Synthesis of 1,6-dihydro-1,6-dihydroxybenzo[1,2-d:3,4-d´]bistriazole, 4- and 5-nitro-1,6-dihydro-1,6-dihydroxybenzo[1,2-d:3,4-d´]bistriazole and 4,7-dihydro-1,4,7-trihydroxy-1*H*-benzo-[1,2-d:3,4-d´:5,6-d"]tris[1,2,3]triazole

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1,6-Dihydro-1,6-dihydroxybenzo[1,2-d:3,4-d']bistriazole and 4- and 5-nitro-1,6-dihydro-1,6-dihydroxybenzo[1,2-d:3,4-d']bistriazole were synthesized starting from 2,4-dinitrosore-sorcinol, whereas 4,7-dihydro-1,4,7-trihydroxy-1H-benzo[1,2-d:3,4-d':5,6-d"]tris[1,2,3]-triazole was synthesized starting from phloroglucinol. The reaction of trinitrosophloroglucinol with hydrazine hydrate in acetic acid led to 2,4,6-tridiazocyclohexane-1,3,5-trione.

Key words: nitrosophenols, 1-hydroxybenzotriazoles, 2*H*-benzotriazole *N*-oxides, dihydrobenzo[1,2-*d*:3,4-*d*']bistriazoles, benzotristriazoles, diazoketones.

An important property of 1-hydroxybenzotriazole is its ability to liberate gaseous products upon heating, which allow one to use it as a blowing agent in the production of gas-filled materials.^{1,2} The range of foaming agents is limited, and a search for new compounds which satisfy practical requirements remains still an actual problem. Introduction into the molecule of 1-hydroxybenzotriazole of groups capable of easy decomposition on heating with the formation of gaseous products could have broaden the scope of such compounds. Additional one or two 1-hydroxytriazole rings annulated to 1-hydroxybenzotriazole could have served as such groups. In order to broaden the range of the gas-generating compounds, we carried out synthesis of such 1-hydroxybenzotriazoles.

The synthesis of 1-hydroxybenzotriazole annulated to another 1-hydroxytriazole ring was effected according to Scheme 1. The nitrosation of resorcinol **1** leads to 2,4-dinitrosoresorcinol **2** (see Ref. 3). (Taking into account that o- and p-nitrosohydroxyarenes exist in the tautomeric equilibrium with quinone oximes,⁴ to make the presentation of the material easier, the nitrosation products of hydroxyarenes further will be called as the corresponding nitroso compounds.)

When compound **2** was treated with 2,4-dinitrophenylhydazine (2,4-DNPH), 2,6-di[(2,4-dinitrophenyl)hydrazono]cyclohex-4-ene-1,3-dione 1,3-dioxime **3** was formed (see Ref. 5). The oxidation of compound **3** with MnO_2 in acetone gave rise to 2,7-dihydro-2,7-di(2,4dinitrophenyl)benzo[1,2-d:3,4-d']bistriazole 1,6-diox-





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

Reagents, conditions, and yields: *i*. NaNO₂, H₂SO₄, 0–3 °C, 92%; *ii*. 2,4-DNPH, MeOH, HCI (gas), 20 °C, 94%; *iii*. MnO₂, acetone, 50 °C, 61%; *iv*. MeONa, MeOH, 40 °C, 61.4%; *v*. K₂CO₃, MeI, MeCN, 54%.

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ide (4). The structure of compound 4 was confirmed by the 1 H and 13 C NMR data, as well as by mass spectrometry and elemental analysis.

Since the molecule is unsymmetric, the signals for the protons of the 4-dinitrophenyl groups in the ¹H NMR spectrum of compound 4 are observed as multiplets at δ 7.80-7.95, 8.30-8.41, and 9.80-9.95, the signals for the protons at positions 4 and 5 as doublets at δ 9.02 and 9.03. The ¹³C NMR spectrum exhibits five signals for the carbon atoms bonded to a hydrogen atom, and 10 signals for the quaternary carbon atoms. Apparently, three signals for the carbon atoms overlapped with other signals. As it has been shown earlier, 2,4-dinitrophenyl group in benzotriazoles could be easily eliminated upon the action of nucleophilic agents.⁶⁻⁹ The action on benzobistriazole 4 of sodium methoxide in methanol led to the elimination of dinitrophenyl groups with the formation of 1,6-dihydro-1,6-dihydroxybenzo[1,2-d:3,4-d']bistriazole (5) (see Scheme 1). It should be noted that in the mass spectrum of compound 5, the peak of molecular ion with the mass 292 is absent and the peak with the mass 264 - $[M-28]^+$ is present. Apparently, molecules of compound 5 in the source of ions of mass spectrometer decompose with elimination of nitrogen.

