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[(3-Nitro-1*H*-1,2,4-triazol-1-yl)-*NNO*-azoxy]furazans: energetic materials containing an N(O)=N–N fragment†

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The strategy for the synthesis of substituted [(3-nitro-1*H*-1,2,4-triazol-1-yl)-*NNO*-azoxy]furazans **4**–**7**, in which the distal nitrogen of the azoxy group is bonded to the nitrogen atom of the azole ring, includes, firstly, the reaction of 1-amino-3-nitro-1*H*-1,2,4-triazole with 2,2,2-trifluoro-*N*-(4-nitrosofurazan-3-yl) acetamide in the presence of dibromisocyanuric acid followed by removing of the trifluoroacetyl protecting group to afford aminofurazan (**4**). Transformation of the amino group in the latter made it possible to synthesize the corresponding nitro (**5**), azo (**6**), and methylene dinitramine (**7**) substituted furazans. The compounds synthesized are thermally stable (decomposition onset temperatures 147–228 °C), exhibit acceptable densities (1.77–1.80 g cm^{-3}) and optimal oxygen balance (the oxidizer excess coefficients $\alpha = 0.42–0.71$). Their standard enthalpies of formation (576–747 kcal kg^{-1}) were determined experimentally by combustion calorimetry and these compounds have been estimated as potential components of solid composite propellants. In terms of the specific impulse level, model solid composite propellant formulations based on nitro and methylene dinitramine substituted furazans **5** and **7** outperform similar formulations based on CL-20 by 1–4 s, and formulations based on HMX and RDX by 5–8 s.

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Introduction

Currently, one of the most dynamically developing areas of the chemistry of energetic materials is the synthesis of nitrogen–oxygen heterocyclic systems.[1] Of particular interest are compounds that combine a high enthalpy of formation (>500 kcal kg^{-1}), high density (≥1.80 g cm^{-3}), and optimal oxygen balance (oxidizer excess coefficients $\alpha \geq 0.6$). Such substances are required for development of solid composite propellants (SCP) with high specific impulses.[2]

The majority of newly synthesized energetic compounds are nitrogen heterocycles with energy-rich functional groups such as $–NO_2$, $–NHNO_2$, $–N_3$, $–C(NO_2)_3$ and others. One such group is the azoxy group –N(O)=N–. The introduction of the azoxy group into a molecule improves its oxygen balance and increases the enthalpy of formation (compare, for example, the enthalpy of formation of 4,4′-dinitro-3,3′-difurazan[3] and 4,4′-dinitro-3,3′-azoxyfurazan (**1**),[3] 3,4-dinitrofurazan[4] and 3-nitro-4-(nitro-*NNO*-azoxy)furazan[4]). In general, the azoxy group can be part of complex explosophoric groups (*e.g.* $–N(O)=N–NO_2$ (ref. 4 and 5) and $–N=N(O)–C(NO_2)_3$ (ref. 6)) or it can be embedded in a heterocycle scaffold (*e.g.* 1,2,3,4-tetrazine 1,3-dioxides,[7,8] 1,2,4,5-tetrazine 2,4-dioxides,[9] *N*-oxides of tetrazole[10]).

Alternatively, the azoxy group can be a bridge between two heterocycles (Fig. 1). The most studied are compounds **A**, in which the terminal N atom of the azoxy group is bonded to the carbon atom of the heterocycle.[11,12] 4,4′-Dinitro-3,3′-azoxyfurazan **1** is one of the representative compounds of this kind.[3] Compounds **B**, in which the terminal N atom of the azoxy group is bonded to the N atom of the heterocycle, are scarcely studied. As far as we know, only two representatives of *N*-(azoxy)azoles have been described: 4-[(2-methylphenyl)-*ONN*-azoxy]-4*H*-1,2,4-triazole (**2a**)[13] and 4-[(2,4,6-trichlorophenyl)-*ONN*-azoxy]-4*H*-1,2,4-triazole (**2b**).[14]

At the same time, compounds **B** exhibit a higher heat of formation than isomeric compounds **A**. According to quantum chemical calculations (semi-empirical PM3 method),

