,[26] were used as the model compounds; the ^{15}N NMR spectra for these compounds were also recorded. The NMR spectral data are presented in Table 2. Three singlet signals for the nitrogen atoms are observed in the ^{15}N NMR spectra of all four compounds. The low-field signals for N(1), apparently, can be assigned to the nitrogen atom from oxime and nitroso groups. Two rest signals N(2) and N(3) represent the signals for the nitrogen atoms of the furazan and furoxan rings. For furoxans, apparently, the high-field N(3) signals belong to the nitrogen atoms that are connected with two oxygen atoms.[24] Judging from the ^{15}N NMR spectral data it can be concluded that compounds **6** and **10** in DMSO exist in the quinone oxime form. The proportion of the nitroso form, obviously, is insignificant.



A



B

2,4-Dinitrophenylhydrazone **11** was obtained upon reaction of compound **10** with 2,4-DNPH, the oxidation of this compound with MnO_2 in acetonitrile afforded compound **12**. Judging by ^1H NMR spectral data, product **12** represents a mixture of two isomers **12a** and **12b** in the ratio 2.9 : 1, which differ from each other in the position of the *N*-oxide oxygen atom of the furoxan ring.

The presence of two isomers is typical of furoxans, especially those annulated by aromatic rings, and is caused by easy isomerization of the furoxan ring.[27] Treatment of compound **12** with sodium methoxide gave a mixture of isomeric hydroxytriazolobenzofuroxans **13a** and **13b**. The ratio of isomers was 6 : 1 judging by ^1H NMR spectral data.

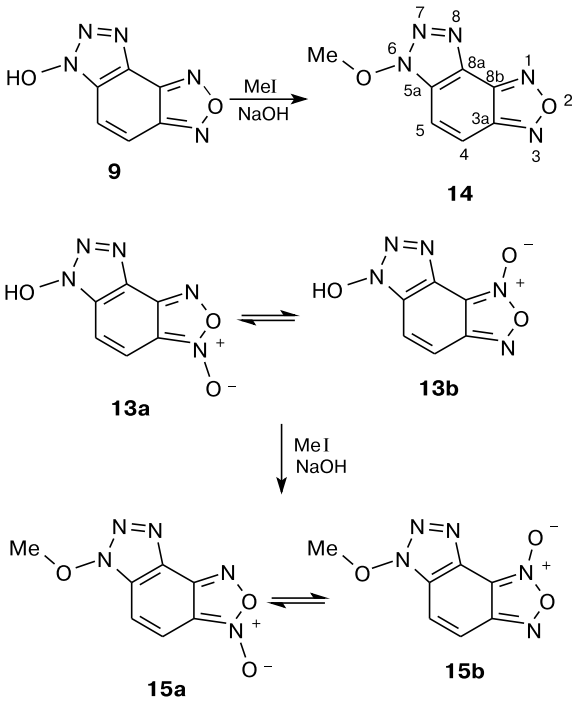
It is known[28] that methylation of 1-hydroxybenzotriazole leads to a mixture of *N*- and *O*-methylated com-

Table 2. Chemical shifts of the nitrogen atom in the ^{15}N NMR spectra (in DMSO-d_6)

Compound	δ		
	N(1)	N(2)	N(3)
A	422.34	410.74	406.02
6	443.61	422.12	409.21
B	406.10	387.88	366.80
10	421.15	370.28	362.52

pounds. The reaction of compound **9** and a mixture **13a,b** with methyl iodide resulted in only *O*-methylated compounds **14** and **15a,b**. The ratio of tautomers **15a** : **15b** was 6.7 : 1 judging by ^{1}H NMR spectral data. (Scheme 4).