It is known¹⁰ that 1-hydroxybenzotriazole **A** exists in the tautomeric equilibrium with its *N*-oxide form **B**, with the form **B** being predominant in polar solvents, whereas the form **A** is predominant in nonpolar. Methylation of 1-hydroxybenzotriazole leads to a mixture of *N*- and *O*-methylated compounds.¹¹



Upon alkylation of compound **5** with methyl iodide, only *O*-methylated compound, *i.e.*, dimethoxy derivative **6**, was isolated (see Scheme 1).

Treatment of compound **3** with nitric acid led to compound **7** (Scheme 2).

The ¹H NMR spectrum of compound **7** exhibits signals for six aromatic protons as multiplets at δ 8.38–8.40, 8.85–8.98, and 9.02–9.09 and a broad singlet at δ 9.00. In the ¹³C NMR spectrum four signals for the carbon atoms bonded to the hydrogen atoms and 11 signals for the quaternary carbon atoms are found. Apparently, other signals for the carbon atoms overlapped. In the mass spectrum of compound **7**, a peak of the molecular ion with the mass 589 is observed. The C₁₈H₇N₁₁O₁₂ molecular formula was obtained from the elemental analysis data. A combination of these data allowed us to suggest that the obtained compound **7** is a mononitro derivative of benzobistriazole.

To clarify which position (4 or 5) the nitro group is situated at, we used recrystallization from dilute nitric acid to grow crystals and performed X-ray diffraction studies of molecule 7. From the X-ray diffraction data, it follows that the product 7 is a mixture of 2,7-dihydro-2,7-bis(2,4-dinitrophenyl)-4-nitrobenzo[1,2-d:3,4-d']-bistriazole 1,6-dioxide (7a) and 2,7-dihydro-2,7-bis(2,4-dinitrophenyl)-5-nitrobenzo[1,2-d:3,4-d']bistriazole 1,6-dioxide (7b) in the ratio of 7 : 3.

The structure of molecules 7a and 7b in the cocrystal is shown in Fig. 1. The benzobistriazole fragment is planar, with the mean square deviation of atoms being 0.048 Å. The dinitrophenyl groups deviate from this plane by the same angle of $65.2(1)^{\circ}$. The nitro group of the benzobistriazole fragment of the molecule is disordered over two positions, with the ratio of occupations being 0.708(7): 0.292(7), which indicates cocrystallization of two isomers, viz., 4-nitro- and 5-nitrobenzobistriazoles (7a and 7b, respectively). The nitro group at position 4 is coplanar to the framework (the angle of $1.1(5)^{\circ}$), whereas the nitro group at position 5 deviates from the plane by the angle of 21.1(8)°. Note that we did not find data on analogous benzobistriazole N-oxides in the Cambridge Structural Database.¹² There are data on the structure of 4,6-dinitro-2-(2,4,6-trinitrophenyl)-2H-benzotriazole 1-oxide,¹³ methyl 3-[3-tert-butyl-5-(6-chloro-1-hydroxybenzotriazol-2-yl)-4-hydroxyphenyl]propionate,¹⁴ and 2-(3-carboxamidofuroxan-4-yl)-4-nitro-5-carboxamido-2H-[1,2,3]triazole 1-oxide.¹⁵ The bond distances of the



Scheme 2

Reagents, conditions, and yields: *i*. HNO₃ (d = 1.42), reflux, 43%; *ii*. MeONa, MeOH, 40 °C, 50.4%.



Fig. 1. Molecular structures of 4- and 5-nitro-2,7-dihydro-2,7-di(2,4-dinitrophenyl)benzo[1,2-d:3,4-d']bistriazole 1,6-dioxides (7a,b) in the cocrystal (the solvent molecules of water are shown). The distances are as follows: O(1)...O(2W) 2.86(2), O(2W)...O(3W) 2.77(4), O(3W)...O(1W) 2.44(5) Å.

triazole oxide fragment of the cocrystal under studies are close to the data given in the literature.

The action on a mixture of benzotriazoles **7a** and **7b** of sodium methoxide in methanol leads to the elimination

of dinitrophenyl groups and formation of a mixture of 1,6-dihydro-1,6-dihydroxy-4-nitrobenzo[1,2-*d*:3,4-*d'*]bistriazole (**8a**) and 1,6-dihydro-1,6-dihydroxy-5-nitrobenzo[1,2-*d*:3,4-*d'*]bistriazole (**8b**), respectively (see Scheme 2). In the ¹H NMR spectrum of the mixture of compounds **8a** and **8b**, the following signals for the hydrogen atoms are observed: for compound **8a** at δ 8.36, for compound **8b** at δ 8.34, as well as a broad signal at δ 10.4 for the hydrogen atoms of two OH groups. Note that both isomeric compounds have identical ¹³C NMR spectra.

