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A rational method of synthesis and chemical properties of 5-(4-aminofurazan-3-yl)-1-hydroxytetrazole

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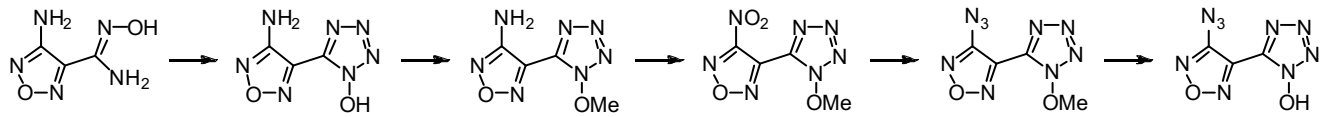


A practical and scalable scheme for the synthesis of 5-(4-aminofurazan-3-yl)-1-hydroxytetrazole was developed, starting from 4-aminofurazan-3-carboxylic acid amidoxime. New methods were proposed for the synthesis of 1-hydroxy-5-(4-nitrofurazan-3-yl)-tetrazole and 5-(4-azidofurazan-3-yl)-1-hydroxytetrazole.

Keywords: aminofurazan, azidofurazan, 1-hydroxytetrazole, nitrofurazan, 1,2,5-oxadiazole.

The chemistry of energetic compounds has shown a trend toward the inclusion of heteroaromatic polynitrogen motifs in their structures.[1] Heterocyclic systems of this type are characterized by positive enthalpies of formation; during their explosive decomposition energy is liberated not only through oxidation of carbon atoms, but also by energetically favorable rearrangement of chemically bonded nitrogen atoms of heterocycle into highly stable nitrogen molecules.[2–9] Another feature of nitrogen heterocycles is the possibility of improving the oxygen balance of energetic compound derived from them by forming *N*-oxides.[10] The introduction of an *N*-oxide group usually increases the density of energetic compounds, as well as in many cases helps to improve their stability.[11]

The values given in Figure 1 for enthalpies of formation (in gas phase) of some azoles[12] illustrate the benefits from introduction of tetrazole and furazan (1,2,5-oxadiazole) rings in the structures of energetic compounds. These types of applications have substantially contributed to the progress in the chemistry of both tetrazoles[13–16] and furazans.[17,18]

The concept of combining furazan and hydroxytetrazole rings in the structures of energetic compounds[12,19–23] has been used for the synthesis of compounds with structures shown in Figure 2. For practical purposes, the preferred compounds were salts of compounds **1**–**5** with nitrogen-containing bases (ammonia, hydroxylamine, hydrazine, guanidine, and others). Some of the obtained salts were characterized by high thermal stability, decreased sensitivity to mechanical stimuli, and calculated detonation velocity similar to RDX.

During the current study, we developed a rational method for the synthesis and studied the reactivity of 5-(4-aminofurazan-3-yl)-1-hydroxytetrazole (**1**).

It should be noted that prior to the publications on energetic properties of dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate (TKX-50, Fig. 3)[24–26] the derivatives of 1-hydroxytetrazole were not thoroughly investigated.[27–29] For example, in the series of oxadiazole derivatives, besides compound **1** studied in this work,[30,31] also the syntheses of compounds combining the structural features of 1-hydroxytetrazole heterocyclic system with 1,2,4-oxadiazole,[32] 1,3,4-oxadiazole,[33] as well as furazan and furoxan rings were considered.[21,22]

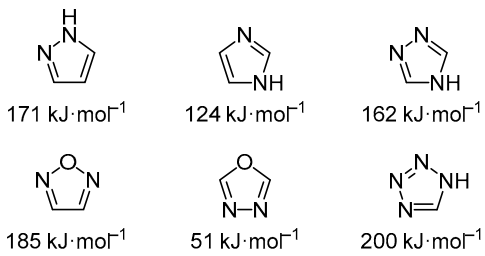


Figure 1. The enthalpies of formation for azoles in gas phase.

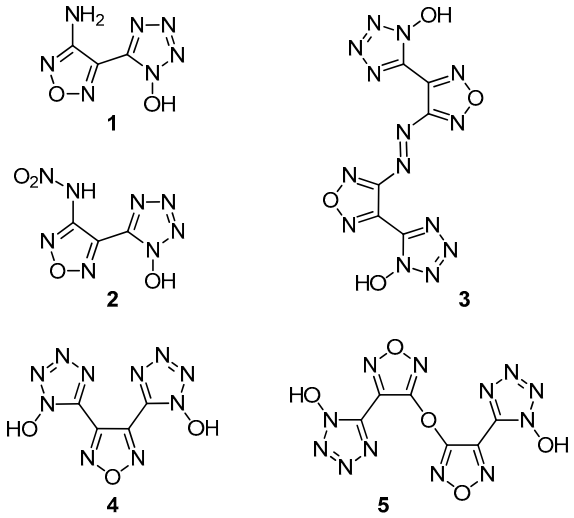


Figure 2. The currently known energetic derivatives of 1-hydroxy-5-(4-R-furazan-3-yl)tetrazole.

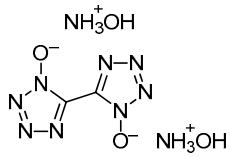
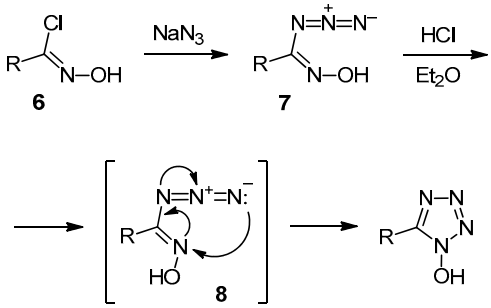
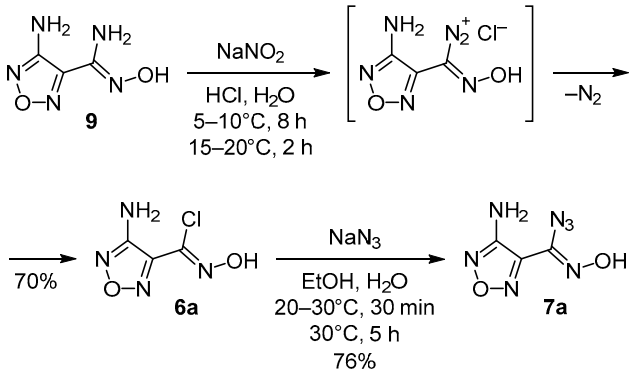


Figure 3. Dihydroxylammonium 5,5'-bistetrazole-1,1'-diolate (TKX-50).

Scheme 1



Scheme 2



The general method for the synthesis of 5-R-substituted 1-hydroxytetrazole derivatives is based on intramolecular cyclization of carboxazidoximes **7**.[30,34,35] The required azidoximes **7** were obtained by nucleophilic substitution of halide in the appropriate halooximes **6** with an azide group *via* reaction with sodium azide.[30,31] Anhydrous hydrogen chloride solution in diethyl ether was used to induce the isomerization of the stable (*Z*)-form of oxime **7** to the labile (*E*)-form **8**, which underwent a spontaneous intramolecular cyclization reaction of azide and oxime groups that produced a 1-hydroxytetrazole ring (Scheme 1).

The synthesis of hydroxytetrazole **1** was first accomplished by Andrianov and coworkers in 1992.[31] In subsequent studies, compound **1** was obtained according to an analogous procedure (for example, in reports[20,34]). The synthesis was laborious, unsafe, and thus unsuitable for further scale-up. For this reason, we started our study from improving the known scheme for the synthesis of compound **1**, including the preparation of chloroxime **6a**, reaction with sodium azide (Scheme 2), and isomerization of azidoxime **7a**.

The preparation of chloroxime **6a** was based on the diazotation of amidoxime **9** in dilute hydrochloric acid with $NaNO_2$ solution at 0–5°C temperature.[36–38] The yield of compound **6a** was 53–59%, the solvent ratio (mass ratio of solvents used in the reaction and the starting material) was in the range from 17 to 24. It has been reported[39] that the solvent ratio can be decreased to 10.8, while the yield of crude product (mp 192–194°C) reached 76%. The possibility of increasing the yield of chloroxime **6a** to 80% has also been described, by further minimizing the use of hydrochloric acid.[40] Our experiments with hundreds of grams of compound **9** showed that performing the reaction in concentrated hydrochloric acid allowed to reduce the solvent ratio to 3. In this case, the yield of crude chloroxime **6a** was 65–70% (mp 195–198°C, Scheme 2). The crude product after filtration and washing with water contained 20–25% of moisture and could be used in the next step of synthesis without drying. The moisture content in the product was determined as loss of mass upon drying in thermostat at 90–100°C.

The step yielding tetrazole **1** involves the use of a compound that is potentially unsafe in anhydrous state – azidoxime **7a**, which was obtained in 76% yield by a reaction of chloroxime **6a** with sodium azide in a mixture of ethanol and water. The obtained azidoxime **7a** contained 24% of moisture and was used without additional drying.

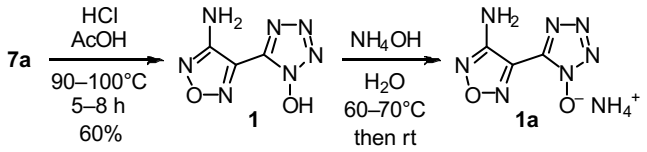
The cyclization of compound **7a** was performed according to a previously published procedure by saturating its suspension in diethyl ether with anhydrous hydrogen chloride.[31,40]

We have shown that the cyclization of azidoxime **7a** can be successfully achieved in a 1:1 (v/v) mixture of acetic acid and concentrated hydrochloric acid at 90–100°C over 5–8 h. The yield of tetrazole **1** after recrystallization from water reached approximately 60%. The treatment of filtrates and mother liquors with aqueous 25% solution of ammonia to pH 8–9 allowed to improve the total yield of tetrazole **1** to 82–85% by precipitating its residual amount as ammonium salt **1a** that was sparingly soluble in water (Scheme 3).

The total yield of hydroxytetrazole **1** reached 40–45%, as calculated from the amidoxime **9**, and was in line with

the previously reported values.[20,31,34] The proposed scheme for the synthesis of hydroxytetrazole **1** substantially improved its synthetic availability for extended exploration of its reactivity.

Scheme 3



Compound **1** had two reactive sites – the hydroxy group of tetrazole ring (A) and the amino group at the furazan ring (B) (Fig. 4). We examined some reactions of hydroxytetrazole **1** that involved these reactive sites.

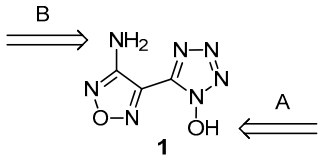


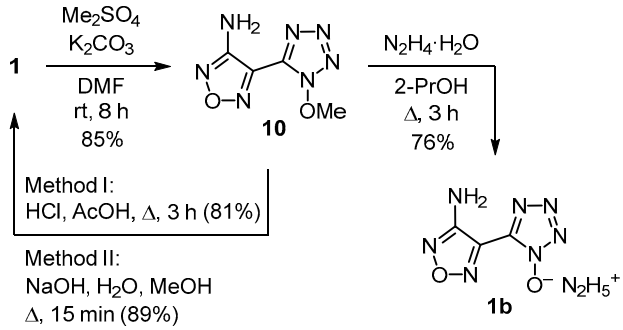
Figure 4. Two reactive sites in the molecule of 5-(4-aminofurazan-3-yl)-1-hydroxytetrazole (**1**).