Scheme 4



Assignment of the signals in the ^{1}H and ^{13}C NMR spectra for compounds **14**, **15a**, and **15b** was made using ^{13}C—^{1}H correlation with direct (HSQC)[29] and long-range (HMBC)[30] SSCC. The NMR methods in this case allow determination of relative positions of carbon and hydrogen atoms of the benzene rings of the examined compounds. However, the NMR spectral data permit alternative assignment of the signal for the benzene rings atoms. Besides, the assignment of signals in the NMR spectra of compounds **15a** and **15b** was ambiguous. In order to eliminate these ambiguities, we carried out quantum chemical calculations (DFT) of geometry and chemical shifts in the ^{13}C NMR spectra of compounds **14**, **15a**, and **15b**; a comparison of the experimental data with the calculated values for different assignments has been made (see Table 1). It can be seen from the Table that only one variant of assignment, which is in good agreement with the experiment, exists for each of the studied compounds, and it is this variant that conforms best of all to the literature data[24,31] on the chemical shifts of analogs. Somewhat better correlation with experimental data in the case of structure **15a,b** is achieved when B3LYP potential is used, which is not surpising, because this potential reproduces well the furoxan geometric parameters.[32] The use of the DFT-potential without the HF term, such as PBE, is also reasonable: the correlation with the experiment is only slightly worse, while the laboriosuess and computation duration (using PRIRODA program)[33] are significantly smaller. According to the calculations, compound **15a** is 0.5—0.9 kcal mol^{-1} more stable than compound **15b**, and this is in accordance with the observed dominance of isomer **15a** in the mixture.

Thus, we described the synthesis and the spectral characteristics of 1-hydroxybenzotriazoles annulated by furazan or furoxan rings. The obtained compounds are analogs of promoters that are widely used in the synthesis of peptides, nucleotides and other organic compounds.

Experimental

IR spectra were recorded on a Bruker Vector in KBr (concentration — 0.25%), the most intensive absorption bands in the spectra are presented. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AM-400 spectrometer (400.13 (^{1}H) and 100.61 MHz (^{13}C)) and on a Bruker Avance DRX-500 spectrometer (500.13 (^{1}H) and 125.77 MHz (^{13}C)) in $CDCl_3$ and DMSO-d_6 for 10% solutions at 25 °C. Chemical shifts were measured relative to the solvent residual signals: $CDCl_3$ (δ_H 7.24 and δ_C 76.90), DMSO-d_6 (δ_H 2.50 and δ_C 39.50). Multiplicity of signals in the ^{13}C NMR spectra was determined in the J-modulation mode (JMOD) and by ^{13}C—^{1}H correlations. ^{15}N NMR spectra were recorded on a Bruker Avance III 600 spectrometer (60.82 MHz). Chemical shifts were measured relative to NH_3 as the external standard. Mass spectra were obtained on a Finnigan MAT-8200 mass spectrometer (ionizing electron energy 70 eV, direct inlet of the sample, ion source temperature 180 °C). The course of the reactions and purity of the compounds were monitored by TLC on Sorbfil UV-254 plates with visualization by UV light and iodine vapor. Compound **2** was synthesized by the known method,[12] using manganous dioxide catalyst (Spec 6-09-01-718-87, Leningrad plant "Krasnyi khimik"). Melting points were determined on a Kofler heating stage. Elemental analysis was carried out in the Laboratory of microanalysis of the Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences.

Geometry optimization in the quantum chemical computations for compounds **14** and **15a,b** was carried out by DFT/B3LYP method (6G-31* basis set ((4s)/[2s] for H, (10s4p1d)/[3s2p1d] basis for C, N, O), GAMESS program),[34] riDFT/B3LYP method (L1 basis set (Λ01)[35] ((6s2p)/[2s1p] for H, (10s7p3d)/[3s2p1d] for C, N, O), PRIRODA program)[37] and DFT/PBE method (see Ref. 36) (L2 basis set (Λ02)[33] ((8s4p2d)/[3s2p1d] for H, (12s8p4d2f)/[4s3p2d1f] for C, N, O), PRIRODA program). Calculations of the chemical shifts was carried out by GIAO/DFT/PBE method (L2 basis set, PRIRODA program).