The synthesis of 1-hydroxybenzotriazole annulated with two 1-hydroxytriazole rings was carried out according to Scheme 3. The nitrosation of phloroglucinol 9 easily leads to the formation of trinitrosophloroglucinol 10. The synthesis of this compound was described in the works.^{16,17} The compound was isolated as a potassium salt. The free trinitrosophloroglucinol was obtained by decomposition of the lead salt with alcoholic sulfuric acid. Both the potassium salt and the free trinitrosophloroglucinol are unstable. The product **10** rapidly decomposes on standing in aqueous solutions and especially during evaporation of these solutions. We found that the free trinitrosophloroglucinol 10 was easily obtained upon nitrosation of phloroglucinol isopropylnitrite in ethanol in the presence of catalytic amounts of acetic acid. The reaction of compound 10 with 2,4-DNPH led to 2,4,6-tri-[(2,4-dinitrophenyl)hydrazono)]cyclohexane-1,3,5-trione 1,3,5-trioxime 11, whose oxidation with MnO_2 in acetone



Scheme 3

R = H (13), OMe (14)

Reagents, conditions, and yields: *i.* PrⁱONO, MeOH, AcOH, 0–5 °C, 95%; *ii.* 2,4-DNPH, MeOH, HCl (gas), 20 °C, 93%; *iii.* MnO₂, acetone, 40 °C, 35%; *iv.* MeONa, MeOH, 40 °C, 54.5%; *v.* NH₂NH₂·H₂O, AcOH, reflux, 20.5%.

or with nitric acid gave benzotristriazole 1,4,7-trioxide 12. The product is a light yellow crystalline compound with melting point above 360 °C, virtually insoluble in water and ethanol. Compound 12 is very poorly soluble in acetone and was recrystallized from 70% aqueous nitric acid. Because of poor the solubility of the compound in organic solvents, the NMR spectra were recorded in concentrated sulfuric acid. The ¹H NMR spectra exhibit three broad signals for the hydrogen atoms of the dinitrophenyl groups in the region δ 7.75–7.95, 8.40–8.60, and 8.75–8.94. The ¹³C NMR spectra exhibit eight signals for the carbon atoms, the three of which belong to the carbon atoms bonded to the hydrogen atoms in the dinitrophenyl groups. Other three signal are attributable to the carbon atoms, which are not bonded to the hydrogen atoms in the dinitrophenyl groups, and other two signals belong to the carbon atoms of the triazole rings.

Elimination of 2,4-dinitrophenyl groups in compound 12 upon the action of MeONa in methanol led to the formation of trihydroxybenzotristriazole 13. This compound was obtained as colorless crystals and is insoluble in most organic solvents, including DMSO and DMF, moderately soluble in water, but well soluble in aqueous solutions of acids and alkali. Compound 13 was recrystallized from water. The ¹³C NMR spectrum recorded in H_2SO_4 exhibits two signals for the carbon atom at δ 129.00 and 123.5. A peak of molecular ion with the mass of 249 is present in the mass spectrum. The $C_6H_3N_9O_3 \cdot 3H_2O$ molecular formula was calculated for the compound from the elemental analysis data. These data allowed us to assign to the compound obtained the structure of 4,7-dihydro-1,4,7trihydroxy-1*H*-benzo[1,2-d:3,4-d':5,6-d"]tris[1,2,3]triazole (13).

The alkylation of compound **13** with methyl iodide easily led to the formation of 4,7-dihydro-1,4,7-trimethoxy-1H-benzo[1,2-d:3,4-d':5,6-d"]tris[1,2,3]triazole (**14**). The structure of compound **14** was confirmed by the X-ray diffraction data (Fig. 2).

The molecular framework of compound 14 is planar within ± 0.021 Å (see Fig. 2). The carbocycle of the molecule demonstrates clear alternation of the bond distances: the bonds common to two rings have the lengths of 1.385(3)-1.389(3) Å, other bonds lie within 1.430(3)-1.432(3) Å. Such an alternation agrees with the quantum chemical calculations, which gives 1.408 and 1.423 Å (DFT/PBE/3z), 1.402 and 1.423 Å (DFT/B3LYP/6-311G*), respectively. Similar alternation of bond distances was observed in the molecule of 2,5,8-tri-n-pentylbenzotris(imidazole)¹⁸ (1.375(6) and 1.408(6) Å), however, in the molecule of 2,5,8-tris(4-methylphenyl)bis-[1,3]dithiolo[4,5-e:4',5'-g][1,3]benzodithiole,¹⁹ the alternation was reverse (1.414(5) and 1.378(5) Å). The bond distances in heterocycles also are close to the calculated values and slightly differ from the data for the molecule of 1-hydroxybenzotriazole.¹⁰ In the molecule 14, the meth-