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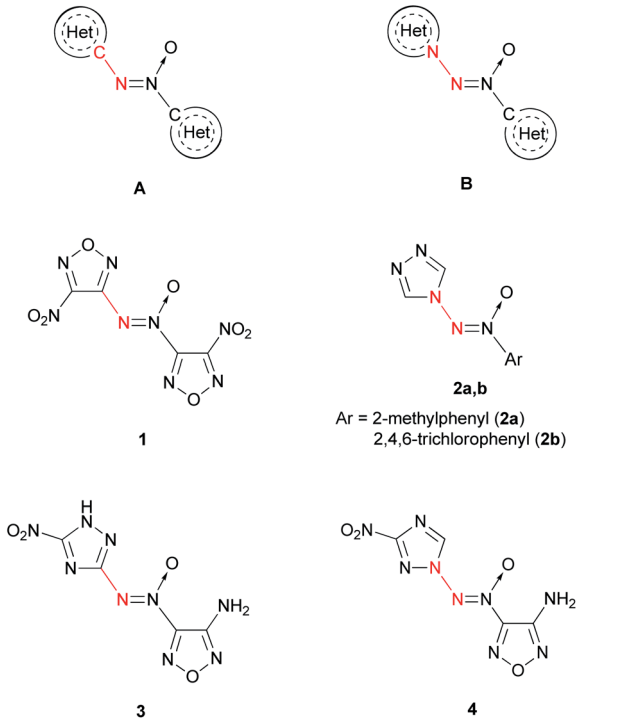


Fig. 1 Two different modes of connection of terminal N atom of the azoxy group with heterocycles: C–N linking (A, 1, 3) and N–N linking (B, 2, 4).

compound **4** is 22 kcal mol^{-1} higher in energy than hypothetical compound **3** (Fig. 1). Apparently, this is due to the presence of an additional N–N bond in the former molecule.

In this work, we report on the synthesis of energetic aminofurazan **4** and related energetic heterocyclic systems.

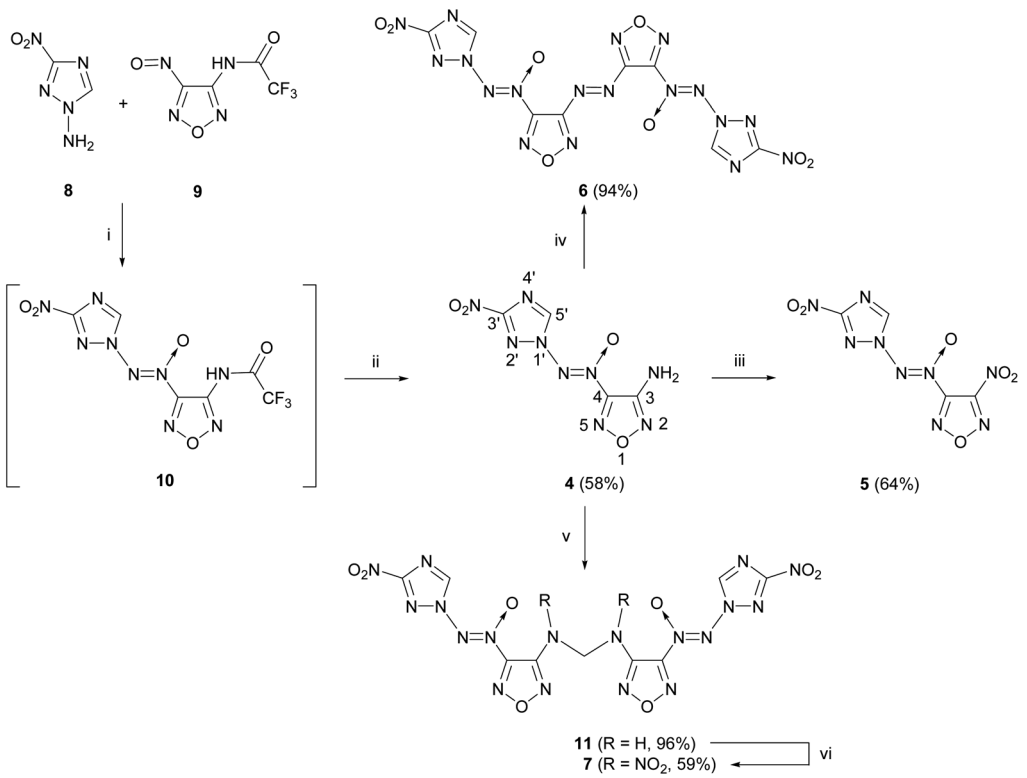
Results and discussion

Synthesis of [(3-nitro-1*H*-1,2,4-triazol-1-yl)-*NNO*-azoxy] furazans (4–7)