Cyclohex-5-ene-1,2,3,4-tetrone 1,2,4-trioxime (4)[14]. A mixture of dinitrosoresorcinol **2** (84 g, 0.5 mol), hydroxylamine hydrochloride (50 g, 0.72 mol), 50% aqueous ethanol (1 L) and conc. HCl (10 mL) was refluxed for 2 h and cooled. The precipitate was filtered off, washed sequentially with water (300 mL), ethanol (100 mL), and ether (200 mL). Compound **4** was obtained (83 g, 90%), m.p. 210 °C (decomp., from ethanol)

(*cf.* Ref. 14: m.p. 210 °C with flash). ^{1}H NMR (DMSO-d_6), δ: 7.15, 7.27 (both d, 1 H each, J = 10.0 Hz); 12.72, 13.40, 13.95 (all br.s, 1 H each, OH).

5-Nitroso-2,1,3-benzoxadiazol-4-ol (6) was synthesized by the modified method.[14] Compound **4** (210 g, 1.15 mol) was added to acetic anhydride (750 mL) and the mixture was heated to 80 °C with vigorous stirring, to the beginning of exothermic reaction. The mixture was kept for 1 h at 80—90 °C with water cooling. Acetic anhydride was distilled off *in vacuo* at ~15 Torr. Water (400 mL) was added to the residue. The mixture was kept for 3 h at ~20 °C for decomposition of acetic anhydride. The precipitate that formed was filtered off, washed with water and dried. **4,5-Dihydro-2,1,3-benzoxadiazole-4,5-dione 5-(*O*-acetyloxime) (5)** was obtained (175 g, 73.5%), m.p. 142—143 °C (from benzene) (*cf.* Ref. 23: m.p. 142—143 °C). Found (%): C, 46.12; H, 2.90; N, 20.10. $C_8H_5N_3O_4$. Calculated (%): C, 46.38, H, 2.43, N, 20.29. IR, ν/cm^{-1}: 1721 (C=O); 1775 (C=O). ^{1}H NMR (DMSO-d_6), δ: 2.30 (s, 3 H, Me); 7.60 (s, 2 H, CH). ^{13}C NMR (DMSO-d_6), δ: 19.30 (Me); 120.67 (CH); 125.02 (CH); 149.87; 151.34; 151.75; 167.25 (C=O); 171.64 (C=O). UV (EtOH), λ_{max}/nm (logε): 233 (3.83).

Methanol (600 mL) and HCl (2 mL) were added to compound **5** (175 g, 0.85 mol) in a 1 L flask. The mixture was refluxed for 1 h until all the starting oxime disappeared from the mixture (TLC, ethyl acetate—hexane, 1 : 1, R_f 0.42 (compound **5**) and 0.54 (compound **6**)). The solvent was evaporated, chloroform (200 mL) was added to the residue, the precipitate was suspended, filtered off, and dried. Compound **6** was obtained (90 g, 48%), m.p. 184—186 °C (from ethanol) (*cf.* Ref. 17: m.p. 185—187 °C). Found (%): C, 43.72; H, 1.90; N, 25.40. $C_6H_3N_3O_3$. Calculated (%): C, 43.64; H, 1.82; N, 25.45. ^{1}H NMR (DMSO-d_6), δ: 7.28, 7.53 (both d, 1 H each, J = 10.4 Hz); 10.65 (br.s, 1 H, OH). ^{13}C NMR (DMSO-d_6), δ: 118.17 (CH); 124.41 (CH); 148.77; 149.84; 152.23; 172.47.

4,5-Dihydro-2,1,3-benzoxadiazole-4,5-dione 4-(2,4-dinitrophenylhydrazone) 5-oxime (7). 2,4-Dinitrophenylhydrazine (2.0 g, 10.1 mmol) was added to a solution of compound **6** (1.65 g, 0.01 mol) in methanol (300 mL). Dry HCl was bubbled through the mixture with stirring at ~20 °C, the mixture was kept for 8 h at ~20 °C. The precipitate that formed was filtered off, washed with methanol, and dried. Compound **7** was obtained (3.05 g, 96.3%), m.p. 234 °C (decomp., from ethanol). Found (%): C, 42.40; H, 1.95; N, 28.30. $C_{12}H_7N_7O_6$. Calculated (%): C, 42.23; H, 2.06; N, 28.70. ^{1}H NMR (DMSO-d_6), δ: 7.49, 7.72 (both d, 1 H each, J = 9.6 Hz); 8.29 (d, 1 H, J = 8.8 Hz); 8.60 (dd, 1 H, J = 8.8 Hz, J = 2.4 Hz); 8.94 (d, 1 H, J = 2.4 Hz); 13.58 (s, 1 H, NH); 14.48 (s, 1 H, OH).