Fig. 2. Molecular structure of 4,7-dihydro-1,4,7-trimethoxy-1H-benzo[1,2-d:3,4-d':5,6-d"]tris[1,2,3]triazole (**14**).

oxy groups deviate from the plane of the framework, the torsional angles CNOC are equal to -88.7(3), 88.2(3), and $100.4(3)^{\circ}$, indicating that one methoxy group comes out of the plane to the opposite side. According to the gas-phase DFT/B3LYP/6-311G* calculations, such a ααβ-conformation is only 0.2 kcal mol⁻¹ more stable than the ααα-conformation, the rotational barrier for the methoxy group is equal to 6.0 kcal mol⁻¹. Molecules in the crystal form stacks along the axis *a* due to the π-stacking (the distances: between planes 3.32 Å, intercentroid 3.425(1), 3.717(1) Å (benzene—triazole) and 3.665(1) Å (triazole—triazole)). The following interactions between stacks C—H...O (C(8)—H...O(2), H...O 2.63 Å, C—H...O 154°; C(9)—H...O(2), 2.61, 140; C(9)—H...O(3), 2.55, 164) combine the stacks in layers.

It is necessary to note that the reaction of trinitrosophloroglucinol **10** with hydrazine hydrate in acetic acid unexpectedly led to 2,4,6-tridiazocyclohexane-1,3,5-trione (**15**) instead of the expected 2,4,6-trihydrazonocyclohexane-1,3,5-trione 1,3,5-trioxime. Compound **15** has been obtained earlier by the reaction of 2-azido-3-ethylbenzothiazolium fluoroborate with phloroglucinol.²⁰ The formation of compound **15** can be explained similarly to the described synthesis of 3-diazo-2,4-chromanedione.²¹ It is possible that the reaction of the nitroso group in trinitrosophloroglucinol with hydrazine hydrate results in the formation the intermediate triazene, elimination of ammonia from which gives rise to compound **15** (Scheme 4).

In conclusion, we for the first time accomplished synthesis of a number (5, 6, 8, 13, 14) of 1-hydroxy- and 1-methoxybenzotriazoles annulated to one and two 1-hydroxytriazole rings. Preliminary testing showed that these compounds are promising gas-generating components in the corresponding devices. Thus, heating of 1 g of compound 5 in an autoclave at 250 °C during 10 min results in





i. NH₂NH₂•H₂O; *ii*. –NH₃.

the liberation of 700 mL of gases, *i.e.*, the compound has high gas number. For comparison, it can be indicated that 1 g of oxygen occupies the volume of 700 mL.

Experimental

IR spectra were recorded on a Bruker Vector spectrometer in KBr pellets (concentration of 0.25%). UV spectra of solutions of compounds in ethanol were recorded on a Specord M-40 spectrophotometer. ¹H and ¹³C NMR spectra were recorded on a Bruker AM 400 spectrometer (400.13 (¹H) and 100.61 MHz (¹³C)) in DMSO-d₆ and H₂SO₄ for 10% solutions at 25 °C. Sulfuric acid of reagent grade (GOST 4204-77) was used for the spectra recording, CH₂Cl₂ was used as an internal standard ($\delta_{\rm H}$ 5.33 and $\delta_{\rm C}$ 54.0). Chemical shifts were measured relative to the residual signals of the solvent: DMSO-d₆ (δ_H 2.50 and δ_C 39.50). Splitting of signals in the ¹³C NMR spectra was determined in the J-modulation regime (JMOD). Mass spectra were recorded on a Finnigan MAT-8200 instrument (70 eV, direct injection of compounds, temperature the source of ions 180 °C). Peaks of molecular ions and peaks with intensities higher than 10% are reported. Reaction progress and individuality of compounds were monitored by TLC on Sorbfil UV-254 plates. Chromatographic plates were visualized with UV light and iodine vapors. Compounds 2 and 3 were synthesized according to the known procedures.^{3,5} Manganese dioxide (TU 6-09-01-718-87) purchased from Leningrad plant Krasnvi khimik was used in the synthesis. Melting points were determined on a Kofler microheating stage. Elemental analysis of compounds was performed in the Laboratory of microanalysis of the Institute of Organic Chemistry. Siberian Branch of the Russian Academy of Sciences.

