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# Synthesis and properties of 3-azido-4-(2*H*-tetrazol-5-yl)furazan

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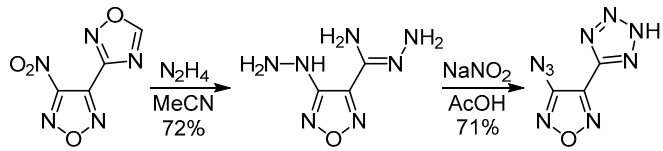



We describe an effective scheme for the synthesis of a new energetic compound – 3-azido-4-(2*H*-tetrazol-5-yl)furazan from 4-amino-*N*'-hydroxyfurazan-3-carboximidamide. The structure of 3-azido-4-(2*H*-tetrazol-5-yl)furazan was proved by $^{1}$H and $^{13}$C NMR spectroscopy, mass spectrometry, and X-ray structural analysis. 3-Azido-4-(2*H*-tetrazol-5-yl)furazan crystallized in monoclinic syngony, space group $P2_1/n$, monocrystal density *d* 1.953 g·cm$^{-3}$ (100 K). According to differential scanning calorimetry data, 3-azido-4-(2*H*-tetrazol-5-yl)furazan melts at 103.3°C, while the maximum of thermal decomposition exotherm was observed at 185.6°C. The sensitivity of 3-azido-4-(2*H*-tetrazol-5-yl)furazan to impact (2 kg, 25 cm, 36% explosion frequency) and to friction (1450 kg·cm$^{-3}$ lower limit) was at the level of pentaerythritol tetranitrate. The salts of 3-azido-4-(2*H*-tetrazol-5-yl)furazan with ammonia and guanylurea were also obtained and characterized.

**Keywords**: amidrazone, azidofurazan, nitrofurazan, 1,2,5-oxadiazole, tetrazole.

Azoles (oxadiazoles, triazoles, tetrazoles, and others), especially derivatives containing explosophoric substituents (nitro, azo, azoxy, and azido groups) represent promising objects for the synthesis of new energetic compounds.[1] In contrast to the usual aromatic systems, azoles are characterized by high positive enthalpies of formation, which is an essential property of energetic compounds.[2] The combination of several azole rings in one molecule of energetic compound,[3,4] in particular tetrazole[5] and furazan (1,2,5-oxadiazole) rings,[6] provides an approach for the design of compounds that simultaneously have the high energy characteristics of tetrazoles and the good thermal stability of furazans.

An important structural feature of furazan ring is the presence of "active oxygen" atom, which has no direct covalent bonds to carbon atoms and thus can provide energy *via* oxidation of carbon-containing moieties. The second carbon atom of furazan ring can be decorated with an explosophoric group, while the presence of an acidic proton in the structure of tetrazole moiety can be exploited for the preparation of various energetic salts either with metals or with various inorganic and organic nitrogenous bases.[2] In particular, such compounds as 4-(2*H*-tetrazol-5-yl)furazan-3-amine[7–10] (**1**), 5-(4-nitrofurazan-3-yl)-2*H*-tetrazole[9] (**2**), *N*-[4-(2*H*-tetrazol-5-yl)furazan-3-yl]nitramine[11] (**3**), 3,4-bis(2*H*-tetrazol-5-yl)furazan[12] (**4**), 1,2-bis[4-(2*H*-tetrazol-5-yl)-furazan-3-yl]diazene[9,13,14] (**5**), 4,4'-oxybis[3-(2*H*-tetrazol-5-yl)furazan][15–18] (**6**) are known in the series of 3-substituted 4-(tetrazol-5-yl)furazan derivatives (Fig. 1). The energetic characteristics of their salts are presented in Table 1. Compound **3** has been used as ligand in pentaaminecobalt(III) complexes.[19]

In this work, we describe the synthesis of a new energetic compound, 3-azido-4-(2*H*-tetrazol-5-yl)furazan (**7**). The synthesis of compound **7** can be accomplished by starting from 4-amino-*N*'-hydroxyfurazan-3-carboximidamide (**8**)[20,21] according to Scheme 1. The azido group can be introduced into furazan ring by nucleophilic substitution of nitro group in compound **2** with sodium azide,[22,23] or by reaction of diazonium salt **10** with sodium azide.[24]

It should be noted that the synthesis of compound **7** according to Scheme 1 includes some problematic and