The starting compounds for the synthesis of [(3-nitro-1*H*-1,2,4-triazol-1-yl)-*NNO*-azoxy]furazans **4–7** are nitrosofurazan **9** with a trifluoroacetyl protecting group and 1-amino-3-nitro-1,2,4-triazole **8** obtained by an improved method based on two previously published methods (Scheme 1).[15,16]

To form an azoxy bridge, nitrosofurazan **9** was condensed with aminotriazole **8** in the presence of dibromisocyanuric acid (DBI) in acetonitrile as a solvent. The intermediate azoxyfurazan **10** was not isolated, and the trifluoroacetyl protecting group was removed by acid hydrolysis to obtain aminofurazan **4** in 58% yield. Further transformation of the amino group of aminofurazan **4** afforded energetic compounds **5–7** (see Scheme 1).

For the oxidation of aminofurazan **4** to nitrofurazan **5**, we used the previously developed method of oxidation of the amino group to the nitro group under the action of an excess of N_2O_5.[17] The reaction in acetonitrile at 0 °C takes 14 days to give nitrofurazan **5** in 64% yield.



Scheme 1 Synthesis of substituted [(3-nitro-1*H*-1,2,4-triazol-1-yl)-*NNO*-azoxy]furazans **4–7**. Reagents and conditions: (i) DBI, MeCN, 0 °C, 2 h; (ii) CF_3CO_2H, MeOH, H_2O, 0 °C, 12 h; (iii) N_2O_5 (10 equiv.), MeCN, −20 °C, then 0 °C, 14 days; (iv) $KMnO_4$, HCl, H_2O, 55 °C, 4 h; (v) CH_2O, H_2SO_4, H_2O, 1,4-dioxane, 20 °C, 40 min; (vi) N_2O_5 (2 equiv.), MeCN, −20 °C, then 0 °C, 1 h.

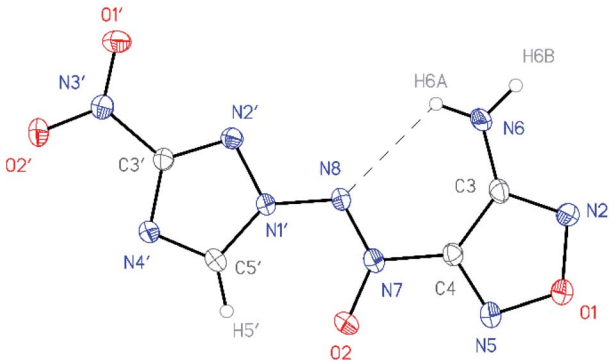


Fig. 2 General view of aminofurazan **4** in a crystal; non-hydrogen atoms are represented by probability ellipsoids of atomic displacements (p = 50%).

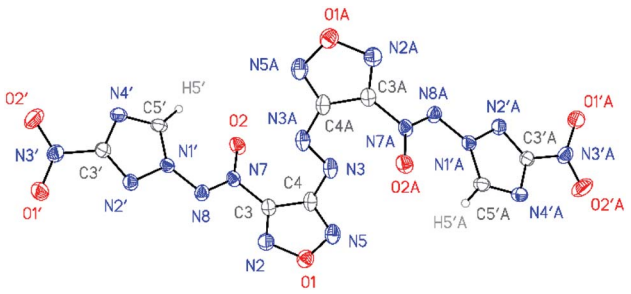


Fig. 4 General view of azofurazan **6** in a crystal; non-hydrogen atoms are represented by probability ellipsoids of atomic displacements (p = 50%). Symmetrically independent is a half of the molecule labeled without A suffix.

Aminofurazan **4** was converted to azofurazan **6** in almost quantitative yield under the action of $KMnO_4$ in conc. hydrochloric acid at 55 °C.

Methylene dinitramine **7** was obtained in two stages with the overall yield of 57% by condensation of aminofurazan **4** with formaldehyde in the presence of sulfuric acid, followed by nitration of the intermediate methylene diamine **11** with N_2O_5 in acetonitrile.

Crystal structures and spectroscopy

All compounds synthesized were characterized by multinuclear NMR and IR spectroscopy and high resolution mass spectrometry. The structures of compounds **4–6** were confirmed by single-crystal X-ray diffraction studies[18] (Fig. 2–4).