X-ray diffraction studies were performed on a Bruker P4 diffractometer (for compounds **7a** and **7b**, graphite monochromator, λ (Mo-K α) = 0.71073 Å, θ /2 θ -scan technique) and Bruker KAPPA APEX II diffractometer (for compound **14**, Mo-K α irradiation, graphite monochromator, φ , ω -scan technique). The structures were solved by direct method using the SHELXS-97 program. Refinement of the structural parameters were performed by the least squares method on all the reflections in full-matrix anisotropic (for all the nonhydrogen atoms) approximation using the SHELXL-97 program. Positions of hydrogen atoms were refined using the riding model. Full tables of the atomic coordinates for compounds **7a**, **7b**, and **14** were deposited with the Cambridge Structural Database (CCDC 822784 and CCDC 822785, respectively).

The gas-phase quantum chemical calculations were performed using the PRIRODA program (DFT/PBE/3z) and the GAMESS program (DFT/B3LYP/6-311G*).

Crystallographic data for the cocrystal of compounds 7a and 7b. Temperature 296 K, $C_{18}H_7N_{11}O_{12} + 0.621(H_2O)$, M = 580.51, triclinic crystal system, space group $P\overline{1}$, a = 10.836(4) Å, b = 11.410(4) Å, c = 11.772(3) Å, $\alpha = 77.72(3)^{\circ}$, $\beta = 63.14(2)^{\circ}$, $\gamma = 80.83(3)^\circ$, V = 1265.4(7) Å³, Z = 2, $d_{calc} = 1.515$ g cm⁻³, $\mu = 0.132 \text{ mm}^{-1}$, scanning range $2\theta < 50^{\circ}$, number of measured reflections 4706 ($R_{int} = 0.0506$), number of reflections with $I \ge 2\sigma(I)$ 2280, number of refined parameters 396, $R_1(I \ge 2\sigma(I)) =$ = 0.0856, $wR_2 = 0.2792$, S = 1.010 (on all the 4432 independent reflections). Allowance for absorption was made using experimental curves of the azimuth scanning $(T_{\min}/T_{\max} = 0.6381/$ 0.8846). The crystalline structure showed the presence of the water solvent molecules placed in three positions. It should be noted that these positions are occurred partially (0.156(9)), 0.337(10), 0.128(9), that is apparently due to the loss of the water molecules on storage of the crystals. This is facilitated by the molecular packing, which creates channels along the axis cwith the overall volume of 231.7 $Å^3$.

Crystallographic data for compound 14. Temperature 200 K, C₉H₉N₉O₃, M = 291.25, monoclinic crystal system, space group $P2_1/c$, a = 4.0975(6), b = 18.109(3), c = 16.891(2) Å, $\beta = 95.281(7)^\circ$, V = 1248.0(3) Å³, Z = 4, $d_{calc} = 1.550$ g cm⁻³, $\mu = 0.123$ mm⁻¹, scanning range $2\theta < 50^\circ$, amount of measured reflections 5200, from them 2190 were independent ($R_{int} =$ = 0.0556), $wR_2 = 0.1182$, S = 0.963, 191 parameter, R = 0.0449for 1409 $F > 4\sigma_F$. Allowance for absorption was made by empirical method using the SADABS program (transmission 0.73–0.93). Note that the Cambridge Structural Database¹² has no information on benzobistriazoles and benzotristriazoles.

2,6-Di[(2,4-dinitrophenyl)hydrazono]cyclohex-4-ene-1,3-dione 1,3-dioxime (3). 2,4-Dinitrophenylhydrazone (3.96 g, 0.02 mol) was added to a solution of dinitrosoresorcinol **2** (1.68 g, 0.01 mol) in methanol (300 mL) and a flow of dry HCl was passed through the mixture with stirring at room temperature, then the mixture was kept at room temperature for 8 h. A precipitate was filtered off, washed with methanol, dried. The yield was 5.0 g (94%), compound **3** turns color to black at 270 °C and does not melt to 360 °C (*cf.* Ref. 5: m.p. 266 °C). Found (%): C, 40.80; H, 2.18; N, 26.42. C₁₈H₁₂N₁₀O₁₀. Calculated (%): C, 40.92; H, 2.29; N, 26.51.