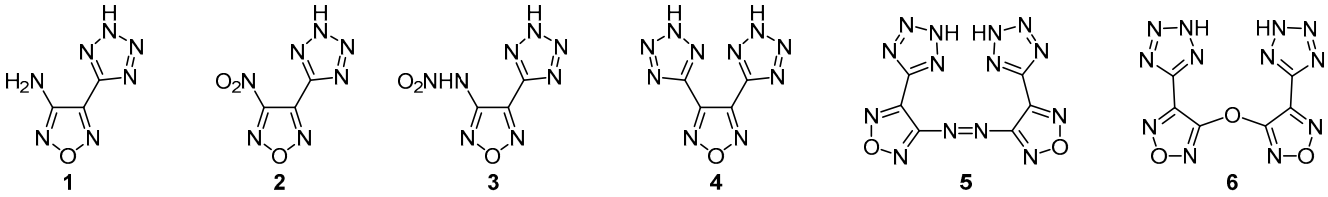


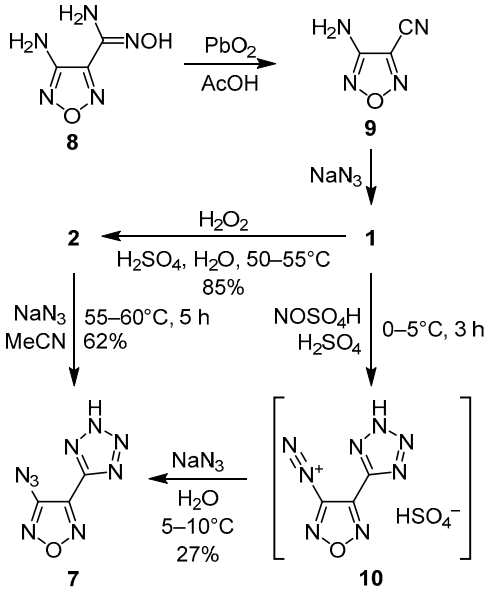
**Figure 1**. Energetic derivatives of 4-(tetrazol-5-yl)furazan.

dangerous procedures. Thus, the methods for the preparation of intermediate 4-aminofurazan-3-carbonitrile (**9**)[7] and nitro compound **2**[9] are quite laborious. Furthermore, the literature procedure[9] for the isolation of compound **2** from reaction mixture by extraction with dichloromethane could not be reproduced. We were able to achieve full extraction of nitro compound **2** from the reaction mixture with ethyl acetate only after its partial neutralization by addition of crystalline $Na_3PO_4$ (see Experimental). According to the known reactivity of aminofurazans,[25] diazotation of amine **1** can be performed with nitrosylsulfuric acid in concentrated $H_2SO_4$ medium. The azidation of diazonium salt **10** involves the use of an excess of aqueous sodium azide solution in an acidic reaction mixture, which invariably leads to the liberation of toxic and explosive $HN_3$.[24]

**Table 1**. Energetic characteristics of salts obtained from 4-(tetrazol-5-yl)furazan derivatives

| Compound | ρ, g·cm$^{-3}$ | $\Delta H_f°_{298}$, kJ·mol$^{-1}$ | $V_D$, m·s$^{-1}$ |
|---|---|---|---|
| **3** (salt with biguanidine)[2] | 1.770 | 441 | 8670 |
| **3** (salt with $NH_2OH$)[11] | 1.815 | 426 | 8830 |
| **5**[14] | 1.747 | 1117 | 7730 |
| **6** (salt with triaminoguanidine)[15] | 1.75 | 1371 | 8620 |
| **6** (salt with carbodihydrazide)[15] | 1.86 | 585 | 8320 |
| Hexogen (RDX)[15] | 1.80 | 93 | 8778 |

**Scheme 1**



Scheme 2 shows an alternative route proposed by us for the synthesis of azide **7**. We used amidoxime **8** as precursor, the condensation of which with triethyl orthoformate[26] in the presence of $BF_3 \cdot Et_2O$ provided 4-(1,2,4-oxadiazol-3-yl)-furazan-3-amine (**11**) in up to 90% yield when using the optimized procedure.[27] Nitrofurazan **12** was obtained in 84% yield by oxidation of compound **11** with a mixture of aqueous 36% $H_2O_2$ solution and concentrated $H_2SO_4$ at elevated temperature.[27] The synthesis of the key intermediate **13** was based on a reductive opening of the 1,2,4-oxadiazole ring with hydrazine.[27] Thus, the treatment of compound **12** with an excess of hydrazine hydrate in MeCN at room temperature resulted both in the opening of 1,2,4-oxadiazole ring and the substitution of nitro group with a hydrazinyl moiety, leading to the formation of compound **13**. The treatment of the latter with aqueous $NaNO_2$ solution in acetic acid medium while cooling gave the target azidotetrazole **7** in 75% yield. The overall yield of tetrazole **7**, as calculated from amidoxime **8**, was approximately 50%.