5-(2,4-Dinitrophenyl)-5*H*-[1,2,3]triazolo[4,5-*e*][2,1,3]-benzoxadiazole 6-oxide (8). To a suspension of hydrazone **7** (4.0 g, 11.6 mmol) in chloroform (400 mL), MnO_2 (10 g) was added; the mixture was stirred at 40—50 °C for ~12 h (until all starting compound has disappeared, TLC monitoring). The precipitate was filtered off and extracted with chloroform in a Soxhlet extractor. The extract was concentrated to 50 mL, the precipitate that formed was filtered off, washed with small volume of chloroform, and dried. Compound **8** was obtained (3.20 g, 80.4%), m.p. 246—248 °C (from $CHCl_3$). Found (%): C, 41.82; H, 1.30; N, 28.90. $C_6H_3N_3O_3$. Calculated (%): C, 41.98; H, 1.46; N, 28.57. IR, ν/cm^{-1}: 1341; 1465; 1498; 1554; 1611. ^{1}H NMR (DMSO-d_6), δ: 7.90, 7.98 (both d, 1 H each, J = 9.60 Hz); 8.34 (d, 1 H, J = 8.8 Hz); 8.88 (dd, 1 H, J = 8.8 Hz, J = 2.4 Hz); 9.03 (d, 1 H, J = 2.4 Hz). ^{13}C NMR (DMSO-d_6), δ: 116.14 (CH); 119.72 (CH); 121.30 (CH); 129.67 (CH); 131.31 (CH); 124.53; 128.99; 131.83; 142.26; 143.58; 148.79; 150.57. UV (EtOH), λ_{max}/nm (logε): 240 (3.90); 295 (4.10). MS, m/z (I_{rel} (%)): 343 [M]$^+$ (100), 327 (10), 313 (15), 237 (15).

6-Hydroxy-6*H*-[1,2,3]triazolo[4,5-*e*][2,1,3]benzoxadiazole (9). To a suspension of compound **8** (3.43 g, 0.01 mol) in methanol (80 mL), $NaOCH_3$ (1.52 g, 0.03 mol) was added; the mixture was stirred for 6 h at 35—40 °C, concentrated to dryness, chloroform (50 mL) was added to the residue. The precipitate was filtered off, washed thoroughly with chloroform, and dried. The precipitate was dissolved in water (15 mL) and acidified with 10% HCl to pH ~5, cooled, the precipitate that formed was filtered off, washed with water, and dried. Compound **9** was obtained (1.25 g, 70.8%), m.p. 206—207 °C (decomp., from water). Found (%): C, 40.50; H, 1.62; N, 39.90. $C_6H_3N_5O_2$. Calculated (%): C, 40.69; H, 1.71; N, 39.54. IR, ν/cm^{-1}: 1423; 1531; 1583; 1639. ^{1}H NMR (DMSO-d_6), δ: 7.79, 7.86 (both d, 1 H each, J = 9.2 Hz); 6.18 (br.s, 1 H, OH). ^{13}C NMR (DMSO-d_6), δ: 116.00 (CH); 129.52 (CH); 128.77; 129.51; 141.99; 149.56. UV (EtOH), λ_{max}/nm (logε): 234 (4.25); 283 (3.62). MS, m/z (I_{rel} (%)): 177 [M]$^+$ (49), 149 (66).