According to X-ray structural data, in compounds **4–6** the azoxy group and the triazole ring are practically co-planar [dihedral angles C(5′)–N(1′)–N(8′)–N(7′) vary from 2.8(2)° in **6** to 10.1(5)° in **5**]. Interestingly, the average value of 8.5(4)° is observed in the aminofurazan **4** where the planar conformation is additionally stabilized by the intramolecular H-bond N(6)–H(6A)···N(8) [N···N 2.930(3) Å]. The lengths of the N(1′)–N(8) bonds in these molecules vary from 1.3716(17) Å in **6** to 1.384(3) Å in **4**, which is somewhat shorter than the length of the single N–N bond in the hydrazine derivatives in solid state (1.400 ± 0.020 Å, calculated for 1220 single-bonded non-charged non-disordered acyclic hydrazine moieties with hydrazine N atoms connected to H, C, N or O atoms, from Cambridge Structural Database,[19] v. 5.41). The distances between the H(5′)···O(2) atoms in molecules **4–6** (2.20 Å with C–H set to 1.089 Å) are lower than the sum of the van der Waals radii[20] of hydrogen and oxygen atoms (2.72 Å).

The densities of the compounds were estimated from unit cell volumes obtained by single-crystal X-ray data at 120 K and powder diffraction data at ambient conditions (approximately 298 K). Aminofurazan **4** was found to have a density of 1.784 g cm^{-3} at 298 K and 1.830 g cm^{-3} at 120 K. Nitrofurazan **5**

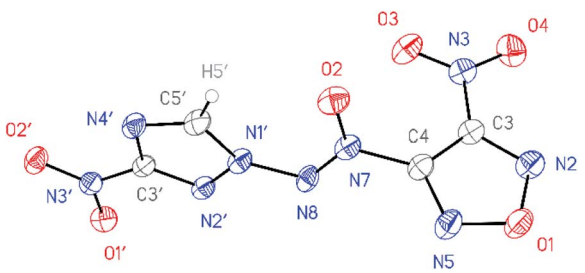


Fig. 3 General view of nitrofurazan **5** in a crystal; non-hydrogen atoms are represented by probability ellipsoids of atomic displacements (p = 50%).

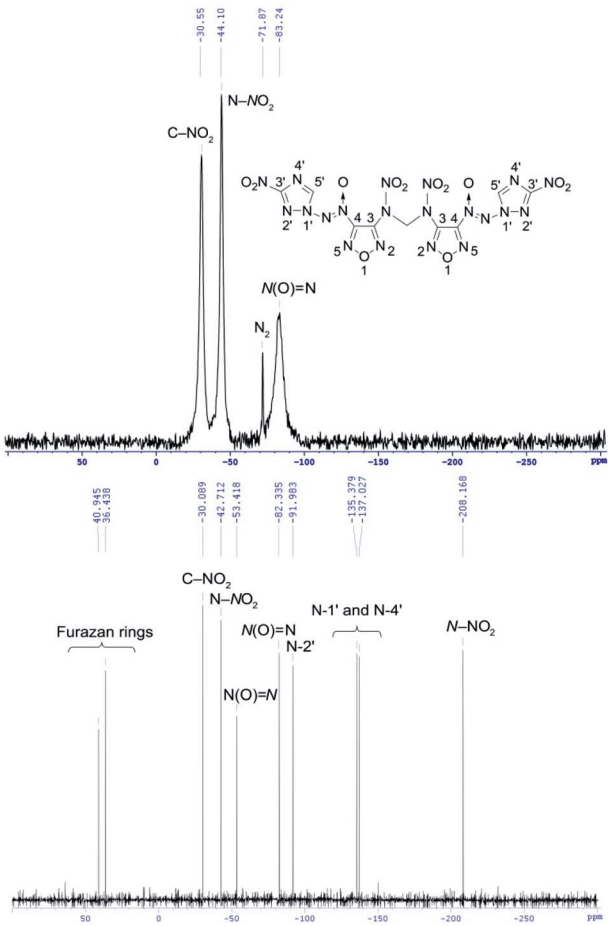


Fig. 5 ^{14}N and ^{15}N NMR spectra of methylene dinitramine **7**.