**Scheme 2**

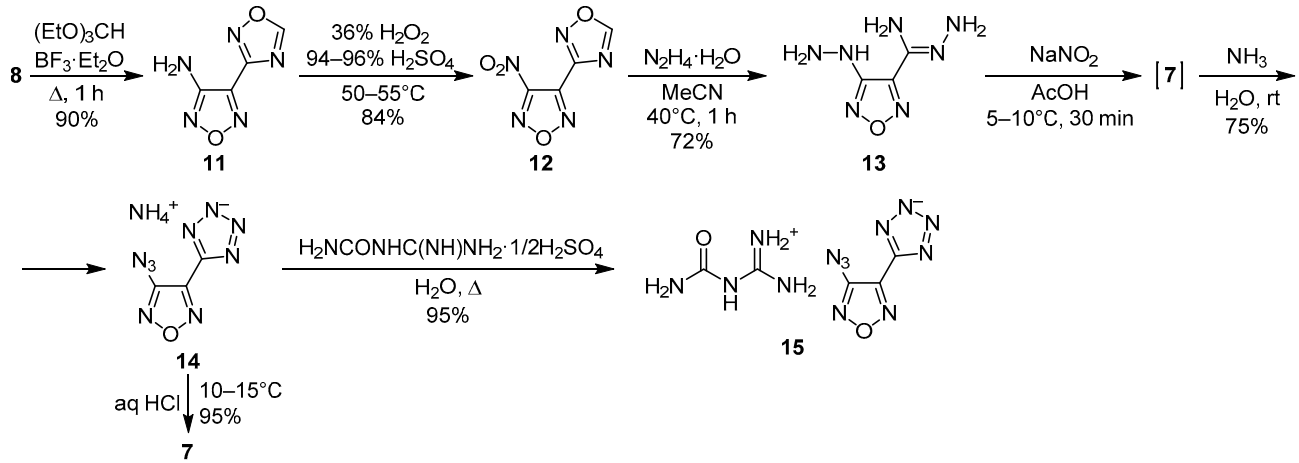


**Table 2**. The spectral characteristics of 3-R-4-(tetrazol-5-yl)furazans **2**, **7**, **14**, and **15**

| Compound | IR spectrum, ν, $cm^{-1}$ | $^1H$ NMR spectrum, δ, ppm | $^{13}C$ NMR spectrum, δ, ppm | | | | Mass spectrum, *m/z* ($I_{rel}$, %) |
|---|---|---|---|---|---|---|---|
| | | | Furazan | | Tetrazole | Cation | |
| | | | C-3 | C-4 | | | |
| **2** | 3223 (NH), 1620 (C=N), 1568 ($NO_2$), 1397, 1386 ($NO_2$), 1329, 1305, 1144, 1115, 1030, 999, 825, 429 | 10.40–8.80 (1H, br. s, NH) | 160.0 | 141.3 | 147.4 | – | 183 $[M]^+$ (0.2), 78 (20), 46 (20), 30 $[NO]^+$ (100), 29 (50) |
| **7** | 3048, 3006, 2934, 2857, 2836, 2766, 2719, 2663, 2591, 2142 ($N_3$), 1544, 1493, 1396, 1315, 1273, 1237, 1184, 1149, 1049, 1029, 1021, 998, 935, 906, 883, 782, 581, 530, 488, 432 | 12.00–9.0 (1H, br. s, NH) | 153.3 | 140.0 | 148.0 | – | 179 $[M]^+$ (1), 151 $[M–N_2]^+$ (8), 67 (11), 30 $[NO]^+$ (100), 29 (33) |
| **14** | 3290, 3154, 3017, 2984, 2839, 2284, 2229, 2166 ($N_3$), 2152 ($N_3$), 2139 ($N_3$), 1899, 1809, 1688, 1535, 1466, 1433, 1395, 1217, 1173, 1145, 1033, 910, 887, 786, 589, 531, 491, 435, 407 | 7.24 (4H, s, $NH_4^+$) | 152.8 | 143.6 | 148.7 | – | – |
| **15** | 3412, 3362, 3191, 2180 ($N_3$), 2141 ($N_3$), 1745, 1704, 1608, 1528, 1400, 1352, 1231, 1189, 1119, 998, 941, 908, 888, 781, 770, 719, 695, 590, 492, 454 | 9.76 (1H, br. s, NH); 8.14 (4H, br. s, $2NH_2$); 7.18 (2H, br. s, $NH_2$) | 155.9 | 143.6 | 148.8 | 154.8; 152.8 | – |

According to the results of potentiometric titration, azide **7** was a stronger NH acid (p$K_a$ 2.32) than amine **1** (p$K_a$ 2.53), but weaker than nitro analog **2** (p$K_a$ 2.22). Similarly to compounds **1** and **2**, azide **7** formed hydrolytically stable salts with metal cations and nitrogenous bases. From practical point of view, the salts easiest to isolate were ammonium salt **14** and the salt with guanylurea **15**, which was sparingly soluble in water (Scheme 2).