4-Hydroxy-5-nitroso-2,1,3-benzoxadiazole 1-oxide (10). To a solution of trioxime **4** (2.0 g, 10.9 mmol) in acetonitrile (200 mL), MnO_2 (5 g) was added, the mixture was stirred for 6 h at ~20 °C. The precipitate was filtered off, the filtrate was concentrated. The residue was chromatographed on silica gel (ethyl acetate) (R_f = 0.75 in ethyl acetate). Benzofuroxan **10** was obtained (1.4 g, 70%), m.p. 162 °C (decomp., from ethanol). Found (%): C, 39.90; H, 1.42; N, 23.00. $C_6H_3N_3O_4$. Calculated (%): C, 39.79; H, 1.67; N, 23.20; IR, ν/cm^{-1}: 1620; 1705. ^{1}H NMR (DMSO-d_6), δ: 6.97, 7.38 (both d, 1 H each, J = 10.4 Hz); 5.56 (br.s, 1 H, OH). ^{13}C NMR (DMSO-d_6), δ: 113.39 (CH); 123.53 (CH); 109.02; 150.45; 153.36; 169.44. UV (EtOH), λ_{max}/nm (logε): 250 (4.04); 280 (4.13); 370 (3.72). MS, m/z (I_{rel} (%)): 181 [M]$^+$ (100), 165 (10), 151 (15).

2,1,3-Benzoxadiazole-4,5-dione 4-(2,4-dinitrophenylhydrazone) 5-oxime 1-oxide (11) was obtained similarly to compound **7**. Yield 80%, m.p. 212—214 °C (from ethanol). Found (%): C, 41.10; H, 2.09; N, 26.90. $C_{12}H_7N_7O_7$. Calculated (%): C, 39.89; H, 1.94; N, 27.15. IR, ν/cm^{-1}: 1340; 1490: 1510; 1595; 1610; 1620. ^{1}H NMR (DMSO-d_6), δ: 7.34, 7.65 (both d, 1 H each, J = 10.4 Hz); 8.25 (d, 1 H, J = 9.2 Hz); 8.63 (dd, 1 H, J = 9.2 Hz, J = 2.4 Hz); 8.94 (d, 1 H, J = 2.4 Hz); 13.62 (s, 1 H, NH); 14.30 (s, 1 H, OH).

5-(2,4-Dinitrophenyl)-5*H*-[1,2,3]triazolo[4,5-*e*][2,1,3]-benzooxadiazole 1(3),6-dioxide (12) was synthesized similarly to compound **8**. Yield 78%, m.p. 232—234 °C (from HNO_3, d = 1.42 g cm^{-3}). Based on ^{1}H NMR data, a mixture of two compounds in the ratio 1 : 2.9 was obtained. Found (%): C, 40.18; H, 1.27; N, 27.68. $C_{12}H_5N_7O_7$. Calculated (%): C, 40.11; H, 1.39; N, 27.30. IR, ν/cm^{-1}: 1348; 1543; 1616; 1637; 1467; 1498. ^{1}H NMR (DMSO-d_6), δ, main isomer: 7.45, 7.62 (both d, 1 H each, J = 9.6 Hz); 8.35 (d, 1 H, J = 8.8 Hz); 8.89 (dd, 1 H, J = 8.8 Hz, J = 2.8 Hz); 9.03 (d, 1 H, J = 2.8 Hz); minor isomer: 7.73, 7.79 (both d, 1 H each, J = 9.6 Hz); 8.27 (d, 1 H, J = 8.8 Hz); 8.86 (dd, 1 H, J = 8.8 Hz, J = 2.8 Hz); 9.00 (d, 1 H, J = 2.8 Hz). ^{13}C NMR (DMSO-d_6), δ, main isomer: 104.72; 113.44 (CH); 116.09 (CH); 121.23 (CH); 125.21; 128.98; 129.62 (CH); 131.29 (CH); 132.70; 143.54; 145.11; 148.80;

minor isomer: 105.98; 118.05 (CH); 119.65 (CH); 121.44 (CH); 123.28; 128.58; 129.85 (CH); 131.13 (CH); 132.28; 143.44; 148.63, 152.63. MS, m/z (I_{rel} (%)): 359 $[M]^+$ (100), 343 (35), 329 (5), 313 (10), 299 (25).