Reactions of compound 1 involving the hydroxy group. According to the results of potentiometric titration, compound **1** exhibited the properties of a strong OH acid (pK_a 2.45) and produced stable salts, the properties of which have been reported previously.[19,20] The ammonium salt **1a** is poorly soluble in water, which can be used for the isolation and purification of tetrazole **1**.

The study of alkylation reactions involving tetrazole **1** showed that the preparation of 1-alkoxy derivatives is only possible by using such potent alkylating agent as dimethyl sulfate in DMF–K_2CO_3 system (Scheme 4). Performing the reaction with less active alkylating agents ($ClCH_2CONH_2$, MeI, CH_2I_2, $PhCH_2Cl$) in DMF–K_2CO_3 or MeONa–MeOH systems did not produce any alkylation products. It should be noted that the ambident character of 1-hydroxytetrazole anion[41] provides possibilities for alkylation reaction occurring either at the oxygen atom of hydroxy group or the nitrogen atoms of tetrazole ring. According to an earlier work,[42] it is important to take into account that alkylation of amino group at the furazan ring is also possible under the conditions of phase-transfer catalysis. NMR spectra of the product obtained by alkylation of compound **1** with dimethyl sulfate in DMF–K_2CO_3 system unequivocally pointed to the exclusive formation of *O*-alkylation product **10** in 85% yield.

The investigation of chemical properties of compound **10** showed low stability of the methoxy group toward hydrolysis, as it could be cleaved both in acidic and basic media. Thus, refluxing a solution of compound **10** in acetic acid in the presence of hydrochloric acid was accompanied by the regeneration of a hydroxy group. The reaction of compound **10** with aqueous alkali and hydrazine proceeded analogously (Scheme 4).

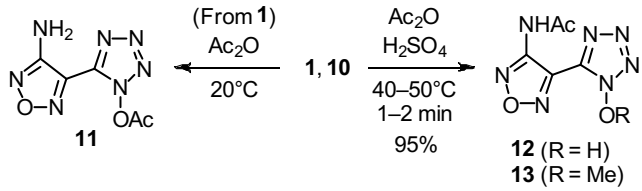
Scheme 4



The reactions of compound 1 and methoxy derivative 10 involving the amino group. *N*-Acylation and *N*-nitration, as well as the oxidation to nitro or azo groups represent typical reactions for an amino group linked to a furazan ring.[17,18,43]

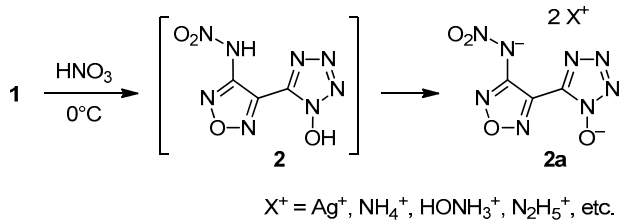
It has been reported earlier[30] that acylation of compound **1** with acetic anhydride without the addition of a catalyst occurs at the hydroxy group of tetrazole ring, leading to the formation of compound **11**. We have found that the acylation of tetrazole **1**, as well as its *O*-methyl derivative **10** with acetic anhydride in the presence of catalytic amounts of sulfuric acid or sodium acetate led to the *N*-acylation products **12** and **13** in 95% yields (Scheme 5).

Scheme 5



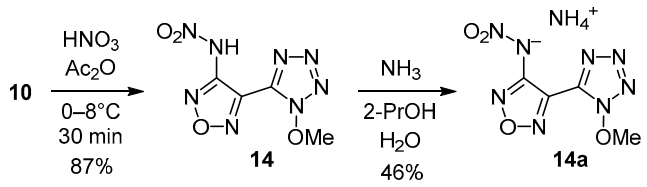
The nitration of tetrazole **1** with 100% HNO_3 was used for the preparation of nitramine **2**[12] (stable only in the form of a solution), isolated as salts **2a** with cations of silver, ammonium, hydroxylammonium, hydrazonium, and guanidinium derivatives (Scheme 6).

Scheme 6



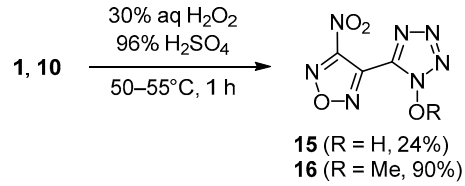
For the nitration of compound **10** we used a system of HNO_3–Ac_2O. Nitramine **14** precipitated when the nitration mixture was poured onto ice, but decomposed during an attempted recrystallization from organic solvents and was isolated as ammonium salt **14a** (Scheme 7).

Scheme 7



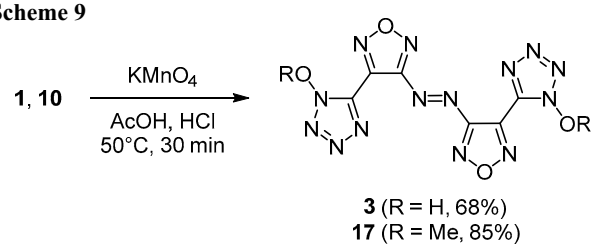
According to literature data, the oxidation of aminofurazans to nitrofurazans can be performed with two-electron oxidants based on peroxide oxygen.[44] The oxidation of compounds **1** and **10** to the respective nitro derivatives was successfully performed by us in a 30% H_2O_2 – 96% H_2SO_4 system under the conditions that were previously used for the synthesis of 4-(5-methyl-1,2,4-oxadiazol-3-yl)-3-nitrofurazan[45] (Scheme 8). The isolation of 1-hydroxy-5-(4-nitrofurazan-3-yl)tetrazole (**15**) from the reaction mixture was quite difficult due to its high solubility in the oxidizing mixture and water, as well as its low affinity for organic solvents. The procedure for isolation of compound **15** included a partial neutralization of the reaction medium with crystalline sodium orthophosphate, followed by multiple extractions of the obtained solution with ethyl acetate. On the other hand, the procedure for the isolation of 1-methoxy-5-(4-nitrofurazan-3-yl)tetrazole (**16**) from the reaction mixture was simple and effective. Product **16** precipitated as a heavy oil upon diluting the reaction mixture with water, and could be separated from the aqueous phase by extraction with dichloromethane. The yield of compound **16** reached 90%.

Scheme 8



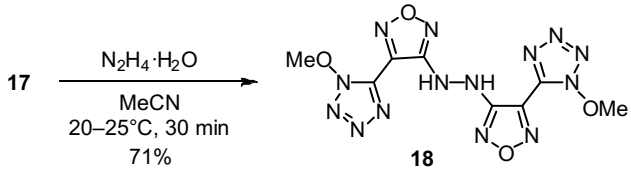
The oxidation of aminofurazans **1** and **10** with potassium permanganate in acidic medium was accompanied by oxidative dimerization of amino groups to an azo group (Scheme 9), which is characteristic for furazans.[43,46–48] The synthesis of 3,3'-bis(1-hydroxytetrazol-5-yl)-4,4'-azofurazan (**3**) has been described before.[12] Compound **3** is stable only as a solution in diethyl ether and was isolated as diammonium salt. On the other hand, performing an analogous oxidation reaction with methoxytetrazole **10** showed that the obtained oxidation product – 3,3'-bis(1-methoxytetrazol-5-yl)-4,4'-azofurazan (**17**) – can be isolated in crystalline form.

Scheme 9



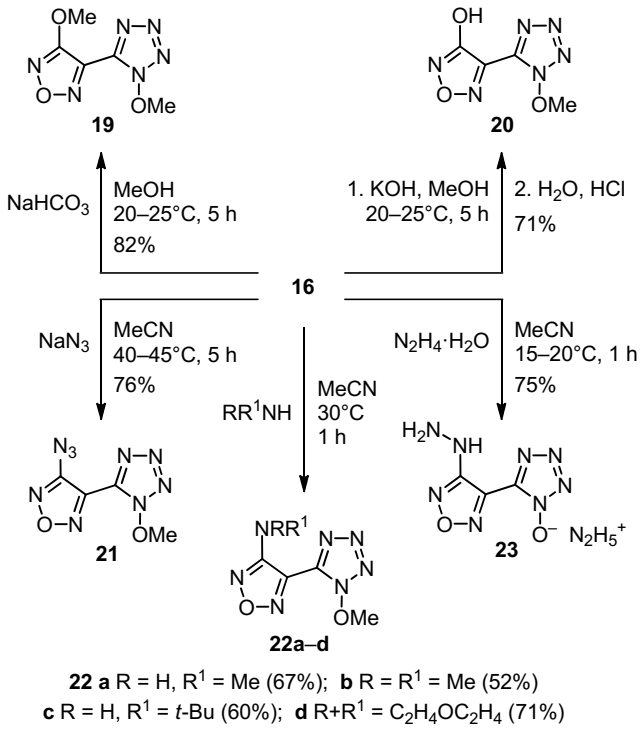
We also noted differences in the chemical properties of compounds **3** and **17** when attempting to obtain their salts. Thus, the treatment of compound **3** in diethyl ether solution with hydrazine or hydroxylamine was accompanied by vigorous evolution of gas and destruction of the starting compound molecule, while acetonitrile solution of dimethoxy derivative **17** reacted with hydrazine differently, resulting in the reduction of azo group and formation of the symmetrical 1,2-di(furazanyl)hydrazine **18** in 71% yield (Scheme 10).

Scheme 10



The availability of nitro derivative **16** enabled us to use it as a precursor for the synthesis of a series of 1-hydroxy-5-(4-R-furazan-3-yl)tetrazole derivatives. For example, the nitro group of compound **16** underwent substitution reactions with *N*- and *O*-nucleophiles, analogously to other nitrofurazans[49,50] (Scheme 11).

Scheme 11

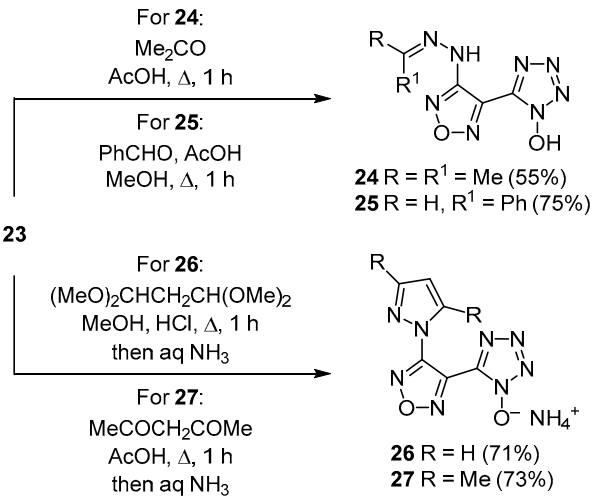


22 a R = H, R^1 = Me (67%); **b** R = R^1 = Me (52%)
c R = H, R^1 = *t*-Bu (60%); **d** R+R^1 = $C_2H_4OC_2H_4$ (71%)

Thus, the substitution of a nitro group with methoxy group was achieved under mild conditions ($NaHCO_3$, MeOH, 20–25°C) (Scheme 11, compound **19**). The use of stronger alkaline reagents (K_2CO_3 or KOH in MeOH) resulted in the formation of hydroxyfurazan **20**. The reaction of compound **16** with NaN_3 in MeCN at 40–45°C led to the formation of azidofurazan **21**. A smooth substitution of nitro group was achieved in reaction with

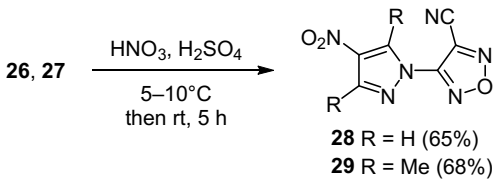
strongly basic amines, leading to the formation of aminofurazans **22a**–**d**. Compound **16** in acetonitrile solution reacted with hydrazine hydrate not only at the nitro group of furazan ring, but also underwent the hydrolysis of methoxy group and formed the respective hydrazinium salt of hydrazinofurazan **23**. Salt **23** was weakly soluble in acetonitrile and precipitated from the reaction mixture. The high aqueous solubility and low affinity for organic solvents did not allow us to isolate free 5-(4-hydrazinofurazan-3-yl)-1-hydroxytetrazole from salt **23**. The presence of a primary hydrazino group in compound **23** was confirmed by condensation reactions with carbonyl and β-dicarbonyl compounds (formation of the respective hydrazones **24**, **25** and pyrazoles **26**, **27**, Scheme 12). Since compound **23** is a hydrazinium salt, the side reactions of carbonyl compounds with hydrazinium cation also produced the respective *N*-unsubstituted hydrazones and pyrazole derivatives. These impurities could be separated by exploiting their better solubility in organic solvents during the recrystallization of the obtained products. Pyrazoles **26** and **27** were isolated as ammonium salts.