The salts of compound **7** with hydrazine and hydroxylamine could not be obtained, because the addition of hydrazine or hydroxylamine to azide **7** caused its vigorous decomposition. The spectral characteristics of 3-azido-4-(2*H*-tetrazol-5-yl)furazan (**7**) and salts **14**, **15** are presented in Table 2.

Since compounds **2** and **7** are strong NH acids, the proton signals in $^1H$ NMR spectra were observed as significantly broadened singlets in the downfield region. The replacement of nitro group with azide group resulted in 4.1–7.2 ppm upfield shift of $^{13}C$ NMR signal for the furazan ring carbon atom bearing the azido group. Deprotonation of the tetrazole ring in salts **14** and **15** did not substantially affect the positions of $^{13}C$ NMR signals due to the furazan and tetrazole ring carbon atoms.

Monocrystals of compound **7** that were suitable for X-ray structural analysis were obtained by slow evaporation of its solution in water. The colorless, well-faceted crystals of compound **7** belonged to monoclinic syngony. The molecule of compound **7** was practically planar: the torsion angle N(1)–C(1)–C(2)–C(3) was equal to 6.3° (Fig. 2). The bond lengths and valence angles in furazan ring containing localized C=N double bonds were in good agreement with the literature data.[28–32] In general, with the exception of known differences between the bond lengths and angles in furazans and furoxans,[33] the molecular geometry of compound **7** was similar to the structure of its closest structural analog, 3-azido-4-(1*H*-tetrazol-5-yl)furoxan.[34] All three N–N bonds in the tetrazole ring had similar lengths, providing evidence of significant delocalization of the double bonds.

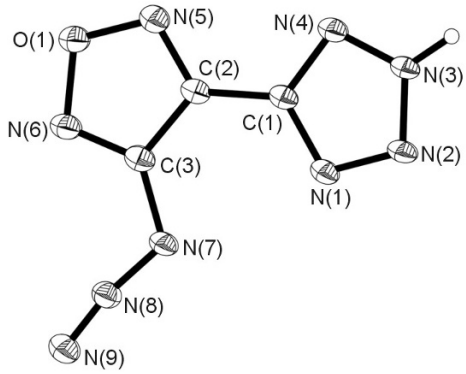



**Figure 2**. The molecular structure of 3-azido-4-(2*H*-tetrazol-5-yl)-furazan (**7**) with atoms represented by thermal vibration ellipsoids of 50% probability.

The molecules related by the symmetry of second order screw axis were linked into infinite chains by relatively strong N(3)–H(3)···N(1) hydrogen bonds with 2.829 Å length. The H(3)···N(1) distance was equal to 1.945 Å, while the angle at hydrogen atom was 164.5°. An illustration of a fragment of the chain is provided in Figure 3.

The crystal lattice of compound **7** had a layered structure. The crystal packing in projection along the monoclinic axis is shown in Figure 4. All of the molecules forming the crystal were located in the (1 0 3) plane with an interlayer distance of 3.15 Å. An analogous layered structure was noted also for the closest structural analog of compound **7** – the ammonium salt of 3-azido-4-(1*H*-tetrazol-5-yl)furoxan,[34] where planar anions were also located in the (1 0 3) plane of crystal, while the hydrogen atoms of ammonium ion provided hydrogen bonds that formed a three-dimensional framework. The hydrogen bond lengths were in the range of 3.03–3.06 Å.

According to calculations,[35] the anion of compound **7**, its triaminoguanidine salt, and ammonium salt **14** had high positive enthalpies of formation (682, 1089, and 799 $kJ \cdot mol^{-1}$, respectively). As shown in Table 3, the target compound, azide **7**, and its salts were characterized by relatively good thermal stability. The sensitivity of compounds **7** and **14** to