Table 1 Standard thermochemical characteristics for compounds 4–7

Compound	$-\Delta U_B'$ [cal g^{-1}][a]	$-\Delta H_c^\circ$ [kcal mol^{-1}][b]	ΔH_f° [kcal mol^{-1}][c]
4	2587.0 ± 1.5	619.4 ± 0.4	140.7 ± 0.4
5	2110.2 ± 2.0	566.5 ± 0.5	156.1 ± 0.5
6	2482.3 ± 2.7	1177.7 ± 1.3	356.9 ± 1.3
7	2290.2 ± 3.5	1326.3 ± 2.0	343.2 ± 2.0

[a] Energy of combustion under bomb conditions. [b] Standard enthalpy of combustion. [c] Standard enthalpy of formation.

has a density of 1.796 g cm^{-3} at 298 K and 1.836 g cm^{-3} at 120 K. The density of azofurazan **6**, measured by powder X-ray diffraction analysis, was 1.765 g cm^{-3} at 298 K and 1.815 cm^{-3} at 120 K.

^{14}N NMR spectroscopy is useful method for identifying positively charged nitrogen atoms in the azoxy and nitro groups (see for example ^{14}N NMR spectrum of methylene dinitramine **7** on Fig. 5).

The ^{14}N NMR spectra of compounds **4–7** and **11** bearing the azoxy groups showed signals at $\delta = -74$ to -88 ppm [*N*(O)═N, $\Delta\nu_{1/2}$ = 80–500 Hz]. Signals of the C–NO$_2$ groups of triazole ring were registered at $\delta = -27$ to -31 ppm ($\Delta\nu_{1/2}$ = 80–580 Hz). Signal at $\delta = -41$ ppm (C–NO$_2$ of furazan ring, $\Delta\nu_{1/2}$ = 10 Hz) was registered in the ^{14}N NMR spectrum of nitrofurazan **5**. Signal at $\delta = -44$ ppm (N–NO$_2$, $\Delta\nu_{1/2}$ = 100 Hz) was registered in the spectrum of methylene dinitramine **7**.

^{15}N NMR spectroscopy is a powerful tool for confirming the structure of molecules consisting of 1,2,4-triazole and furazan cores, azoxy and azo bridges, amino and nitramino groups. This analysis allows detecting the signals of nitrogen atoms that are not visible in the ^{14}N NMR spectra (see for example ^{15}N NMR spectrum of methylene dinitramine **7** on Fig. 5). The ^{15}N NMR spectra of compounds **4–7** and **11** containing a 1,2,4-triazole core showed signals at $\delta = -91.0$ to -92.0 ppm [N(2′) atom of triazole ring] and signals at $\delta = -134.8$ to -137.8 ppm [N(1′) and N(4′) atoms of triazole ring]. The ^{15}N NMR spectra of compounds **4–7** and **11** containing a furazan core showed signals at δ = 44.0 to −4.8 ppm (nitrogen atoms of furazan ring). Signal at δ = 143.4 ppm (N═N) was registered in the ^{15}N NMR spectrum of azofurazan **6** containing azo bridge. Signals at $\delta = -48.6$ to -57.3 ppm [N(O)═*N*] ppm were registered in the ^{15}N NMR spectra of compounds **4–7** and **11** bearing the azoxy bridge. The ^{15}N NMR spectrum of compound **11** containing a methylene diamino moiety showed signal at $\delta = -316.1$ ppm (NH). The ^{15}N NMR spectrum of methylene dinitramine **7** containing a nitramino group showed signal at $\delta = -208.2$ ppm (*N*–NO$_2$) (for details see ESI†).

Thermal stability and energetic properties

The thermal stability of compounds **4–7** was determined with differential scanning calorimetry (DSC) (for details see ESI†). All these compounds exhibited good thermal stability. DSC analysis showed that the decomposition of these compounds begins in the range of 147–226 °C. Nitrofurazan **5** was found to be the most stable (T_m = 117 °C, T_{onset} = 228 °C). Aminofurazan **4** melts with decomposition (T_{onset} = 200 °C). Azofurazan **6** decompose without melting (T_{onset} = 184 °C), whereas methylene dinitramine **7** is least stable (T_{onset} = 147 °C).