2,7-Dihydro-2,7-bis(2,4-dinitrophenyl)benzo[1,2-d:3,4-d']bistriazole 1,6-dioxide (4). Manganese dioxide (20 g) was added to a solution of compound 3 (3.80 g, 0.00715 mol) in acetone (1 L) and the mixture was stirred for 24 h at 40–50 °C. A precipitate was filtered off, placed into the Soxhlet extractor and extracted with hot acetone. Acetone was evaporated, the residue was suspended in hexane, and a precipitate was filtered off. The yield of bistriazole 4 was 2.38 g (61%), m.p. 167-169 °C (decomp., ethanol). Found (%): C, 41.32; H, 1.73; N, 26.24. C₁₈H₈N₁₀O₁₀. Calculated (%): C, 41.22; H, 1.53; N, 26.72. UV, λ_{max}/nm (lg ϵ): 272 (3.30); 330 (3.15). ¹H NMR (DMSO-d₆), δ: 7.80-7.95 (m, 2 H, CH); 8.30-8.40 (m, 2 H, CH); 9.80-9.95 (m, 2 H, CH); 9.02 (d, 1 H, J = 2.0 Hz); 9.03 (d, 1 H, J = 2.0 Hz). ¹³C NMR (DMSO-d₆), δ: 116.87, 119.84, 121.34, 129.70, 131.45 (all CH); 114.87, 123.31, 129.16, 129.37, 131.37, 143.06, 143.50, 143.66, 148.69, 148.76 (all C). MS, m/z (I_{rel} (%)): 524 [M]⁺ (40); 299 (10); 195 (20).

1,6-Dihydro-1,6-dihydroxybenzo[1,2-*d*:3,4-*d*']bistriazole (5). The compound MeONa (13.5 g, 0.25 mmol) was added to

a suspension of benzobistriazole **4** (20 g, 0.038 mol) in methanol (500 mL), and the mixture was stirred for 6 h at 35–40 °C, followed by evaporation to dryness. Chloroform (300 mL) was added to the residue, a precipitate formed was filtered off, thoroughly washed with chloroform, and dried. A precipitate was dissolved in water (200 mL), acidified with 10% aqueous HCI to pH 5. A precipitate formed was filtered off, washed with water, and dried to obtain compound **5** (4.50 g, 61.4%), m.p. 250 °C (decomp., ethanol). Found (%): C, 37.20; H, 2.08; N, 42.92. C₆H₄N₆O₂. Calculated (%): C, 37.50; H, 2.10; N, 43.74. UV, λ_{max}/mm (lg ε): 230 (4.08). ¹H NMR (DMSO-d₆), δ : 7.61 (d, 1 H, J = 10.0 Hz); 7.99 (d, 1 H, J = 10.0 Hz); 11.70 (br.s, 2 H, OH). ¹³C NMR (DMSO-d₆), δ : 107.89, 119.75 (all CH); 119.27, 127.80, 128.99, 141.58 (all C). MS, m/z (I_{rel} (%)): 164 [M – 28]⁺ (3.6).

1,6-Dihydro-1,6-dimethoxybenzo[1,2-d:3,4-d´]bistriazole (6). A. Finely powdered calcined potash (1.4 g, 0.01 mol) and methyl iodide (1.4 g, 0.01 mol) were added to a solution of compound 5 (0.3 g, 0.0016 mol) in anhydrous acetonitrile with stirring. The mixture was stirred for 24 h at 25-30 °C. A precipitate formed was filtered off, the solvent was evaporated in vacuo of a water-jet pump, the residue was subjected to chromatography on SiO₂, using chloroform as an eluent, to isolate compound 6 (0.25 g, 54%), m.p. 166-168 °C (ethyl acetate). Found (%): C, 43.46; H, 3.68; N, 38.27. C₈H₈N₆O₂. Calculated (%): C, 43.63; H, 3.64; N, 38.18. UV, λ_{max}/nm (lg ε): 230 (4.60), 283 (3.05). ¹H NMR (DMSO-d₆), δ: 4.46 (s, 3 H, OCH₃); 4.53 (s, 3 H, OCH_3 ; 7.85 (d, 1 H, J = 9.0 Hz); 8.19 (d, 1 H, J = 9.0 Hz). 13 C NMR (DMSO-d₆), δ : 68.35 (OCH₃); 69.03 (OCH₃); 107.97, 120.84 (all CH), 117.82, 126.98, 128.18, 141.53 (all C). MS, m/z $(I_{rel} (\%))$: 220 [M]⁺ (17), 192 (70), 164 (17), 161 (10), 118(62), 103(69). HRMS: found m/z = 220.0707; C₈H₈N₆O₂; calculated, M = 220.0703.

B. Dimethyl sulfate (2 g, 0.0158 mol) was added to a solution of compound **5** (0.3 g, 0.0016 mol) in 10% aq. NaOH (10 mL), the mixture was stirred at room temperature for 12 h, diluted with water (10 mL), and extracted with ethyl acetate (3×15 mL). A combined ethyl acetate extract was washed with saturated aq. NaCl (2×20 mL) and dried with MgSO₄. The solvent was evaporated *in vacuo* of a water-jet pump, the residue was subjected to chromatography on SiO₂, using chloroform as an eluent to isolate compound **6** (0.21 g, 61%).