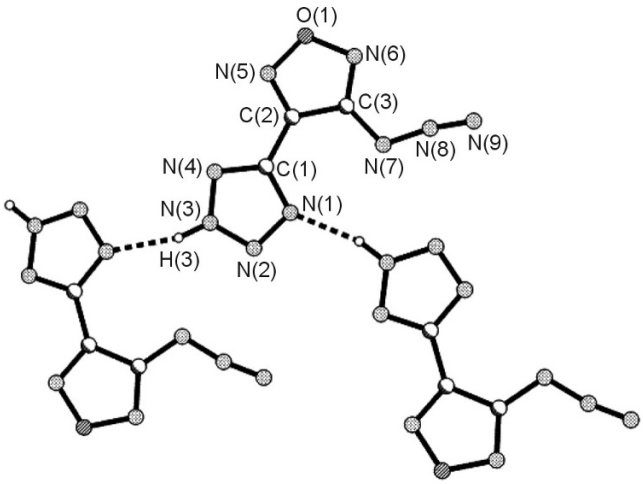



**Figure 3**. A fragment from the infinite chain formed by molecules of compound **7**.

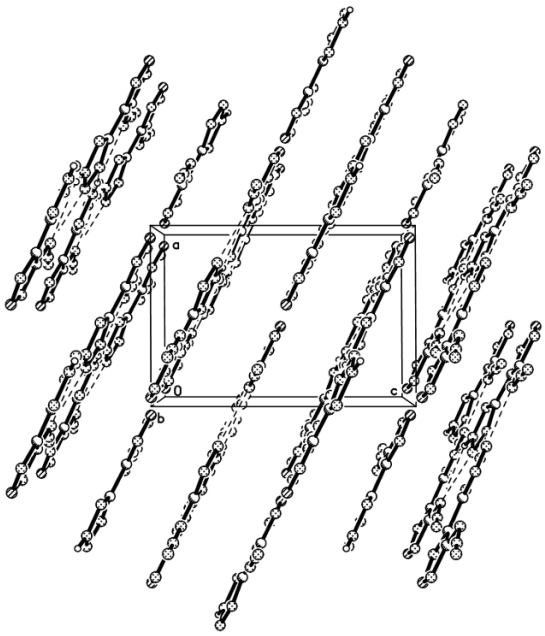


**Figure 4**. The structure of compound **7** projected along the *b* axis of unit cell.

mechanical stimuli was at the level of pentaerythritol tetranitrate (PETN), while the guanylammonium salt **15** in this regard was similar to picric acid.

The proposed scheme for the synthesis of 3-azido-4-(2*H*-tetrazol-5-yl)furazan is suitable for scale-up, thus enabling further practical studies of this compound and a series of its salts as nitrogen-rich components of energetic compositions.

## Experimental

IR spectra were recorded on an FSM-1201 FT-IR spectrometer in KBr pellets. $^1$H and $^{13}$C NMR spectra were acquired in DMSO-$d_6$ solutions on a Bruker DRX 400 spectrometer (400 and 100 MHz, respectively). The chemical shifts of $^1$H and $^{13}$C nuclei were determined relative to the solvent signals (2.51 and 40.0 ppm, respectively). Mass spectra were recorded on a Finnigan MAT Incos 50 instrument (EI ionization, 70 eV). Elemental analysis was performed on a PerkinElmer 2400 elemental analyzer. The dissociation constants for compounds **1**, **2**, and **7** were determined by method of potentiometric titration in aqueous solutions with 0.1 N NaOH solution. Calorimetric studies were performed in aluminum crucible under argon flow (100 ml/min) at the heating rate of 5 K/min, using a Netzsch TG 209 F1 Libra analyzer. The sensitivity to mechanical stimuli was determined according to GOST 4545-88 and GOST R 50835-95 standards.[36] Melting points were determined in capillary tubes. The reaction progress and the purity of the obtained compounds were controlled on a Shimadzu Series 20 HPLC instrument with a diode matrix detector. The following analytical conditions were used: Luna C18(2) 250 × 4.6 mm column, 5 μm Phenomenex stationary phase. The mobile phase was MeOH–$H_2O$–$CF_3CO_2H$ at the volume ratio of 74.95:24.95:0.10. The thermostat and detector temperatures were set at 40°C. Detection was performed at 209, 230, and 254 nm wavelengths. The retention time of compound **7** was 4.2 min at 0.8 ml/min flow rate.

**Table 3**. Physicochemical properties of 3-R-4-(tetrazol-5-yl)furazans **2**, **7**, **14**, and **15**

| Compound | Mp, °C | Starting temperature of vigorous decomposition, °C | Oxygen balance, % | Sensitivity | |
|---|---|---|---|---|---|
| | | | | impact*, % | friction**, kg·cm$^{-2}$ |
| **2**[9] | 123–124 | – | –30.6 | 20 | 3100 |
| **7** | 102.5–103.5 | 185.6 | –49.1 | 36 | 1450 |
| **14** | – | 185.2 | –57.1 | 24 | 1900 |
| **15** | – | 206.0 | –65.4 | (32, 10 kg) | 3400 |
| PETN | 141.3 | 140–145 | –10.1 | 20–36 | 1500 |
| Picric acid | 121.9 | | –45.4 | (25, 10 kg) | 4500 |

* Fall hammer apparatus K-44-II (apparatus No. 1, hammer mass 2 kg at drop height 25 cm), explosion frequency, %.
** Apparatus K-44-III (lower limit).