Table 2 Physical and detonation properties of compounds 4–7 in comparison with RDX

	4	**5**	**6**	**7**	RDX
Formula	$C_4H_3N_9O_4$	$C_4HN_9O_6$	$C_8H_2N_{18}O_8$	$C_9H_4N_{20}O_{12}$	$C_3H_6N_6O_6$
FW [g mol^{-1}][a]	241	271	478	584	222
d [g cm^{-3}][b]	1.78	1.80	1.77	1.79[o]	1.82[q]
T_m [°C][c]	200	117	—	—	204[q]
T_d [°C][d]	200	228	184	147	204[q]
α[e]	0.42	0.71	0.47	0.6	0.67
N [%][f]	52.28	46.49	52.72	47.95	37.84
Ω_{CO} [%][g]	−9.96	8.86	−3.35	2.74	0
Ω_{CO_2} [%][h]	−36.51	−14.76	−30.13	−21.92	−21.62
$-\Delta H_c^\circ$ [kcal mol^{-1}][i]	+584	+576	+747	+588	+72[q]
v_D [km s^{-1}][j]	8.71[p]	8.83[p]	8.69[p]	8.79[p]	8.96[p] 8.75[q]
P_{C-J} [GPa][k]	33.9[p]	36.2[p]	34.0[p]	35.5[p]	36.6[p] 35.0[q]
Q_D [kcal kg^{-1}][l]	1425[p]	1609[p]	1539[p]	1570[p]	1479[p] 1512[q]
IS [J][m]	9	2	1	2	7.5[q]
FS [N][n]	210	35	23	65	120[q]

[a] Formula weight. [b] Density measured by powder diffraction at 298 K. [c] Melting temperature (DSC). [d] Decomposition temperature (extrapolated onset temperature at a heating rate of 5 °C min^{-1}). [e] Oxidizer excess coefficient. [f] Nitrogen content. [g] Oxygen balance (based on CO). [h] Oxygen balance (based on CO_2). [i] Experimentally measured standard enthalpy of formation. [j] Detonation velocity. [k] Detonation pressure. [l] Heat of detonation. [m] Impact sensitivity. [n] Friction sensitivity. [o] Density measured by gas pycnometer at 298 K. [p] Calculated with Shock and Detonation (S&D) Version 4.5. [q] Ref. 25.

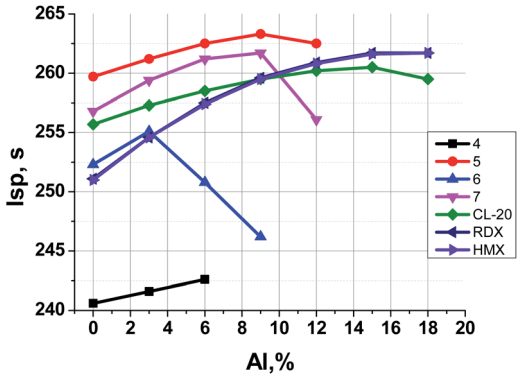


Fig. 6 Formulations of the organic energetic filler + the active binder (18 vol%, 14.5–15.5 wt%) + aluminum. Dependence of I_{sp} on the kind of the organic energetic filler and on the content of aluminum in the formulation.

The standard enthalpies of combustion (ΔH_c°) for compounds **4–7** were determined experimentally by the method of combustion (bomb) calorimetry and the standard enthalpies of formation (ΔH_f°) were calculated from ΔH_c° (for details see ESI†).[21] Standard thermochemical characteristics (ΔH_c° and ΔH_f°) for compounds **4–7** are shown in Table 1.

Azofurazan **6** has the highest enthalpy of formation ($\Delta H_f^\circ = +747$ kcal kg^{-1}) (Table 2). Furazans **4**, **5** and **7** have almost the same enthalpies of formation in the range from +576 to +588 kcal kg^{-1}. Thus, new compounds **4–7** significantly exceed the commonly used energetic materials and CL-20 ($\Delta H_f^\circ = +205$ kcal kg^{-1})[22] in terms of the enthalpy of formation.

All calculations concerning the detonation parameters were carried out using the Shock and Detonation (S&D) Version 4.5 Program package[23] and were based on the standard enthalpies of formation and attributed to the corresponding densities. Compounds **4–7** show calculated detonation velocities in the range of 8.69–8.83 km s^{-1} and detonation pressures in the range of 33.9–36.2 GPa, which is close to the calculated values for RDX (8.96 km s^{-1} and 36.6 GPa) (see Table 2).