Scheme 12



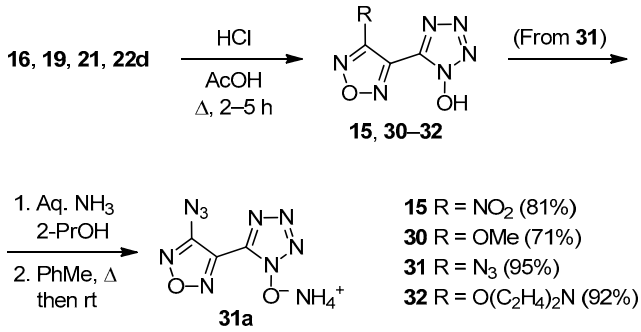
The nitration of pyrazoles **26** and **27** in a system of concd HNO_3 (*d* 1.5) – concd H_2SO_4 (*d* 1.84) at 5–10°C proceeded quite unusually. The nitration of pyrazole ring under these conditions was accompanied by the destruction of 1-hydroxytetrazole ring, leading to the formation of a nitrile group (Scheme 13).

Scheme 13



The aforementioned hydrolytic susceptibility of methoxy group in the tetrazole ring allowed us to consider it as a protecting group during the synthesis of the respective hydroxytetrazoles. The potential of this approach is illustrated in Scheme 14. The methoxy group can be removed by refluxing solutions of methoxytetrazoles **16**, **19**, **21**, **22d** for 2–5 h in a 1:1 (v/v) mixture of AcOH and concd HCl.

Scheme 14



The oily nitrofurazan **15** obtained from hydrolysis of the methoxy derivative **16** contained 15–20% of impurities according to HPLC analysis and NMR spectral data. The crystalline ammonium salt of this compound was obtained in 65% yield by exchange reaction with ammonium acetate in acetic acid. The treatment of nitrofurazan **15** with aqueous ammonia or ammonium bicarbonate was accompanied by substitution of nitro group with amino group and was not applicable for the preparation of its ammonium salt. The azido derivative **31** was a strong OH acid (pK_a 2.07) and could be isolated in pure form or converted into the stable ammonium salt **31a**.

The structures of the synthesized compounds were proved by the methods of IR and ^{1}H, ^{13}C NMR spectroscopy, data of elemental analysis, and high-resolution mass spectrometry. The assignment of carbon atom signals in the furazan ring was performed while taking into account the literature data.[51] Azido derivative **31** was also characterized by ^{15}N NMR spectrum (Fig. 5). The assignment of ^{15}N NMR signals was based on comparison with the data[12,20,52] for analogous structures: 422.0 (N-5); 388.1 (N-3); 365.5 (N-6); 360.0 (N-2); 331.0 (N-4); 269.7 (N-1); 238.3 (N-8); 235.2 (N-9); 80.0 (N-7) (atom numbering according to Fig. 6).

Several of the obtained compounds could not be characterized by mass spectrometric methods of analysis due to their decomposition during the introduction into the mass spectrometer input device.

Nitro and azido derivatives **15a**, **16**, **21**, **31**, which are of interest as potential high-energy compounds, were characterized by methods of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). According to TGA and DSC data, the ammonium salt of 5-(4-nitrofurazan-3-yl)-1-hydroxytetrazole (**15a**) started losing mass at 160°C, while the maximum of decomposition exotherm was at 175°C. 1-Methoxy-5-(4-nitrofurazan-3-yl)tetrazole (**16**) existed in liquid form and noticeably evaporated already at 120–130°C, while the evaporation of sample was complete at 175°C without decomposition. 5-(4-Azidofurazan-3-yl)-1-methoxytetrazole (**21**) melted at 84°C, the evaporation process was observed above 100°C, with two exotherms of decomposition at 183 and 197°C. 5-(4-Azidofurazan-3-yl)-

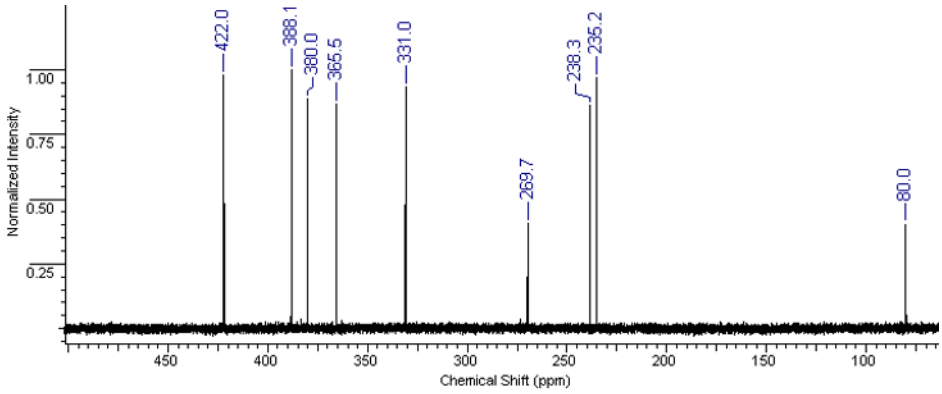


Figure 5. ^{15}N NMR spectrum of compound **31** (DMSO-d_6, the chemical shift values of nitrogen atoms are reported relative to NH_3).

1-hydroxytetrazole monohydrate (**31**) showed loss of mass above 55°C (loss of solvate water), with the exotherm of decomposition observed at 187–188°C. The ammonium salt of 5-(4-azidofurazan-3-yl)-1-hydroxytetrazole (**31a**) underwent vigorous sublimation at 163°C and decomposed explosively at 179°C. The impact sensitivity of compounds **31** and **31a** was at the level of pentaerythritol tetranitrate (PETN), while the friction sensitivity was considerably lower (Table 1).

The crystal structures of 5-(4-azidofurazan-3-yl)-1-hydroxytetrazole (**31**) and its ammonium salt **31a** were unequivocally confirmed by X-ray structural analysis. Suitable monocrystals were grown by slow evaporation of solvent from aqueous solutions of the respective compounds. The molecular structures of compounds **31** and **31a** are shown in Figures 6 and 7.

Both molecules are practically planar: the torsion angles N(1)–C(1)–C(2)–N(5) are equal to –3.25° (compound **31**) and –0.75° (compound **31a**). The bond lengths and valence angles in the furazan ring with localized C=N double bonds are in a good agreement with the data obtained for azidofurazan derivatives[55–58] and have values typical for the respective atoms.[59] Compound **31** contains a solvated water molecule, which forms a crystal lattice with the main molecule *via* hydrogen bonding, forming a packed structure in the (1 0 0) plane. The calculated monocrystal density for compound **31** is equal to 1.760 g·cm^{-3} (100 K). The calculated monocrystal density of compound **31a** is 1.757 g·cm^{-3} (100 K).

Thus, we have developed a safe method for the preparation of 5-(4-aminofurazan-3-yl)-1-hydroxytetrazole on the scale of several hundreds of grams. Based on the reactivity study of 5-(4-aminofurazan-3-yl)-1-hydroxytetrazole and its 1-*O*-methyl derivative, new routes have been proposed for expanding the library of energetic furazanotetrazole derivatives. The synthesis of a series of previously unknown 5-furazanyl-substituted 1-hydroxytetrazole derivatives has been accomplished. The proposed schemes for the synthesis of 1-hydroxy-5-(4-nitrofurazan-3-yl)tetrazole and 5-(4-azidofurazan-3-yl)-1-hydroxytetrazole allow us to consider the obtained compounds not only from the theoretical point of view, but also as physical samples for further practical investigation of their energetic properties.

Table 1. Physicochemical properties of compounds **31** and **31a**

Compound	Beginning of vigorous decomposition, °C	Oxygen balance, %	Sensitivity	
			to impact* %	to friction** kg·cm^{-2}
31	187–188	–36.9	20 ± 4	3600 ± 200
31a	179	–45.3	20 ± 4	2200 ± 200
PETN	140–145	–10.1	20–36	1500

* Drop hammer apparatus K-44-II (apparatus No. 1, weight of 2 kg at 25 cm height), frequency of exposions.[53]
** Drop hammer apparatus K-44-III (lower limit).[54]

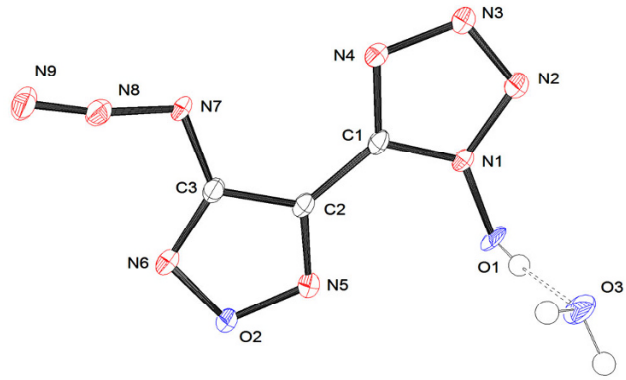


Figure 6. The molecular structure of compound **31** with atoms represented by thermal vibration ellipsoids of 50% probability.

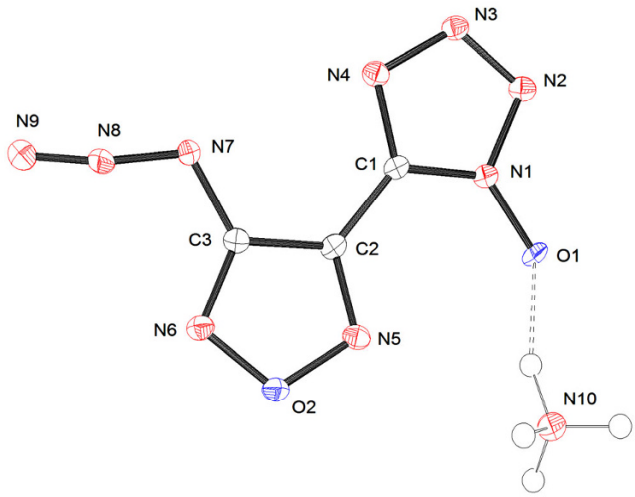


Figure 7. The molecular structure of compound **31a** with atoms represented by thermal vibration ellipsoids of 50% probability.