The synthesis of compound **1** was performed as described previously,[27] the synthesis of amidoxime **8** – according to another publication.[21] The synthesis of 4-(1,2,4-oxadiazol-3-yl)furazan-3-amine (**11**) was accomplished according to optimized literature procedure.[26]

**5-(4-Nitrofurazan-3-yl)-2*H*-tetrazole (2)**. Concd $H_2SO_4$ (40.0 ml, 73.6 g, 0.72 mol, *d* 1.84 g/cm$^3$) was added dropwise to a vigorously stirred and externally cooled 30% aqueous $H_2O_2$ solution (32.6 ml, 36.3 g, 0.32 mol), while maintaining the temperature in the solution below 50–55°C. Compound **1** (12.2 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 completing the addition of compound **1**, the mixture was stirred for 1 h at 50–55°C, cooled to room temperature, and poured into a mixture of ice and water (50 ml). The quenched mixture was partially neutralized by adding crystalline sodium orthophosphate (100 g, approximately 0.26 mol) and then

extracted with ethyl acetate (4×30 ml). The combined organic layers were washed with water (2×10 ml) and dried over anhydrous $MgSO_4$. The solvent was evaporated at reduced pressure, the oily residue was crystallized from 1,1,1-trichloroethane. Yield 12.4 g (85%), yellow, needle-shaped crystals, mp 123–124°C ($MeCCl_3$) (mp 123–124°C (EtOAc)[9]).

**4-(1,2,4-Oxadiazol-3-yl)furazan-3-amine (11)**. Compound **8** (143 g, 1.00 mol) was added with vigorous stirring to $(EtO)_3CH$ (160 g, 1.08 mol), followed by the addition of $BF_3 \cdot Et_2O$ (1 ml, 8.00 mmol). The stirred mixture was slowly heated to reflux temperature and was refluxed for 1 h. The mixture was then diluted with an equal volume of hot water, again heated to reflux, and then allowed to slowly crystallize. The precipitate was filtered off and recrystallized from 2-PrOH. Yield 138 g (90%), white, fine crystalline powder, mp 126–127°C ($H_2O$) (mp 126–127°C ($H_2O$)[26]). IR spectrum, ν, $cm^{-1}$: 3480, 3320 ($NH_2$), 3120 (CH), 1647 ($NH_2$), 1014 (oxadiazole). $^1H$ NMR spectrum, δ, ppm: 10.00 (1H, s, CH); 6.50 (2H, s, $NH_2$). $^{13}C$ NMR spectrum, δ, ppm: 168.7; 158.6; 156.0; 137.4. Mass spectrum, *m*/*z* ($I_{rel}$, %): 154 $[M+H]^+$ (2.5), 153 $[M]^+$ (100), 123 $[M–NO]^+$ (23), 96 (94), 69 (20), 58 (91), 54 (13), 53 (28), 42 (15), 30 $[NO]^+$ (55), 29 $[CHO]^+$ (41).

**3-(4-Nitrofurazan-3-yl)-1,2,4-oxadiazole (12)**. Compound **11** (76.5 g, 0.5 mol) was added to a vigorously stirred mixture that was prepared from 36% $H_2O_2$ solution (105 ml) and 94–96% $H_2SO_4$ (107 ml), while maintaining the temperature in reaction mixture in the range of 50–55°C. After the exothermic effect ceased, the mixture was maintained for 30 min at 50–55°C, cooled to room temperature, diluted with water (400 ml), and extracted with $CH_2Cl_2$ (2×100 ml). The organic layers were washed with water, evaporated under vacuum, the solid residue was recrystallized from methanol. Yield 76.9 g (84%), colorless, round crystals, mp 54–55°C ($CCl_4$). IR spectrum, ν, $cm^{-1}$: 3430, 3138, 1609, 1564, 1539, 1505, 1422, 1408, 1307, 1270, 1116, 1035, 965, 910, 883, 823, 773, 742, 616, 586, 475, 418, 404. $^1H$ NMR spectrum, δ, ppm: 10.08 (1H, s, CH). $^{13}C$ NMR spectrum, δ, ppm: 169.2 (CH); 160.0 ($CNO_2$); 156.5; 141.1. Mass spectrum, *m*/*z* ($I_{rel}$, %): 183 $[M]^+$ (1.2), 137 $[M–NO_2]^+$ (1.6), 77 (22), 46 (100), 38 (13), 30 $[NO]^+$ (99).