The sensitivity of compounds **4–7** toward impact (IS) and friction (FS) was determined according to the STANAG[24] standards. Aminofurazan **4** was found to be the least sensitive to mechanical stimuli (IS = 9 J, FS = 210 N). Thus, **4** is less sensitive than benchmark RDX explosive (IS = 7.5 J, FS = 120 N).[25] Methylene dinitramine **7** (IS = 2 J, FS = 65 N) and nitrofurazan **5** (IS = 2 J, FS = 35 N) show the response to mechanical hazards on the level of nitroether compounds (PETN: IS = 3 J, FS = 60 N).[25] Azofurazan **6** has the impact and friction sensitivity values approaching the primary explosives (lead azide: IS = 1 J, FS < 5 N).[26]

Energetic properties of compounds 4–7 as components of solid composite propellants

Compounds **4–7** have oxidizer excess coefficients $\alpha = 0.42$–0.71, therefore the most effective is to use them as components of solid composite propellants (SCP) with so called active binders.[27] We have considered SCP formulations containing such a percentage (that is about 13.5–16.0 wt%) of the active binder $C_{18.96}H_{34.64}N_{19.16}O_{29.32}$; ($\Delta H_f^\circ = -757$ kJ kg^{-1}, $\rho = 1.49$ g cm^{-3}),[28] so that the volume percentage of the binder is always 18 ± 0.1%. In addition to compounds **4–7**, CL-20, HMX, and RDX were also considered as components of SCP to compare their effectiveness.

The formulations containing ammonium perchlorate (AP) together with compounds **4–7**, CL-20, HMX, and RDX have been also considered as well as formulations containing aluminum (up to 18%).

The specific impulses values (I_{sp}) were calculated with the standard code TERRA[29] (at pressures in combustion chamber and the exit nozzle section 4.0 and 0.1 MPa accordingly).

Fig. 6 illustrates the dependence of calculated I_{sp} values of propellants on content of Al. The data for analogous formulations with RDX, HMX and CL-20 are also shown for comparison. Table 3 represents the main characteristics of binary formulations of propellants containing the organic energetic filler and the active binder (18 vol%, 14.5–15.5 wt%).

It can be seen (Fig. 6, Table 3) that for binary systems: energetic filler + active binder (without aluminum) formulations with nitrofurazan **5** and methylene dinitramine **7** have I_{sp} higher (by 1–8 s) than formulations with CL-20, HMX, and RDX, and azofurazan **6** demonstrates I_{sp} a bit higher (by 1 s) than formulations with HMX, and RDX. Aminofurazan **4** has I_{sp} less than all other formulations. The addition of Al increases I_{sp} of all compositions, but it does not change their relative effectiveness.

In Fig. 7 one can see that the most effective compounds (**5**, **7**, CL-20) do not need AP for I_{sp} increase, the formulations with less effective compounds such as **6**, RDX and HMX can increase I_{sp} a bit, while in formulations with aminofurazan **4**, which is

Table 3 The main energetic characteristics of binary formulations containing the organic energetic filler + the active binder (18 vol%, 14.5–15.5 wt%)

Organic energetic filler	wt% of organic energetic filler	Density, g cm^{-3}	Temperature in the combustion chamber, K	I_{sp}, s
5	84.75	1.761	3680	**259.7**
7	84.55	1.736	3580	**256.8**
CL-20	86.20	1.944	3450	255.7
6	84.47	1.728	3540	252.3
HMX	85.35	1.832	3175	251.0
RDX	84.75	1.761	3180	251.1
4	84.55	1.736	3080	240.6

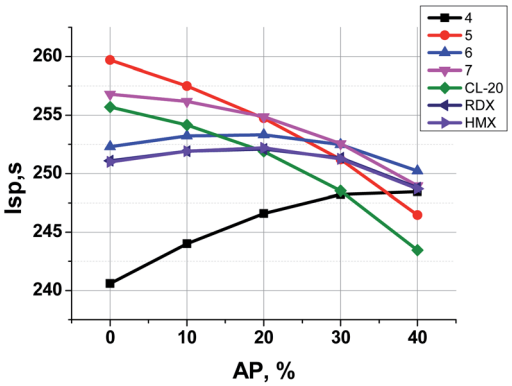


Fig. 7 Formulations of the organic energetic filler + the active binder (18 vol%, 14.5–15.5 wt%) + ammonium perchlorate (AP). Dependence of I_{sp} on the kind of the organic energetic filler and on the content of AP in the formulation.

the less energetic among all others, the AP introducing allows to increase I_{sp} considerably.