Experimental

IR spectra were recorded on an FSM-1201 FT-IR spectrometer in KBr pellets. ^{1}H, ^{13}C, and ^{15}N NMR spectra were acquired on a Bruker DRX-400 spectrometer (400, 100, and 40 MHz, respectively) in DMSO-d_6. The chemical shifts of ^{1}H and ^{13}C nuclei were determined relative to the solvent signal (2.51 and 40.0 ppm, respectively), the chemical shifts of ^{15}N nuclei were determined relative to liquid NH_3. Mass spectra were recorded on a Finnigan MAT Incos 50 instrument (EI ionization, 70 eV). High-resolution mass spectra were recorded on a Bruker micrOTOF II instrument using electrospray ionization. Elemental analysis was performed on a PerkinElmer 2400 elemental analyzer. Calorimetric analyses were performed in aluminum crucibles on a Netzsch TG 209 F1 instrument under argon flow (100 ml/min) at the heating rate of 5 K/min. Melting points were determined in a capillary. The dissociation constants for compounds **1** and **31** were determined in aqueous solutions by potentiometric titration method with 0.1 N NaOH solution. The reaction progress and purity of the obtained compounds were controlled by HPLC method on a Shimadzu 20 chromatograph with a diode matrix detector. The analytical conditions: Phenomenex Luna 5 μm C18(2) 250 × 4.6 mm column, MeOH–H_2O–CF_3COOH (74.95:24.95:0.10) mobile phase, thermostat and detector temperature set at 40°C. The UV wavelengths of 209, 230, and 254 nm were used for detection.

The synthesis of compound **9** was performed according to a published procedure.[60]

4-Amino-*N*-hydroxyfurazan-3-carboximidoyl chloride (6a). Amidoxime **9** (350 g, 2.45 mol) was added with vigorous stirring to 38% HCl (1 l, 452 g of HCl, 12.40 mol), while maintaining the temperature of mixture at or below 20°C by external cooling with water bath. The reaction mixture was then cooled to 5–10°C and treated at this temperature by dropwise addition of saturated aqueous $NaNO_2$ solution (169 g, 2.45 mol) over 8 h. After completing the addition of $NaNO_2$, the reaction mixture was maintained at 15–20°C for 2 h, the precipitate that formed was filtered off and washed on filter with cold water (250–300 ml). The yield of crude compound **6a** with 20–25% moisture was 259–279 g (65–70% yield calculated for dry product), mp 195–198°C. This product was used without additional purification for the preparation of azide **7a**. Analytically pure sample of compound **6a** was obtained by recrystallization from 1:1 mixture of AcOH–H_2O, mp 204–205°C (decomp.) (mp 203–206°C (decomp., Et_2O – petroleum ether),[30] mp 197–212°C (decomp., DSC)[61]). IR spectrum, ν, cm^{-1}: 3460; 3338; 3250; 1640; 1628 1532; 1435; 1332; 1301; 1040; 1010; 945; 915; 868; 739; 718; 438. ^{13}C NMR spectrum, δ, ppm: 154.0; 141.9; 126.5.

4-Amino-*N*-hydroxyfurazan-3-carboximidoylazide (7a). Compound **6a** from the previous step (crude mass 195 g including 20% moisture content, dry mass 162.5 g, 1 mol of anhydrous product) was added to EtOH (300 ml) with vigorous stirring, followed by the addition of H_2O (100 ml). The obtained suspenion was maintained at 20–30°C by external cooling with water bath and treated by adding 10–20-g portions of sodium azide over 30 min (for the total amount of 80 g, 1.23 mol). After the end of exothermic effect, the mixture was stirred for 5 h at 30°C and diluted with water (1 l). The precipitate was filtered off, washed with water, and pressed on filter. Azide **7a** was obtained in 159 g (76%) yield with 24% of moisture and was used without additional drying in the synthesis of compound **1**. An analytically pure sample of compound **7a** was obtained by recrystallization of wet product from 1:2 mixture of AcOH–H_2O, mp 176–177°C (mp 170–171°C[30], mp 177–178°C[31]). IR spectrum, ν, cm^{-1}: 3451, 3339, 2155, 2096, 1630, 1593, 1538, 1419, 1356, 1252, 1029, 959, 910, 858, 692, 561, 439. (IR spectrum (thin film), ν, cm^{-1}: 3461 and 3322 (NH_2), 3248 (OH), 2169 (N_3), 986 (furazan).[31]) ^{1}H NMR spectrum, δ, ppm: 12.57 (1H, s, OH); 6.24 (2H, s, NH_2). (^{1}H NMR spectrum (acetone-d_6), δ, ppm: 11.30 (1H, s, OH); 5.75 (2H, s, NH_2).[30]) ^{13}C NMR spectrum, δ, ppm: 154.9; 140.1; 135.7. Found, *m*/*z*: 192.0247 $[M+Na]^+$. $C_3H_3N_7NaO_2$. Calculated, *m*/*z*: 192.0240.

5-(4-Aminofurazan-3-yl)-1-hydroxytetrazole (1) and its ammonium salt 1a. Wet azidoxime **7a** (150 g, 0.71 mol, 20% water content) and concd HCl (200 ml) were added to stirred AcOH (200 ml). The mixture was heated to 90–100°C. The reaction mixture was stirred at this temperature for 5–8 h until complete dissolution of the starting material. The obtained solution was cooled to room temperature, the precipitated product was filtered off, the filtrate was evaporated at reduced pressure to one half of the initial volume. The precipitate that formed was filtered off, combined with the first precipitate, and recrystallized from water. Yield 72 g (60%), agglomerates of fine, irregularly shaped crystals, mp 182–183°C (mp 182–183°C[31]). IR spectrum, ν, cm^{-1}: 3459, 3340, 2548, 1642, 1612, 1538, 1471, 1434, 1393, 1262, 1107, 1049, 989, 907, 860, 714, 448. (IR spectrum (thin film), ν, cm^{-1}: 3463, 3325 (NH_2), 3250 (NH), 1670 (C=N), 999 (furazan).[31]) ^{1}H NMR spectrum, δ, ppm: 6.94 (3H, br. s, OH, NH_2). (^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.36 (2H, s, NH_2); 7.06 (1H, s, OH).[20] ^{1}H NMR spectrum (acetone-d_6), δ, ppm: 6.58 (2H, s, NH_2); 11.20 (1H, s, OH).[30]) ^{13}C NMR spectrum, δ, ppm: 156.0 (C-4'); 138.0 (C-3'); 134.6 (C-5).* (^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 156.1; 138.0; 134.7.[20]) Mass spectrum, *m*/*z* (I_{rel}, %): 169 $[M]^+$ (1), 111 $[M–N_2–NO]^+$ (44), 53 $[HNCCN]^+$ (40), 42 $[CNO]^+$ (15), 30 $[NO]^+$ (100).

An additional amount of tetrazole **1** was isolated as ammonium salt **1a** that was sparingly soluble in water by combining the filtrates, evaporating to dryness at reduced pressure, dissolving the residue in hot water (100 ml, 60–70°C), and adjusting to pH 8 by adding aqueous 25% ammonia solution. The mixture was cooled to room temperature, the precipitate that formed was filtered off and recrystallized from water. The ammonium salt **1a** was obtained as white, fibrous solid (30–35 g, 16–19% yield, mp 266–267°C (decomp.) (mp 257°C (decomp., DSC)[20]). IR spectrum, ν, cm^{-1}: 3455, 3339, 3157, 3058, 2994, 2920, 1861, 1634, 1603, 1478, 1461, 1430, 1397, 1302, 1239, 1148, 1059, 984, 896, 867, 769, 584, 568, 446. ^{1}H NMR

* The furazan ring carbon atoms in ^{13}C NMR spectra are denoted as C-3' and C-4', the tetrazole ring carbon atom – as C-5.

spectrum, δ, ppm: 7.21 (4H, br. s, NH_4^+); 7.08 (2H, s, NH_2). (^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.10 (6H, s, NH_2, NH_4^+).[20]) ^{13}C NMR spectrum, δ, ppm: 156.2 (C-4'); 137.7 (C-3'); 135.0 (C-5). (^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 156.3; 137.9; 135.0.[20]).

5-(4-Aminofurazan-3-yl)-1-methoxytetrazole (10). Tetrazole **1** (169 g, 1.0 mol) and anhydrous K_2CO_3 (207 g, 1.5 mol) were added with vigorous stirring to DMF (300 ml). The reaction mixture was stirred at room temperature until the evolution of CO_2 ceased (approximately 30 min), cooled to 10°C, and treated at this temperature by dropwise addition of Me_2SO_4 (176 g, 1.4 mol). After the addition of Me_2SO_4 was complete, the stirring at room temperature was continued for 8 h. The mixture was then diluted with ice water (1 l), the precipitate that formed was filtered off, washed with cold water (2×500 ml) and recrystallized from MeOH. Yield 155 g (85%), white plates, mp 140–141°C. IR spectrum, ν, cm^{-1}: 3453, 3340, 2956, 2920, 2853, 1642, 1615, 1468, 1451, 1427, 1269, 1094, 1034, 987, 951, 867, 559, 480, 419. ^{1}H NMR spectrum, δ, ppm: 6.65 (2H, s, NH_2); 4.40 (3H, s, OCH_3). ^{13}C NMR spectrum, δ, ppm: 156.1 (C-4'); 138.9 (C-3'); 134.2 (C-5); 69.8 (OCH_3). Mass spectrum, *m*/*z* (I_{rel}, %): 184 $[M+1]^+$ (2), 183 $[M]^+$ (22), 153 $[M–NO]^+$ (18), 126 $[M–NHCNO]^+$ (99), 53 $[HNCCN]^+$ (24), 43 $[HN_3]^+$ (100), 30 $[NO]^+$ (64), 15 $[CH_3]^+$ (21). Found, *m*/*z*: 184.0578 $[M+H]^+$, 206.0401 $[M+Na]^+$. $C_4H_6N_7O_2$, $C_4H_5N_7NaO_2$. Calculated, *m*/*z*: 184.0578, 206.0397.

Hydrolysis of 5-(4-aminofurazan-3-yl)-1-methoxytetrazole (10). Method I (hydrolysis in acidic medium). Compound **10** (2.00 g, 11 mmol) was dissolved in AcOH (5 ml), concd HCl (5 ml) was added and the mixture was refluxed for 3 h, cooled to room temperature, the solvents were evaporated at reduced pressure. The residue was recrystallized from water. Yield of compound **1** 1.50 g (81%).

Method II (hydrolysis in alkaline medium). Compound **10** (2.00 g, 11 mmol) was added to a solution of NaOH (0.50 g, 12.5 mmol) in a mixture of H_2O (2 ml) and MeOH (2 ml). The obtained solution was refluxed for 15 min, cooled to room temperature, and acidified with concd HCl to pH 1. The precipitate that formed was filtered off. Yield of compound **1** 1.65 g (89%).