**4-Hydrazinylfurazan-3-carbohydrazonamide (13)**. A solution of compound **12** (10 g, 0.055 mol) in acetonitrile (50 ml) was vigorously stirred and maintained at 20–25°C, while 100% hydrazine hydrate (11 ml, 0.22 mol) was added dropwise over 10 min. After the exothermic effect and gas evolution ceased, the obtained suspension was stirred for 1 h at 40°C. The reaction mixture was then worked up by diluting with water (100 ml), cooling to room temperature, and collecting the precipitate by filtration. The precipitate was washed with water and recrystallized from a 1:1 mixture of DMF–MeOH. Yield 6.2 g (72%), light-beige amorphous powder, mp 204–205°C ($CCl_4$). IR spectrum, ν, $cm^{-1}$: 3380, 3336, 3154, 1664, 1605, 1572, 1544, 1322, 1289, 1193, 1102, 953, 856, 650, 417. $^1H$ NMR spectrum, δ, ppm: 7.24 (1H, s, NH); 5.84 (2H, s, $NH_2$); 4.74 (4H, br. s, $2NH_2$). $^{13}C$ NMR spectrum, δ, ppm: 158.9 (C-3); 140.5; 136.8. Mass spectrum, *m*/*z* ($I_{rel}$, %): 158 $[M+H]^+$ (7.7), 157 $[M]^+$ (100), 140 (11), 111 (15), 85 (37), 68 (19), 67 (12), 58 (12), 53 (16), 43 (32), 42 (12), 32 (29), 31 (23), 30 (28), 29 (17).

**Preparation of ammonium 5-(4-azidofurazan-3-yl)-tetrazolide (14)**. Amidrazone **13** (3.14 g, 20 mmol) was added to acetic acid (20 ml). The reaction mixture was cooled to 5°C, vigorously stirred at 5–10°C and treated by dropwise addition of $NaNO_2$ (3.0 g, 43.5 mmol) in water (10 ml). After completing the addition of $NaNO_2$, the reaction mixture was stirred for 30 min at 10–15°C, then acidified with concd HCl to pH 1. The solvent was evaporated at reduced pressure, water (20 ml) was added to the residue and the oil that separated was extracted with $CH_2Cl_2$ (2×20 ml). The combined organic layers were washed with water (2×20 ml) and extracted with 10% aqueous ammonia solution (20 ml). The aqueous layer was separated, evaporated under vacuum, and the residue was dissolved in anhydrous 2-PrOH (50 ml). The obtained solution was evaporated at atmospheric pressure to 20 ml volume, cooled, and the precipitate that formed was separated. An analytical sample of salt **14** was obtained by recrystallization from anhydrous EtOH. Yield 2.9 g (75%), colorless, fine agglomerates of needle-shaped crystals, mp 184°C (decomp.) (EtOH). Found, %: C 18.11; H 2.27; N 71.65. $C_3H_4N_{10}O$. Calculated, %: C 18.37; H 2.06; N 71.42.

**Amino(carbamoylamino)methanaminium 5-(4-azidofurazan-3-yl)tetrazolide (15)**. Method I (from reaction mixture after diazotation of amidrazone **13**). After the diazotation reaction of amidrazone **13** with $NaNO_2$ solution, followed by maintaining for 30 min at 10–15°C, the reaction mixture was basified to pH 7.0–7.5 by the addition of 25% aqueous ammonia solution (20–25 ml). The obtained solution was heated to reflux and treated by adding a hot solution of guanylurea sulfate (2.26 g, 15 mmol) in water (25 ml). The solution was cooled to room temperature, the precipitate that formed was filtered off, washed with ethanol (20 ml), and the product was recrystallized from water. The yield of salt **15** was 3.9 g (70%), agglomerates of fine, colorless irregularly shaped crystals, mp 206°C (decomp.). Found, %: C 21.22; H 2.68; N 64.88. $C_5H_7N_{13}O_2$. Calculated, %: C 21.36; H 2.51; N 64.75.

Method II (from ammonium salt **14**). Compound **14** (1 g, 5 mmol) was dissolved in water (5 ml), and the solution was treated with a hot solution of guanylurea (0.75 g, 5 mmol) in water (5 ml). The precipitate that formed after cooling to room temperature was filtered off and washed with cold water. The guanylammonium salt **15** was isolated in 1.33 g (95%) yield as agglomerates of fine, needle-shaped crystals.