4- and 5-Nitro-2,7-dihydro-2,7-bis(2,4-dinitrophenyl)benzo-[1,2-d:3,4-d']bistriazole 1,6-dioxide (7a,b). Compound 3 (11.6 g, 0.025 mol) was added in portions to 70% ag. nitric acid (100 mL) with stirring, the mixture was stirred for 2 h at room temperature, then was heated to boiling, the reflux was continued for 30 min, and the mixture was allowed to stand for 16 h. A precipitate formed was filtered off, washed with nitric acid, water, and dried to obtain a mixture of bistriazoles 7a,b (6.12 g, 43%), m.p. 316 °C (decomp., 70% HNO₃). Found (%): C, 37.62; H, 1.38; N, 27.16. C₁₈H₇N₁₁O₁₂. Calculated (%): C, 37.96; H, 1.23; N, 27.07. ¹H NMR (DMSO-d₆), δ: 8.38-8.40 (m, 2 H, CH); 8.85-8.98 (m, 2 H, CH); 9.02-9.09 (m, 2 H, CH); 9.00 (br.s, 1 H, CH). ¹³C NMR (H₂SO₄), δ : 117.58, 122.31, 130.70, 132.83 (all CH); 120.37; 125.99; 128.21; 128.54; 129.86; 135.39; 139.02; 143.06; 143.14; 149.74; 149.94 (all C). MS, *m/z* (*I*_{rel} (%)): 569 [M]⁺ (18); 195 (20).

4- and 5-Nitro-1,6-dihydro-1,6-dihydroxybenzo[1,2-d:3,4-d']bistriazole (8a,b) was obtained according to the procedure similar to that for the synthesis of compound 5. The yield was 50.4%, m.p. 220 °C (decomp. from ethanol). Found (%): C, 30.20; H, 2.08; N, 41.66. $C_6H_3N_7O_4$. Calculated (%): C, 30.39; H, 1.28; N, 41.35. UV, λ_{max}/nm (lg ε): 270 (4.00); 340 (3.90). ¹H NMR (DMSO-d₆), δ : 8.34 (**8b**: s, 1 H, CH); 8.36 (**8a**: s, 1 H, CH); 10.4 (br.s, 2 H, OH). ¹³C NMR (DMSO-d₆), δ : 107.76 (CH); 120.70, 125.70, 130.69, 133.95, 137.72. MS, m/z (I_{rel} (%)): 237 [M]⁺ (41).

2,4,6-Trinitrosobenzene-1,3,5-triol (10). Acetic acid (0.5 mL) was added to a solution of phloroglucinol dihydrate **9** (8.1 g, 0.05 mol) in methanol (80 mL). The mixture was cooled to 0 °C, followed by a dropwise addition of isopropyl nitrite (21.6 mL, 0.208 mol) with stirring and keeping the temperature in the mass around 0–3 °C. The addition time was ~1.5 h. The mixture was stirred for 0.5 h at 0 °C and another 0.5 h at room temperature. The solvent was evaporated *in vacuo* of a water-jet pump, keeping the temperature of the water bath below 35 °C. The residue was suspended in diethyl ether, a precipitate was filtered off, washed with some diethyl ether, and dried to obtain compound **10** · H₂O (11.0 g, 95%), m.p. 126 °C (decomp., ethanol). Found (%): C, 31.20; H, 2.08; N, 18.32. C₆H₃N₃O₆·H₂O. Calculated (%): C, 31.17; H, 2.16; N, 18.18. UV, λ_{max}/nm (lg ε): 243 (4.13), 290 (4.29). ¹³C NMR (DMSO-d₆), δ : 147.59, 172.48.

2,4,6-Tris[(2,4-dinitrophenyl)hydrazono]cyclohexane-1,3,5trione 1,3,5-trioxime (11) was obtained according to the procedure similar to that for the synthesis of compound 3. The yield of compound 11 was 93%, dark red crystalline compound, m.p. > 360 °C, insoluble in water, ethanol, moderately soluble in acetone. Found (%): C, 38.20; H, 2.08; N, 27.42. $C_{24}H_{15}N_{15}O_{15}$. Calculated (%): C, 38.25; H, 1.99; N, 27.89.

5,8-Dihydro-2,5,8-tris(2,4-dinitrophenyl)-2*H*-benzo[**1**,2*d*:**3,4-***d*':**5,6-***d*"]tris[**1,2,3**]triazole **1,4,7-trioxide (12)**. *A*. Benzotristriazole **12** (35%) was obtained from compound **11** according to the procedure similar to that for compound **4**, m.p. > 360 °C (70% HNO₃). Found (%): C, 38.20; H, 1.08; N, 27.82. $C_{24}H_9N_{15}O_{15}$. Calculated (%): C, 38.55; H, 1.20; N, 28.11. ¹H NMR (H₂SO₄), δ : 7.75–7.95 (br.s, 3 H, CH); 8.40–8.60 (br.s, 3 H, CH); 8.75–8.94 (br.s, 3 H, CH). ¹³C NMR (H₂SO₄), δ : 122.15, 130.54, 132.45 (all CH); 118.84, 128.30, 130.33, 143.10, 149.53 (all C).