Hydrazinium salt of 5-(4-aminofurazan-3-yl)-1-hydroxytetrazole (1b). Method I. Tetrazole **10** (5.00 g, 27 mmol) was dissolved in 2-PrOH (50 ml) and hydrazine hydrate (2.00 g, 40 mmol) was added. The reaction mixture was refluxed for 3 h; then approximately 20–25 ml of solvent was removed. The residue was cooled to room temperature, the precipitate that formed was filtered off and recrystallized from MeOH. Yield 4.10 g (76%), fine, colorless needle-shaped crystals, mp 213–214°C. IR spectrum, ν, cm^{-1}: 3718, 3697, 3401, 3348, 3166, 2617, 1639, 1625, 1604, 1589, 1566, 1458, 1399, 1303, 1236, 1145, 1092, 980, 932, 888, 862, 771, 681, 590, 572, 495, 454. ^{1}H NMR spectrum, δ, ppm: 7.07 (7H, br. s, NH_2, $N_2H_5^+$). ^{13}C NMR spectrum, δ, ppm: 156.2 (C-4'); 137.7 (C-3'); 135.1 (C-5). Found, %: C 17.71; H 3.68; N 62.31. $C_3H_7N_9O_2$. Calculated, %: C 17.91; H 3.51; N 62.67.

Method II. Tetrazole **1** (1.00 g, 5.9 mmol) was added to 2-PrOH (10 ml). The mixture was neutralized to pH 7 by the addition of hydrazine hydrate (0.30 g, 6.0 mmol), stirred at room temperature for 10 min, the solvent was evaporated at reduced pressure. The residue was recrystallized from MeOH, giving fine, colorless needle-shaped crystals, mp 213–214°C. Yield 1.05 g (89%).

5-[4-(*N*-Acetylamino)furazan-3-yl]-1-hydroxytetrazole (12). Tetrazole **1** (1.00 g, 5.9 mmol) was added at room temperature to stirred Ac_2O (5 ml), then the reaction mixture was treated with concd H_2SO_4 (0.01 g). After the exothermic reaction was complete (1–2 min), the reaction mixture was cooled to room temperature, the precipitate that formed was filtered off, washed with water, and recrystallized from MeOH. Yield 1.18 g (95%), white irregular plates, mp 99–100°C. IR spectrum, ν, cm^{-1}: 3486, 3324, 3287, 1847, 1729, 1690, 1558, 1535, 1359, 1275, 1262, 1239, 1121, 1106, 996, 908, 804, 754, 596, 583. ^{1}H NMR spectrum, δ, ppm: 11.65 (1H, s, NH); 4.53 (1H, br. s, OH); 2.09 (3H, s, CH_3). ^{13}C NMR spectrum, δ, ppm: 169.4 (C=O); 150.5 (C-4'); 138.4 (C-3'); 138.0 (C-5); 23.2 (CH_3). Found, *m*/*z*: 212.0531 $[M+H]^+$, 234.0348 $[M+Na]^+$. $C_5H_6N_7O_3$, $C_5H_5N_7NaO_3$. Calculated, *m*/*z*: 212.0527, 234.0346.

5-[4-(*N*-Acetylamino)furazan-3-yl]-1-methoxytetrazole (13). Methoxytetrazole **10** (1.80 g, 0.01 mol) was added at room temperature to stirred Ac_2O (5 ml), then the reaction mixture was treated with concd H_2SO_4 (0.01 g). After the exothermic reaction was complete (1–2 min), the reaction mixture was cooled to room temperature and the precipitate that formed was filtered off, washed with water, and recrystallized from MeOH. Yield 2.10 g (95%), colorless rhombic crystals, mp 109–110°C. IR spectrum, ν, cm^{-1}: 3450, 3327, 3249, 3025, 2955, 1733, 1561, 1531, 1445, 1354, 1259, 1223, 1113, 1056, 994, 939, 909, 721, 678, 650, 594, 585, 548, 408, 401. ^{1}H NMR spectrum, δ, ppm: 11.50 (1H, s, NH); 4.37 (3H, s, OCH_3); 2.11 (3H, s, $COCH_3$). ^{13}C NMR spectrum, δ, ppm: 169.9 (C=O); 150.6 (C-4'); 138.8 (C-3'); 137.7 (C-5); 70.2 (OCH_3); 23.1 (CH_3). Found, *m*/*z*: 248.0494 $[M+Na]^+$. $C_6H_7N_7NaO_3$. Calculated, *m*/*z*: 248.0502.

1-Methoxy-5-[4-(*N*-nitramino)furazan-3-yl]tetrazole (14) and its ammonium salt (14a). A nitrating mixture was prepared by slow addition of Ac_2O (5 ml) to 95% HNO_3 (5 ml) while cooling to 0–10°C. The nitrating mixture was vigorously stirred and externally cooled with dry ice/acetone bath. Methoxytetrazole **10** (1.0 g, 5.9 mmol) was slowly added, while maintaining the temperature of reaction mixture in the range of 0–8°C. After the addition of the starting material was complete, the mixture was stirred at the same temperature for 30 min and poured into 25 ml of ice water. The precipitate that formed was immediately filtered off, washed with water (2×10 ml), and dried at room temperature. Yield of the crude product 1.1 g (87%), white, amorphous powder, mp 90–97°C (decomp.). According to ^{1}H NMR and HPLC data, the nitration product contained up to 20% of impurities. IR spectrum, ν, cm^{-1}: 3352, 2957, 2919, 2850, 1641, 1509, 1441, 1425, 1295, 1100, 998, 947, 781, 704, 614, 575, 559. ^{1}H NMR spectrum, δ, ppm: 6.80–6.40 (1H, br. s, NH); 4.40 (3H, s, OCH_3). ^{13}C NMR spectrum, δ, ppm: 153.5 (C-4'); 139.4 (C-3'); 137.8 (C-5); 70.6 (OCH_3).

For the purpose of preparing the ammonium salt **14a**, the precipitate of nitramine **14** after filtration and washing with water was transferred into 2-PrOH (10 ml), the obtained suspension was adjusted to pH 8 by adding aqueous 25% ammonia solution, the precipitate that formed was filtered off and recrystallized from 95% EtOH. Yield 0.63 g (46%), light-yellow fine crystalline powder, mp 175–176°C (decomp.). IR spectrum, ν, cm^{-1}: 3175, 1616, 1525, 1385, 1365, 1277, 1116, 996, 930, 878, 824, 773, 597, 500, 430. ^{1}H NMR spectrum, δ, ppm: 7.16 (4H, br. s, NH_4^+); 4.35 (3H, s, OCH_3). ^{13}C NMR spectrum, δ, ppm: 159.2 (C-4'); 139.7 (C-3'); 138.8 (C-5); 70.1 (OCH_3). Found, %: C 19.38; H 3.06; N 51.87. $C_4H_7N_9O_4$. Calculated, %: C 19.60; H 2.88; N 51.42.

1-Hydroxy-5-(4-nitrofurazan-3-yl)tetrazole (15). Method I. Oxidation of 5-(4-aminofurazan-3-yl)-1-hydroxytetrazole (**1**). Oxidizing mixture was prepared from aqueous 30% H_2O_2 solution (32.6 ml, 36.3 g, 0.32 mol) and 96% H_2SO_4 (*d* 1.84 g/ml, 40.0 ml, 73.6 g, 0.72 mol). Tetrazole **1** (13.5 g, 0.08 mol) was added in 2–3-g portions to the oxidizing mixture, while the temperature of the reaction mixture was maintained in the range of 50–55°C. After the addition of compound **1** was complete, the mixture was further stirred at 50–55°C for additional 1 h, then cooled to room temperature and poured into a mixture of ice and water (200 ml). The obtained solution was partially neutralized by adding crystalline $Na_3PO_4 \cdot 12H_2O$ (300.0 g, 0.80 mol) and extracted with EtOAc (5×25 ml). The combined organic extracts were washed with saturated aqueous NaCl solution (2×25 ml) and dried over anhydrous Na_2SO_4. The solution was passed through a layer of alumina (column length 3 cm, diameter 1 cm), the solvent was removed at reduced pressure. The product was dried to constant mass (for approximately 48 h) at room temperature in a vacuum desiccator over P_2O_5. Yield 3.8 g (24%), light-yellow, viscous hygroscopic liquid, soluble in water, $CHCl_3$, EtOH, n_D^{25} 1.511. IR spectrum, ν, cm^{-1}: 2982, 2934, 1574, 1412, 1390, 1339, 1245, 1109, 1005, 926, 904, 825, 806, 534, 502, 466, 455, 439, 420, 401. ^{1}H NMR spectrum, δ, ppm: 9.60 (1H, br. s, OH). ^{13}C NMR spectrum, δ, ppm: 159.6 (br., C-4'); 138.2 (C-3'); 134.6 (C-5). Found, %: C 14.96; H 2.37; N 41.23. $C_3HN_7O_4 \cdot 2H_2O$. Calculated, %: C 15.33; H 2.14; N 41.70.

Method II. Demethylation of 1-methoxy-5-(4-nitrofurazan-3-yl)tetrazole (**16**). Compound **16** (2.13 g, 0.01 mol) was dissolved in AcOH (5 ml), then concd HCl (5 ml) was added and the mixture was heated at reflux for 2 h in a flask with reflux condenser. The mixture was cooled to room temperature, the solvents were evaporated at reduced pressure. Yield 1.60 g (81%), light-yellow, viscous liquid, n_D^{25} 1.513.

Ammonium salt of 1-hydroxy-5-(4-nitrofurazan-3-yl)-tetrazole (15a). Tetrazole **15** (2.0 g, 10 mmol) was dissolved in AcOH (5 ml) and NH_4OAc (1.0 g, 13 mmol) was added. The obtained solution was evaporated at reduced pressure on a rotary evaporator (bath temperature 90–95°C), the residue was dissolved in H_2O (5 ml) and again evaporated at reduced pressure. The addition of water followed by evaporation was repeated twice, the residue was dissolved in refluxing 2-PrOH. The precipitate that formed upon cooling was filtered off, washed with Et_2O (10 ml), and recrystallized from 2-PrOH. Yield 1.4 g (65%), amorphous light-yellow powder, mp 189–191°C (decomp.). IR spectrum, ν, cm^{-1}: 3238, 3052, 2911, 1822, 1607, 1575, 1518, 1478, 1438, 1409, 1341, 1242, 1225, 1119, 1057, 992, 886, 823, 761, 611, 527, 463, 406. ^{1}H NMR spectrum, δ, ppm: 7.18 (1H, br. s, NH_4^+). ^{13}C NMR spectrum, δ, ppm: 156.2 (C-4'); 139.7 (C-3'); 130.7 (C-5). Found, %: C 16.51; H 1.94; N 52.09. $C_3H_4N_8O_4$. Calculated, %: C 16.67; H 1.87; N 51.85.

1-Methoxy-5-(4-nitrofurazan-3-yl)tetrazole (16). Aqueous 30% solution of H_2O_2 (32.6 ml, 36.3 g, 0.32 mol) was vigorously stirred and treated by dropwise addition of 96% H_2SO_4 (*d* 1.84 g/ml, 40.0 ml, 73.6 g, 0.72 mol), while keeping the temperature in the solution at or below 50–55°C by external cooling. Methoxytetrazole **10** (14.6 g, 0.08 mol) was then added in 2–3-g portions, while maintaining the temperature of reaction mixture in the range of 50–55°C. After finishing the addition of compound **10**, the mixture was stirred for another 1 h at 50–55°C, cooled to room temperature and poured into a mixture of ice and water (50 ml). The reaction product was extracted with CH_2Cl_2 (4×30 ml). The combined organic extracts were washed with water (2×10 ml), dried over anhydrous $MgSO_4$, and the solvent was evaporated at reduced pressure. Yield 15.3 g (90%), light-yellow, low viscosity liquid, insoluble in water, soluble in polar organic solvents, n_D^{25} 1.512. IR spectrum, ν, cm^{-1}: 3450, 3327, 3249, 3025, 2955, 1733, 1561, 1531, 1445, 1354, 1259, 1223, 1113, 1056, 994, 939, 909, 721, 678, 650, 594, 585, 548, 408, 401. ^{1}H NMR spectrum, δ, ppm: 4.46 (3H, s, OCH_3). ^{13}C NMR spectrum, δ, ppm: 160.1 (br., C-4'); 137.8 (C-3'); 136.3 (C-5); 70.6 (OCH_3).