6-Hydroxy-6*H*-[1,2,3]triazolo[4,5-*e*][2,1,3]benzoxadiazole 1(3)-oxide (13) was synthesized similarly to compound **9**. Yield 82%, m.p. 186—188 °C (decomp., from ethanol). Based on ^{1}H NMR data, a mixture of isomers in the ratio 6 : 1 was obtained. Found (%): C, 37.11; H, 1.31; N, 36.85. $C_6H_3N_5O_3$. Calculated (%): C, 37.31; H, 1.57; N, 36.27. IR, ν/cm^{-1}: 1645. ^{1}H NMR (DMSO-d_6), δ, main isomer: 7.45, 7.61 (both d, 1 H each, J = 9.2 Hz); minor isomer: 7.70, 7.76 (both d, 1 H each, J = 9.2 Hz). ^{13}C NMR (DMSO-d_6), δ, main isomer: 112.70 (CH); 112.88; 114.99 (CH); 129.29; 130.07; 144.92; minor isomer: 104.89; 117.33 (CH); 118.40 (CH); 127.05; 127.11; 152.17. UV (EtOH), λ_{max}/nm (logε): 240 (3.99); 259 (3.96); 348 (3.86). MS, m/z (I_{rel} (%)): 193 $[M]^+$ (50), 177 (50), 165 (5), 135 (70).

6-Methoxy-6*H*-[1,2,3]triazolo[4,5-*e*][2,1,3]benzoxadiazole (14). Dichloromethane (20 mL), methyl iodide (4.26 g, 0.015 mol), and tetrabutylammonium bromide (0.1 g) were added to a solution of compound **9** (0.91 g, 0.005 mol) in 5% NaOH (15 mL). The mixture was vigorously stirred for 4 h at ~20 °C, the layers were separated. the organic layer was washed with water, dried with $MgSO_4$, and concentrated. The residue was suspended in hexane, the precipitate was filtered off. Compound **14** was obtained (0.88 g, 82%), m.p. 135—136 °C (from ethanol). Found (%): C, 44.20; H, 2.31; N, 36.85. $C_6H_3N_5O_3$. Calculated (%): C, 43.98; H, 2.64; N, 36.64. IR, ν/cm^{-1}: 1442; 1455; 1527; 1566; 2953; 3087. ^{1}H NMR (DMSO-d_6), δ: 8.06, 8.13 (both d, 1 H each, H(4), H(5), J = 9.6 Hz); 4.61 (s, 3 H, OCH_3); ^{1}H NMR ($CDCl_3$), δ: 7.64, 7.83 (both d, 1 H each, J = 9.6 Hz); 4.50 (s, 3 H). ^{13}C NMR (DMSO-d_6) see Table 1. ^{13}C NMR ($CDCl_3$), δ: 68.12 (OCH_3); 116.21 (CH); 117.30 (CH); 123.68; 130.48; 141.76; 149.23. UV (EtOH), λ_{max}/nm (logε): 290 (3.68); 235 (4.24). MS, m/z (I_{rel} (%)): 191 $[M]^+$ (15); 163 (55), 148 (18), 132 (30).

6-Methoxy-6*H*-[1,2,3]triazolo[4,5-*e*][2,1,3]benzoxadiazole 1(3)-oxide (15a,b) was synthesized similarly to compound **14**. Yield 76%. Based on ^{1}H NMR, a mixture of isomers in the ratio 6.7 : 1 was obtained. M.p. 133—134 °C (from $CHCl_3$). Found (%): C, 40.30; H, 2.44; N, 33.50. $C_6H_3N_5O_3$. Calculated (%): C, 40.58; H, 2.43; N, 33.81. IR, ν/cm^{-1} : 1550; 1599; 1627; 3089. ^{1}H NMR for compound **15a** (DMSO-d_6), δ: 7.57, 7.76 (both d, 1 H each, H(4), H(5), J = 9.6 Hz); 4.43 (s, 3 H, OCH_3). ^{1}H NMR for compound **15b** (DMSO-d_6), δ: 7.91, 7.82 (both d, 1 H each, H(4), H(5), J = 9.6 Hz); 4.43 (s, 3 H, OCH_3). ^{13}C NMR spectra see Table 1. UV (EtOH), λ_{max}/nm (logε): 252 (4.02); 344 (3.88). MS, m/z (I_{rel} (%)): 207 $[M]^+$ (15); 179 (48); 149 (100).

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