**3-Azido-4-(2*H*-tetrazol-5-yl)furazan (7)**. Method I (from 5-(4-nitrofurazan-3-yl)-2*H*-tetrazole (**2**)). $NaN_3$ (1.62 g, 25 mmol) was added to a solution of compound **2** (1.83 g, 10 mmol) in acetonitrile (15 ml). The reaction mixture was stirred for 5 h at 55–60°C. The solvent was evaporated at reduced pressure, the residue was dissolved in water (10 ml), acidified with concd HCl to pH 1 and cooled to 0°C. The precipitate that formed was filtered off and

recrystallized from water. Yield 1.1 g (62%), white prismatic crystals, mp 102–103°C ($H_2O$).

Method II (through the diazonium salt **10**). Aminofurazan **1** (3.06 g, 0.02 mol) was dissolved in concd $H_2SO_4$ (30 ml, 55.2 g, 0.56 mol, *d* 1.84 g/cm$^3$). The obtained solution was treated at a temperature not exceeding 5°C by dropwise addition of nitrosylsulfuric acid solution, which was prepared by dissolving finely ground $NaNO_2$ (1.66 g, 0.024 mol) in concd $H_2SO_4$ (25 ml, 46 g, 0.47 mol, *d* 1.84 g/cm$^3$) at 0–5°C. After the addition was complete, the reaction mixture was stirred for 3 h at 0–5°C. The obtained solution of 4-(2*H*-tetrazol-5-yl)-furazan-3-diazonium hydrogen sulfate (**10**) was vigorously stirred with cooling and treated by dropwise addition of $NaN_3$ (3.25 g, 0.05 mol) that was dissolved in a minimum amount of water, while maintaining the reaction mixture temperature at 5–10°C (*Caution: evolution of $HN_3$!*). After completing the addition, the mixture was stirred for 1 h at room temperature and poured onto crushed ice (150 g). The mixture was extracted with $CH_2Cl_2$ (2×30 ml). The organic layers were combined and washed with water (20 ml). The solvent was evaporated at reduced pressure. The residue was dissolved in hot water (5 ml), treated with activated carbon (0.1 g), filtered, and the obtained filtrate was cooled to 0°C. The precipitate that formed was filtered off. Yield 0.97 g (27%), beige prismatic crystals, mp 100–101°C.

Method III (isolation from ammonium salt **14**). The ammonium salt **14** (10 g, 50 mmol) was dissolved in water (25 ml), then NaCl (4 g) was added, the solution was cooled to 10–15°C, vigorously stirred, and acidified with concd HCl to pH 1. The precipitate that formed was filtered off. Azide **7** was isolated as agglomerates of white, prismatic crystals. Yield 8.5 g (95%), mp 102.5–103.5°C ($H_2O$). Found, %: C 19.94; H 0.93; N 70.13. $C_3HN_9O$. Calculated, %: C 20.12; H 0.56; N 70.39.

**X-ray structural study of compound 7** was performed on an Oxford Diffraction Xcalibur CCD diffractometer with an EOS detector (Agilent Technologies UK, Ltd.), using a crystal with dimensions of 0.25 × 0.20 × 0.16 mm. The data collection was performed at 100(1) K. The data processing, solving and refinement of unit cell parameters were performed with the CrysAlis PRO program (Agilent Technologies UK, Ltd., 2011). A total of 5280 reflections were collected, of which 1769 were independent ($R_{int}$ 0.0359). The structure was solved by direct method using the SIR92[37] program, followed by a series of electron density map calculations. The hydrogen atom positions were determined objectively from the difference electron density synthesis and refined in isotropic approximation. The full-matrix anisotropic refinement of non-hydrogen atoms by method of least squares was performed with the SHELXL-97 program[38] at $R_1$ 0.0596, $wR_2$ 0.1759 by 1436 reflections with $I \geq 2\sigma(I)$ and $R_1$ 0.0712, $wR_2$ 0.1871 by all 1769 reflections. *GOOF* 1.110. The number of refined parameters was 122. The maximum electron density from the difference electron density synthesis maps was equal to 0.408 e/Å$^3$. The main crystallographic parameters: space group $P2_1/n$; *a* 6.9664(11), *b* 9.3410(11), *c* 10.2002(15) Å; β 90.27°; *V* 663.75(16) Å$^3$; *Z* 4; *d* 1.953 g/cm$^3$; μ 0.167 mm$^{-1}$. The complete crystallographic dataset for compound **7** was deposited at the Cambridge Crystallographic Data Center (deposit CCDC 1038997).

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