Diammonium salt of 3,3'-bis(1-hydroxytetrazol-5-yl)-4,4'-azofurazan (3). Tetrazole **1** (1.69 g, 0.01 mol) was dissolved in AcOH (10 ml), then concd HCl (10 ml) was added. The obtained solution was vigorously stirred at 20–30°C temperature and treated by the addition of $KMnO_4$ (1.58 g, 0.01 mol) in 100–200-mg portions. The reaction mixture was heated to 50°C and stirred at this temperature for 30 min. The excess of $KMnO_4$ was destroyed by adding several drops of aqueous 30% H_2O_2 solution. The mixture was diluted with H_2O (50 ml), cooled to room temperature and extracted with EtOAc (3×15 ml). The combined organic extracts were washed with a saturated aqueous NaCl solution (3×10 ml). The organic phase was carefully adjusted to pH 8 by dropwise addition of aqueous 25% ammonia solution. The precipitate that formed was filtered off and recrystallized from 10:1 mixture of 2-PrOH–H_2O. Yield 1.25 g (68%), fine orange crystals, mp 252–253°C (decomp.) (mp 266°C (decomp., DSC)[12]). IR spectrum, ν, cm^{-1}: 3182, 3045, 2831, 1597, 1498, 1434, 1414, 1377, 1280, 1224, 1127, 1071, 1015, 993, 910, 855, 772, 697, 624, 524, 404. (IR spectrum (KBr), ν, cm^{-1}: 3188, 3145, 1686, 1597, 1498, 1435, 1405, 1276, 1224, 1124, 989, 854, 769).[12] ^{1}H NMR spectrum, δ, ppm: 7.12 (8H, br. s, $2NH_4^+$). (^{1}H NMR spectrum (DMSO-d_6), δ, ppm: 7.10.[12]) ^{13}C NMR spectrum, δ, ppm: 162.3 (C-4'); 138.2 (C-3'); 131.9 (C-5).

(^{13}C NMR spectrum (DMSO-d_6), δ, ppm: 162.1; 138.1; 131.8.[12])

3,3'-Bis(1-methoxytetrazol-5-yl)-4,4'-azofurazan (17). Tetrazole **10** (1.83 g, 0.01 mol) was dissolved in AcOH (10 ml), then concd HCl (10 ml) was added. The obtained solution was vigorously stirred at 20–30°C and $KMnO_4$ (1.60 g, 0.01 mol) was added. The reaction mixture was heated to 50°C and stirred for 30 min at this temperature. The excess of $KMnO_4$ was decomposed by adding several drops of aqueous 30% H_2O_2 solution. The mixture was diluted with H_2O (50 ml), cooled to room temperature, the precipitate that formed was filtered off and recrystallized from MeOH. Yield 1.55 g (85%), red needle-shaped crystals, mp 127–128°C. IR spectrum, ν, cm^{-1}: 3437, 3027, 2958, 2920, 1618, 1452, 1439, 1422, 1382, 1254, 1112, 1046, 1003, 944, 905, 870, 611. ^{1}H NMR spectrum, δ, ppm: 4.40 (6H, s, 2OCH$_3$). ^{13}C NMR spectrum, δ, ppm: 162.2 (C-4'); 138.2 (C-3'); 137.4 (C-5); 70.3 (OCH$_3$). Found, *m/z*: 385.0590 [M+Na]$^+$. $C_8H_6N_{14}NaO_4$. Calculated, *m/z*: 385.0589.

***N*,*N*'-Bis[4-(1-methoxytetrazol-5-yl)furazan-3-yl]-hydrazine (18)**. Azotetrazole **17** (1.0 g, 2.76 mmol) was dissolved in MeCN (5 ml) and hydrazine hydrate (0.4 g, 8.00 mmol) was added at 20–25°C. The color of solution faded after 1–2 min and white precipitate appeared. The mixture was stirred at 20–25°C for 30 min, diluted with H_2O (10 ml), the precipitate was filtered off and recrystallized from MeOH. Yield 0.71 g (71%), white powder, mp 238–240°C (decomp.). IR spectrum, ν, cm^{-1}: 3342, 1636, 1600, 1489, 1462, 1266, 1112, 996, 947, 803, 579. ^{1}H NMR spectrum, δ, ppm: 9.38 (2H, s, 2NH); 4.44 (6H, s, 2OCH$_3$). ^{13}C NMR spectrum, δ, ppm: 157.0 (C-4'); 138.2 (C-3'); 133.3 (C-5); 70.0 (OCH$_3$). Mass spectrum, *m/z* (I_{rel}, %): 364 [M]$^+$ (25), 263 (13), 232 (55), 168 [M/2–CH$_2$]$^+$ (14), 164 (14), 141 (30), 139 (22), 137 (45), 126 (28), 122 (100), 110 (20), 99 (22), 98 (32), 96 (20), 95 (31), 83 (16), 53 [HNCCN]$^+$ (18), 30 [NO]$^+$ (37). Found, *m/z*: 365.0931 [M+H]$^+$, 387.0744 [M+Na]$^+$. $C_8H_9N_{14}O_4$, $C_8H_8N_{14}NaO_4$. Calculated, *m/z*: 365.0926, 387.0745.

1-Methoxy-5-(4-methoxyfurazan-3-yl)tetrazole (19). Tetrazole **16** (2.13 g, 10 mmol) was dissolved in MeOH (20 ml) and $NaHCO_3$ (1.50 g, 18 mmol) was added. The reaction mixture was stirred for 5 h at 20–25°C, then diluted with H_2O (50 ml) and cooled to 10°C. The precipitate that formed was filtered off and recrystallized from aqueous MeOH. Yield 1.60 g (82%), fine white plates, mp 116–117°C (MeOH–H_2O, 1:1). IR spectrum, ν, cm^{-1}: 3437, 2920, 2853, 1622, 1577, 1472, 1454, 1414, 1261, 1194, 1154, 1106, 1044, 996, 977, 938, 916, 873, 590, 572, 462, 418. ^{1}H NMR spectrum, δ, ppm: 4.40 (3H, s, OCH$_3$ (tetrazole)); 4.23 (3H, s, OCH$_3$ (furazan)). ^{13}C NMR spectrum, δ, ppm: 164.6 (C-4'); 137.8 (C-3'); 134.7 (C-5); 70.0 (OCH$_3$ (tetrazole)); 60.8 (OCH$_3$ (furazan)). Found, *m/z*: 199.0576 [M+H]$^+$, 221.0392 [M+Na]$^+$. $C_5H_7N_6O_3$, $C_5H_6N_6NaO_3$. Calculated, *m/z*: 199.0574, 221.0393.

5-(4-Hydroxyfurazan-3-yl)-1-methoxytetrazole (20). A solution of tetrazole **16** (2.13 g, 10 mmol) in MeOH (20 ml) was treated by dropwise addition of KOH (1.40 g, 25 mmol) solution in MeOH (10 ml). The reaction mixture was stirred for 5 h at 20–25°C, then diluted with H_2O (20 ml), acidified with concd HCl to pH 1 and evaporated at reduced pressure. The residue was extracted with refluxing 2-PrOH (2×10 ml), the inorganic solids were removed by filtration, the hot filtrate was treated by dropwise addition of water until the crystallization started, then the mixture was cooled to 10°C. The precipitate that formed was filtered off and recrystallized from aqueous MeOH. Yield 1.30 g (71%), agglomerates of fine, irregularly shaped crystals, mp 161–162°C (MeOH–H_2O, 1:1). IR spectrum, ν, cm^{-1}: 3557, 3473, 2958, 1638, 1439, 1352, 1304, 1221, 1106, 985, 948, 763, 738, 700, 630, 581, 441, 413. ^{1}H NMR spectrum, δ, ppm: 7.11 (1H, br. s, OH); 4.38 (3H, s, OCH$_3$). ^{13}C NMR spectrum, δ, ppm: 164.8 (C-4'); 138.5 (C-3'); 135.9 (C-5); 70.0 (OCH$_3$). Calculated, %: C 26.09; H 2.19; N 45.65. $C_4H_4N_6O_3$. Found, %: C 25.93; H 2.28; N 45.38. The potassium salt of compound **20** was obtained by mixing a solution of compound **20** (1.00 g, 5.4 mmol) in 2-PrOH (10 ml) with a solution of KOH (0.34 g, 6.0 mmol) in MeOH (2 ml). The precipitate that formed was filtered off, washed with acetone (10 ml), and air-dried. Yield 1.05 g (88%), white fine crystalline powder, mp 271–272°C (with explosion).

5-(4-Azidofurazan-3-yl)-1-methoxytetrazole (21). Tetrazole **16** (2.13 g, 10 mmol) was dissolved in MeCN (20 ml) and NaN_3 (1.00 g, 15 mmol) was added. The reaction mixture was stirred for 5 h at 40–45°C, then diluted with H_2O (50 ml) and cooled to 10°C. The precipitate that formed was filtered off and recrystallized from aqueous MeOH. Yield 1.60 g (76%), agglomerates of fine crystals, mp 84–85°C (MeOH–H_2O, 1:1). IR spectrum, ν, cm^{-1}: 3023, 2957, 2922, 2148, 1546, 1454, 1432, 1383, 1291, 1183, 1097, 1034, 997, 941, 903, 878, 771, 589. ^{1}H NMR spectrum, δ, ppm: 4.43 (3H, s, OCH$_3$). ^{13}C NMR spectrum, δ, ppm: 153.6 (C-4'); 137.7 (C-3'); 137.2 (C-5); 70.2 (OCH$_3$). Found, *m/z*: 210.0485 [M+H]$^+$, 232.0296 [M+Na]$^+$. $C_4H_4N_9O_2$, $C_4H_3N_9NaO_2$. Calculated, *m/z*: 210.0482, 232.0302.

Preparation of compounds 22a–d by reaction of 1-methoxy-5-(4-nitrofurazan-3-yl)tetrazole (16) with amines. The appropriate amine (22 mmol, amines that are gaseous at room temperature were used as aqueous solutions) was added dropwise to a stirred solution of tetrazole **16** (2.13 g, 10 mmol) in MeCN (15 ml), while cooling the reaction mixture in order to maintain the temperature in the range of 25–30°C. The reaction mixture was stirred for 1 h at 30°C and poured into H_2O (50 ml). The precipitated product was filtered off and recrystallized from aqueous MeOH.