B. Compound **11** (20 g, 0.0268 mol) was added in portions to 70% aq. nitric acid (300 mL) and the mixture of was stirred at room temperature for 3 h. Then, the reaction mass gradually was heated to boiling and refluxed until a homogeneous solution was formed. After cooling, a precipitate formed was filtered off, washed with water and ethanol, and dried to obtain benzotristriazole **12** (9 g, 45%).

4,7-Dihydro-1,4,7-trihydroxy-1*H***-benzo[1,2-***d***:3,4-***d***':5,6-***d"***]tris[1,2,3]triazole (13)** was obtained according to the procedure similar to that for the synthesis of compound **5**. The yield of compound **13** was 54.5%, m.p. 230 °C (decomp.). Found (%): C, 23.88; H, 2.56; N, 42.00. $C_6H_3N_9O_3 \cdot 3H_2O$. Calculated (%): C, 23.76; H, 2.97; N, 41.58. ¹³C NMR (H₂SO₄), δ : 129.00, 123.52. MS, *m/z* (I_{rel} (%)): 249 [M]⁺ (5.3).

4,7-Dihydro-1,4,7-trimethoxy-1*H***-benzo**[**1,2**-*d***:3,4**-*d***':5,6**-*d*"]tris[**1,2,3**]triazole (14). Finely powdered calcined $K_2CO_3(1.5 \text{ g})$ and methyl iodide (6.84 g, 0.048 mol) were added to a suspension of compound **13** (0.30 g, 0.00103 mmol) in DMF (15 mL) and the mixture was stirred at room temperature for 12 h. The solvent was evaporated *in vacuo*, the residue was diluted with water (30 mL), a precipitate was filtered off, washed with water, and dried. Purification was made by chromatography on SiO₂, using ethyl acetate—hexane (1 : 1) as an eluent to obtain compound **14** (0.22 g, 76%), m.p. 231–232 °C (from ethyl acetate).

Found (%): C, 37.17; H, 3.03; N, 43.43. C₉H₉N₉O₃. Calculated (%): C, 37.11; H, 3.09; N, 43.30. UV, λ_{max}/nm (lg ε): 230 (4.69). ¹H NMR (DMSO-d₆), δ : 4.57 (s, 9 H, 3 OCH₃). ¹³C NMR (DMSO-d₆), δ : 69.30 (OCH₃); 119.65, 128.41. MS, *m/z* (*I*_{rel} (%)): 291 [M]⁺ (32), 263 (25), 146 (72), 130 (31), 119 (32), 114 (100). MS: found *m/z* = 291.0820. C₉H₉N₉O₃; calculated, M = 291.0823.

2,4,6-Tridiazocyclohexane-1,3,5-trione (15). Hydrazine hydrate (2.5 mL, 0.05 mol) was added to a solution of trinitrosophloroglucinol **10** (2.31 g, 0.01 mol) in acetic acid (100 mL). After the exothermic the reaction reached completion, the reaction mass was refluxed for 20 min. A precipitate was filtered off and discarded. The filtrate was concentrated, the residue was subjected to chromatography on SiO₂, using ethyl acetate as an eluent to obtain compound **15** (0.42 g, 20.5%), m.p. 228–229 °C (decomp., ethyl acetate; *cf.* Ref. 20: m.p. 220 °C (benzene)). Found (%): C, 35.60; N, 41.44. C₆N₆O₃. Calculated (%): C, 35.29; N, 41.18. IR (KBr), v/cm⁻¹: 1620 (C=O); 2150 (C=N=N). UV, λ_{max}/nm (lg ε): 255 (4.58). ¹³C NMR (H₂SO₄), δ : 85.64 (C=N=N), 169.98 (C=O). MS, *m/z* (*I*_{rel.} (%)): 204 [M]⁺ (100).

Determination of amount of gases during decomposition of 1,6-dihydro-1,6-dihydroxybenzo[1,2-d:3,4-d']bistriazole (5). Compound 5 (1.0 g) was placed in a 0.5-L autoclave, which was capped and heated at 250 °C for 10 min using the Wood's alloy. After cooling to room temperature, a connecting pipe was used to collects the liberated gas in a turned upside down and filled with water graduated cylinder. It was found that 700 mL of the gas was liberated.

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