5-[4-(*N*-Methylamino)furazan-3-yl]-1-methoxytetrazole (22a) was obtained by treatment of tetrazole **16** with aqueous 34% $MeNH_2$ solution. Yield 1.30 g (67%), agglomerates of fine, white irregularly shaped crystals, mp 133–134°C. IR spectrum, ν, cm^{-1}: 3401, 3362, 2964, 2921, 1629, 1604, 1510, 1458, 1441, 1417, 1263, 1159, 1112, 1021, 998, 942, 862, 589, 576. ^{1}H NMR spectrum, δ, ppm (*J*, Hz): 6.61 (1H, q, *J* = 4.9, NH); 4.40 (3H, s, OCH$_3$); 2.95 (3H, d, *J* = 4.9, NHC<u>H</u>$_3$). ^{13}C NMR spectrum, δ, ppm: 157.0 (C-4'); 136.8 (C-3'); 133.6 (C-5); 69.8 (OCH$_3$); 31.3 (NHCH$_3$). Mass spectrum, *m/z* (I_{rel}, %): 197 [M]$^+$ (5), 166 [M–NO–H]$^+$

(4), 98 $[C_2N_2ONHCH_3]^+$ (12), 72 $[HN_2CNOH]^+$ (15), 68 $[C_2N_2O]^+$ (17), 53 $[HNCCN]^+$ (31), 42 $[CNO]^+$ (36), 30 $[NO]^+$ (100); 15 $[CH_3]^+$ (23). Found, *m*/*z*: 198.0738 $[M+H]^+$. $C_5H_8N_7O_2$. Calculated, *m*/*z*: 198.0733.

5-[4-(*N*,*N*-Dimethylamino)furazan-3-yl]-1-methoxytetrazole (22b) was obtained by treating tetrazole **16** with aqueous 33% solution of Me_2NH. Yield 1.10 g (52%), fine colorless needle-shaped crystals, mp 63–64°C. IR spectrum, ν, cm^{-1}: 3430, 3037, 3010, 2970, 2959, 2932, 2828, 1603, 1579, 1463, 1440, 1429, 1269, 1100, 997, 950, 570. ^1H NMR spectrum, δ, ppm: 4.42 (3H, s, OCH_3); 2.97 (6H, s, $N(CH_3)_2$). ^{13}C NMR spectrum, δ, ppm: 159.5 (C-4'); 138.8 (C-3'); 134.1 (C-5); 70.2 (OCH_3); 41.2 ($N(CH_3)_2$). Found, *m*/*z*: 234.0715 $[M+Na]^+$. $C_6H_9N_7NaO_2$. Calculated, *m*/*z*: 234.0710.

5-[4-(*N*-*tert*-Butylamino)furazan-3-yl]-1-methoxytetrazole (22c) was obtained by treatment of tetrazole **16** with *tert*-butylamine. Yield 1.40 g (60%), white, fine irregularly shaped plates, mp 62–63°C. IR spectrum, ν, cm^{-1}: 3380, 2976, 1633, 1580, 1527, 1464, 1455, 1435, 1408, 1371, 1364, 1297, 1266, 1230, 1113, 995, 956, 918, 575. ^1H NMR spectrum, δ, ppm: 6.07 (1H, s, NH); 4.40 (3H, s, OCH_3); 1.43 (9H, s, $C(CH_3)_3$). ^{13}C NMR spectrum, δ, ppm: 153.8 (C-4'); 138.8 (C-3'); 134.2 (C-5); 69.7 (OCH_3); 52.4 ($\underline{C}(CH_3)_3$); 28.1 ($C(\underline{C}H_3)_3$). Found, *m*/*z*: 262.0999 $[M+Na]^+$. $C_8H_{13}N_7NaO_2$. Calculated, *m*/*z*: 262.1023.

1-Methoxy-5-[4-(morpholin-4-yl)furazan-3-yl]tetrazole (22d) was obtained by treatment of tetrazole **16** with morpholine. Yield 1.80 g (71%), coarse, irregularly shaped colorless plates, mp 95–96°C. IR spectrum, ν, cm^{-1}: 3436, 3018, 2973, 2915, 2866, 1596, 1547, 1447, 1437, 1269, 1114, 1070, 1028, 996, 952, 913, 583. ^1H NMR spectrum, δ, ppm: 4.42 (3H, s, OCH_3); 3.77–3.73 (4H, m, CH_2OCH_2); 3.38–3.34 (4H, m, CH_2NCH_2). ^{13}C NMR spectrum, δ, ppm: 159.3 (C-4'); 138.8 (C-3'); 135.5 (C-5); 70.1 (OCH_3); 65.7 (CH_2OCH_2); 49.4 (CH_2NCH_2). Found, *m*/*z*: 276.0817 $[M+Na]^+$. $C_8H_{11}N_7NaO_3$. Calculated, *m*/*z*: 276.0815.

Hydrazinium salt of 5-(4-hydrazinofurazan-3-yl)-1-hydroxytetrazole (23). Tetrazole **16** (2.13 g, 10 mmol) was dissolved in MeCN (20 ml), then hydrazine hydrate (1.50 g, 30 mmol) was added dropwise at 15–20°C. The reaction mixture was stirred at this temperature for 1 h. The precipitate that formed was filtered off and recrystallized from MeOH. Yield 1.60 g (75%), light-gray agglomerates of fine irregularly shaped crystals, mp 224–225°C. IR spectrum, ν, cm^{-1}: 3437, 3321, 3303, 3242, 3205, 3017, 2961, 2916, 2676, 1663, 1640, 1585, 1552, 1509, 1456, 1400, 1364, 1281, 1233, 1192, 1141, 1113, 1008, 989, 976, 860, 781, 421. ^1H NMR spectrum, δ, ppm: 9.05 (1H, s, NH); 7.10 (5H, br. s, $N_2H_5^+$); 4.58 (2H, br. s, NH_2). ^{13}C NMR spectrum, δ, ppm: 160.2 (C-4'); 136.2 (C-3'); 134.8 (C-5). Mass spectrum, *m*/*z* (I_{rel}, %): 184 $[M]^+$ (2), 69 (11), 68 (10), 53 $[HNCCN]^+$ (33), 43 $[HN_3]^+$ (22), 31 $[N_2H_3]^+$ (63), 30 $[NO]^+$ (100), 29 (31). Found, *m*/*z*: 229.0170 $[M–H+2Na]^+$. $C_3H_3N_8Na_2O_2$. Calculated, *m*/*z*: 229.0169.

1-Hydroxy-5-{4-[2-(1-isopropylidene)hydrazino]furazan-3-yl}tetrazole (24). Salt **23** (1.00 g, 4.6 mmol) was added to acetone (10 ml), followed by the addition of AcOH (0.2 ml). The reaction mixture was refluxed for 1 h, then the solvent was evaporated at reduced pressure, the residue was washed with water and recrystallized from aqueous MeOH. Yield 0.65 g (55%), white amorphous powder, mp 161–162°C (MeOH–H_2O, 1:1). IR spectrum, ν, cm^{-1}: 3276, 3181, 3076, 3004, 2755, 2645, 1694, 1607, 1582, 1532, 1456, 1443, 1417, 1338, 1291, 1260, 1232, 1125, 989, 970, 930, 869, 793, 751, 678, 571, 447. ^1H NMR spectrum, δ, ppm: 7.05 (2H, br. s, NH, OH); 4.17 (6H, s, $2CH_3$). ^{13}C NMR spectrum, δ, ppm: 168.8 (C-4'); 157.4 (C-3'); 136.2 ($N=\underline{C}(CH_3)_2$); 134.6 (C-5); 20.8 ($2CH_3$). Found, %: C 32.35; H 3.71; N 49.67. $C_6H_8N_8O_2$. Calculated, %: C 32.15; H 3.60; N 49.98.

5-{4-[2-(1-Benzylidene)hydrazino]furazan-3-yl}-1-hydroxytetrazole (25). Salt **23** (1.00 g, 4.6 mmol) was added to MeOH (10 ml), followed by the addition of benzaldehyde (1.00 g, 9.4 mmol) and AcOH (0.2 ml). The reaction mixture was refluxed for 1 h, then diluted with H_2O (50 ml), the oil that separated was decanted and crystallized from aqueous MeOH. Yield 0.94 g (75%), fine gray plates, mp 223–225°C (decomp.) (MeOH–H_2O, 1:1). IR spectrum, ν, cm^{-1}: 3437, 3289, 3026, 2960, 2917, 2851, 2594, 1615, 1450, 1385, 1113, 1090, 1070, 1059, 999, 990, 952, 872, 762, 696. ^1H NMR spectrum, δ, ppm: 11.54 (1H, s, NH); 8.15 (1H, s, N=CH); 7.54–7.45 (5H, m, H Ph); 4.71 (1H, br. s, OH). ^{13}C NMR spectrum, δ, ppm: 155.4 (C-4'); 145.6 (N=CH); 137.8 (C-3'); 134.6 (C-1 Ph); 134.4 (C-5); 130.1 (C-4 Ph); 129.2 (C-3,5 Ph); 127.0 (C-2,6 Ph). Found, %: C 43.95; H 3.13; N 41.31. $C_{10}H_8N_8O_2$. Calculated, %: C 44.12; H 2.96; N 41.16.

Ammonium salt of 1-hydroxy-5-[4-(pyrazol-1-yl)-furazan-3-yl]tetrazole (26). Salt **23** (1.00 g, 4.6 mmol) was added to MeOH (10 ml), followed by 1,1,3,3-tetramethoxypropane (3.28 g, 20.0 mmol). The reaction mixture was heated to 40°C, acidified with concd HCl to pH 1 and refluxed for 1 h. The mixture was then evaporated to dryness at reduced pressure, the residue was extracted with aqueous 10% ammonia solution (10 ml). The insoluble impurities were removed by filtration and the filtrate was washed with CH_2Cl_2 (2×5 ml). The aqueous layer was separated, evaporated to dryness at reduced pressure, and the dry residue was recrystallized from MeOH. Yield 0.77 g (71%), fine white needles, mp 194–195°C. IR spectrum, ν, cm^{-1}: 3436, 3201, 3122, 3045, 2940, 2848, 2818, 2773, 1607, 1576, 1506, 1455, 1417, 1406, 1391, 1379, 1230, 1211, 1171, 1120, 1053, 1021, 1001, 929, 883, 785, 756, 642, 606, 516, 450, 422. ^1H NMR spectrum, δ, ppm (*J*, Hz): 8.48 (1H, d, *J* = 2.5, H-5'); 7.88 (1H, d, *J* = 1.8, H-3'); 7.33 (4H, br. s, NH_4^+); 6.65 (1H, dd, *J* = 2.5; *J* = 1.7, H-4'). ^{13}C NMR spectrum, δ, ppm: 152.5 (C-4'); 144.4 (C-3 (pyrazole)); 139.9 (C-3'); 132.7 (C-5 (pyrazole)); 132.0 (C-5); 109.8 (C-4 (pyrazole)). Found, *m*/*z*: 221.0524 $[M+H]^+$. $C_6H_5N_8O_2$. Calculated, *m*/*z*: 221.0529.

Ammonium salt of 1-hydroxy-5-[4-(3,5-dimethyl-pyrazol-1-yl)furazan-3-yl]tetrazole (27). Salt **23** (1.00 g, 4.6 mmol) was added to AcOH (10 ml), followed by the addition of acetylacetone (2.00 g, 20.0 mmol). The reaction mixture was refluxed for 1 h, then worked up as described

above for the preparation of pyrazole **26**. Yield 0.89 g (73%), fine white irregularly shaped crystals, mp 221–222°C. IR spectrum, ν, cm^{-1}: 3195, 3121, 2984, 2854, 1601, 1572, 1474, 1454, 1437, 1424, 1410, 1373, 1342, 1293, 1223, 1033, 1016, 1007, 984, 864, 809, 781, 749, 454. ^1H NMR spectrum, δ, ppm: 7.24 (4H, br. s, NH_4^+); 6.19 (1H, s, H-4'); 2.30 (3H, s, CH_3); 2.07 (3H, s, CH_3). ^{13}C NMR spectrum, δ, ppm: 152.1 (C-4'); 151.8 (C-3 (pyrazole)); 144.7 (C-3'); 143.0 (C-5 (pyrazole)); 132.2 (C-5); 109.2 (C-4 (pyrazole)); 13.7 (CH_3); 11.8 (CH_3). Found, *m*/*z*: 249.0838 $[M+H]^+$, 271.0659 $[M+Na]^+$. $C_8H_9N_8O_2$, $C_8H_8N_8NaO_2$. Calculated, *m*/*z*: 249.0843, 271.0662.

Preparation of nitriles 28, 29. The appropriate tetrazole **26** or **27** (10 mmol) was added in small portions to stirred HNO_3 (d = 1.5 g/cm^3) (20 ml), while maintaining the temperature in the range of 5–10°C. Then at the same temperature concd H_2SO_4 (20 ml) was added dropwise, resulting in vigorous evolution of gas. The mixture was maintained for 5 h at room temperature and poured onto crushed ice (50 g). The precipitated product was filtered off, washed with water, dried at room temperature, and recrystallized from 1:1 mixture of PhH–hexane.

4-(4-Nitro-1*H*-pyrazol-1-yl)furazan-3-carbonitrile (28). Yield 1.34 g (65%), agglomerates of fine, needle-shaped crystals, mp 93–94°C. IR spectrum, ν, cm^{-1}: 3136, 3122, 3105, 3087, 2719, 1593, 1531, 1522, 1439, 1418, 1402, 1336, 1300, 1198, 1059, 999, 933, 886, 816, 752, 580. ^1H NMR spectrum, δ, ppm: 9.97 (1H, s, H-5'); 8.92 (1H, s, H-3'). ^{13}C NMR spectrum, δ, ppm: 152.9 (C-4); 140.0 (C-3 (pyrazole)); 139.9 (C-5 (pyrazole)); 131.8 (C-4 (pyrazole)); 129.3 (C-3); 107.6 (CN). Mass spectrum, *m*/*z* (I_{rel}, %): 206 $[M]^+$ (100), 121 (70), 38 $[NCN]^+$ (10), 30 $[NO]^+$ (45). Found, %: C 35.14; H 1.13, N 40.98. $C_6H_2N_6O_3$. Calculated, %: C 34.96; H 0.98; N 40.77.

4-(3,5-Dimethyl-4-nitro-1*H*-pyrazol-1-yl)furazan-3-carbonitrile (29). Yield 1.59 g (68%), long needles, mp 59–60°C. IR spectrum, ν, cm^{-1}: 3008, 2936, 2853, 2262, 1595, 1527, 1506, 1483, 1410, 1401, 1378, 1361, 1346, 1260, 1156, 1143, 1053, 1018, 883, 843, 787, 767, 599. ^1H NMR spectrum, δ, ppm: 2.90 (3H, s, CH_3); 2.57 (3H, s, CH_3). ^{13}C NMR spectrum, δ, ppm: 152.7 (C-4); 149.4 (C-3 (pyrazole)); 145.2 (C-5 (pyrazole)); 134.2 (C-4 (pyrazole)); 130.4 (C-3); 107.8 (CN); 14.2 (CH_3); 13.0 (CH_3). Found, %: C 40.85; H 2.72; N 36.03. $C_8H_6N_6O_3$. Calculated, %: C 41.03; H 2.58; N 35.89.

1-Hydroxy-5-(4-methoxyfurazan-3-yl)tetrazole (30). The dimethoxy derivative **19** (1.98 g, 10.00 mmol) was dissolved in AcOH (5 ml) and concd HCl (5 ml) was added. The mixture was refluxed for 5 h, cooled to room temperature. The solvents were evaporated at reduced pressure. The residue was treated with aqueous 15 N ammonia solution (3 ml), filtered, and the filtrate was evaporated at reduced pressure. The solid residue of ammonium salt **30a** was recrystallized from 1:5 mixture of 2-PrOH–PhMe. The yield of salt **30a** was 1.53 g (71%), elongated irregularly shaped plates, mp 214–215°C. IR spectrum, ν, cm^{-1}: 3183, 3058, 2852, 1646, 1613, 1585, 1458, 1444, 1406, 1227, 1132, 1067, 991, 760, 580, 501. ^1H NMR spectrum, δ, ppm: 6.90 (4H, br. s, NH_4^+); 4.12 (3H, s, CH_3). ^{13}C NMR spectrum, δ, ppm: 164.8 (C-4'); 137.0 (C-3'); 132.1 (C-5); 60.1 (OCH_3). In order to isolate the free tetrazole **30**, a part of the obtained ammonium salt (1.00 g, 4.65 mmol) was dissolved in 2-PrOH (2 ml), acidified with concd HCl to pH 1, and evaporated to dryness. The residue was extracted with Et_2O (2×5 ml), filtered, the filtrate was diluted with CCl_4 (5 ml) and allowed to slowly evaporate at room temperature. The precipitate that formed was filtered off and washed with hexane (5 ml). Yield 0.57 g (62%), colorless fine crystals, mp 83–84°C. IR spectrum, ν, cm^{-1}: 3385, 3012, 2952, 1797, 1616, 1575, 1457, 1415, 1392, 1263, 1198, 1169, 1138, 1069, 998, 975, 867, 586, 533, 481, 436, 407. ^1H NMR spectrum, δ, ppm: 6.65 (1H, br. s, OH); 4.12 (3H, s, OCH_3). ^{13}C NMR spectrum, δ, ppm: 164.7 (C-4'); 136.6 (C-3'); 134.9 (C-5); 60.7 (OCH_3). Found, %: C 25.87; H 2.36; N 45.21. $C_4H_4N_6O_3$. Calculated, %: C 26.09; H 2.19; N 45.65.

5-(4-Azidofurazan-3-yl)-1-hydroxytetrazole (31). The azido derivative **21** (2.09 g, 10.0 mmol) was dissolved in AcOH (5 ml) and treated with concd HCl (5 ml). The mixture was refluxed for 3 h, cooled to room temperature, the solvents were evaporated at reduced pressure. The residue was dissolved in 2-PrOH (15 ml), adjusted to pH 8 with aqueous 15 N ammonia solution, diluted with PhMe (20 ml), heated to reflux and slowly evaporated until the start of crystallization. The mixture was cooled to room temperature, the precipitate of ammonium salt **31a** was filtered off, washed on filter with CH_2Cl_2 (5 ml), and dried. Yield 2.01 g (95%), white needles, mp 178–179°C (decomp.). IR spectrum, ν, cm^{-1}: 3171, 3057, 2837, 2149, 1607, 1546, 1467, 1444, 1416, 1386, 1229, 1181, 988, 876, 779, 530, 440. ^1H NMR spectrum, δ, ppm: 7.36–7.11 (4H, m, NH_4^+). ^{13}C NMR spectrum, δ, ppm: 153.1 (C-4'); 139.3 (C-3'); 132.2 (C-5). Found, %: C 16.51; H 2.02; N 66.14. $C_3H_4N_{10}O_2$. Calculated, %: C 16.99; H 1.90; N 66.03. In order to isolate free tetrazole **31**, the ammonium salt **31a** (1.00 g, 4.7 mmol) was dissolved in ice water (3 ml) and acidified with concd HCl to pH 1. The mixture was stirred and cooled to 0°C, the precipitate that formed was filtered off, recrystallized from water, and dried in vacuum at 70°C. Yield 0.84 g (92%), fine white plates, mp 185–187°C. IR spectrum, ν, cm^{-1}: 3549, 3326, 3319, 2152, 1582, 1539, 1478, 1445, 1434, 1418, 1387, 1297, 1267, 1196, 1061, 1045, 996, 887, 865, 858, 782, 530, 441. ^1H NMR spectrum, δ, ppm: 6.65 (1H, br. s, OH). (^1H NMR spectrum (acetone-d_6), δ, ppm: 8.45.[30]) ^{13}C NMR spectrum, δ, ppm: 153.5 (C-4'); 137.3 (C-3'); 136.4 (C-5). Found, %: C 18.27; H 0.94; N 64.82. $C_3HN_9O_2$. Calculated, %: C 18.47; H 0.52; N 64.61.

1-Hydroxy-5-[4-(morpholin-4-yl)furazan-3-yl]tetrazole (32). Compound **22d** (1.26 g, 5 mmol) was dissolved in AcOH (5 ml), and then concd HCl (5 ml) was added. The mixture was refluxed for 3 h, cooled to room temperature, and poured into H_2O (25 ml). The precipitate that formed was filtered off and recrystallized from MeOH. Yield 1.10 g (92%), white needles, mp 235–236°C. IR spectrum, ν, cm^{-1}: 2993, 2976, 2932, 2878, 2855, 2696, 1557, 1447, 1379, 1302, 1266, 1169, 1118, 1111, 1066, 1034, 1019, 998, 910, 881, 845, 755, 566, 436. ^1H NMR spectrum, δ, ppm: 8.14

(^{1}H, br. s, OH); 3.73–3.68 (4H, m, CH_2OCH_2); 3.26–3.22 (4H, m, CH_2NCH_2). ^{13}C NMR spectrum, δ, ppm: 159.2 (C-4'); 137.8 (C-3'); 135.4 (C-5); 65.7 (CH_2OCH_2); 48.9 (CH_2NCH_2). Found, *m*/*z*: 240.0833 $[M+H]^+$, 262.0658 $[M+Na]^+$. $C_7H_{10}N_7O_3$, $C_7H_9N_7NaO_3$. Calculated, *m*/*z*: 240.0839, 262.0659.

X-ray structural studies of compounds 31 and 31a were performed by using an Oxford Diffraction Xcalibur monocrystal diffractometer with an Eos two-dimensional CCD detector and MoKα radiation (0.71073 Å wavelength). The crystal was thermostated with an Oxford Cryosystems Cryostream cooler at 100 K. Monocrystals suitable for analysis were obtained by slow evaporation of solvent from aqueous solutions of the respective compounds under isothermal conditions (20°C). Primary processing of experimental data was performed with the Agilent Technologies CrysAlisPro software suite.[62] The structures were solved and refined by using the Olex2 program from the SHELX software suite.[63] The colorless, well-faceted crystals of compound **31** belong to monoclinic syngony. The main crystallographic data: space group $P2_1/n$; *a* 10.0019(14), *b* 6.2195(7), *c* 13.5749(18) Å; β 107.701°; *V* 804.48(19) Å^3; *Z* 4; *d* 1.760 g/cm^3; μ 0.154 mm^{-1}. The colorless, well-faceted crystals of compound **31a** belong to rhombic syngony. The main crystallographic data: space group $P2_1/2_1/2_1$; *a* 4.7397(3), *b* 12.0960(6), *c* 13.9889(6) Å; β 90°; *V* 802.01(7) Å^3; *Z* 4; *d* 1.757 g/cm^3; μ 0.149 mm^{-1}. The complete crystallographic datasets for compounds **31** and **31a** were deposited at the Cambridge Crystallographic Data Center (deposits CCDC 1523288 and CCDC 1533574, respectively).

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