It should be noted that the main characteristics that determine the effectiveness of compound as organic energetic filler of propellant are enthalpy of formation, molecular composition and coefficient of oxygen excess α. Therefore, compounds **5** and **7** having high enthalpies of formation [$\Delta H_f^\circ = +576$ kcal kg^{-1} (for **5**), $+588$ kcal kg^{-1} (for **7**)] in combination with optimal oxygen balance [$\alpha = 0.71$ (for **5**), 0.6 (for **7**)] outperform RDX, HMX and CL-20 as energetic fillers of propellants.

Conclusions

In summary, substituted [(3-nitro-1*H*-1,2,4-triazol-1-yl)-*NNO*-azoxy]furazans **4**–**7**, in which the distal nitrogen of the azoxy group is bonded to the nitrogen atom of the azole, have been synthesized and fully characterized. The compounds obtained exhibit good thermal stability, optimal oxygen balance, and high experimental enthalpies of formation. Model solid propellant compositions containing compounds **5** and **7** have promising calculated specific impulses exceeding ones with CL-20, HMX and RDX. The sensitivity to mechanical stimuli for compounds obtained varies from moderate to high depending on substituents in the furazan ring.

Experimental section

Safety precautions

While we have experienced no difficulties in syntheses and characterization of these energetic materials, proper protective measures should be used. Manipulations must be carried out in a hood behind a safety shield. Face shield and leather gloves must be worn. Mechanical actions involving scratching or scraping must be avoided.

General methods

^{1}H, ^{13}C, ^{14}N and ^{15}N NMR spectra were recorded with a Bruker DRX-500 spectrometer with frequencies of 500.1, 125.8, 36.1, 50.7 MHz and Bruker AV600 spectrometer with frequencies of 600.1, 150.9, 43.4, 60.8 MHz, respectively. *Chemical shifts* are reported in delta (δ) *units*, parts per million (ppm) downfield from internal TMS (^{1}H, ^{13}C) or external CH_3NO_2 (^{14}N, ^{15}N negative values of δ_N correspond to upfield shifts). J and $\Delta\nu_{1/2}$ values are given in Hz. The IR spectra were recorded with a Bruker ALPHA-T spectrometer in the range 400–4000 cm^{-1} (resolution 2 cm^{-1}) as pellets with KBr or as a thin layer. High-resolution mass spectra (HRMS) were recorded by electrospray ionization (ESI) with a Bruker micrOTOF II instrument. Thermochemical measurements were carried out on a precision automatic combustion calorimeter with an isothermal coating specifically developed for the combustion of energetic compounds.[21] Melting points were determined with a Kofler melting point apparatus and are uncorrected. Thermal behavior was studied using Netzsch DSC 204 HP in nitrogen flow. A sample of *ca.* 0.5 mg were placed in closed aluminium crucibles with pierced lids and heated linearly with 5 K min^{-1} rate up to 400 °C. The impact and friction sensitivities of compounds **4**–**7** were determined using a STANAG protocol and BAM-type impact and friction machines.[24] Density was measured with a Micromeritics AccuPyc II 1340 gas pycnometer. Silica gel 60 Merck (15–40 μm) was used for preparative column and thin-layer chromatography. Silica gel "Silpearl UV 254" was used for preparative column and thin-layer chromatography. Analytical thin-layer chromatography (TLC) was carried out on Merck silica gel 60 F254 and "Silufol" TLC silica gel UV-254 aluminum sheets. All reagents were purchased from Acros and Sigma-Aldrich. Solvents were purified before use, according to standard procedures. All other reagents were used without further purification. 2,2,2-Trifluoro-*N*-(4-nitrosofurazan-3-yl)acetamide (**9**)[4] was prepared according to the reported procedure.

Single crystal X-ray diffraction data were collected on a Bruker APEX DUO diffractometer (λ(MoKα) = 0.71072 Å, graphite monochromator, ω-scans). A semiempirical absorption correction was applied with the SADABS program[30] using intensity data of the equivalent reflections. Structures were solved with a dual-space method with SHELXT program[31] and refined on F^2 in anisotropic approximation with SHELXL program.[31] Hydrogen atoms of the amino groups in aminofurazan **4** were found from difference Fourier synthesis and refined in isotropic approximation. All other hydrogen atoms were placed in calculated positions and refined in a riding model with isotropic displacement parameters U_{iso}(H) equal 1.2U_{eq}(C). Full crystallographic data have been deposited with the Cambridge Crystallographic Data Center, CCDC 2067440 (for compound **4**), CCDC 2067439 (for compound **5**), CCDC 2067441 (for compound **6**). Detailed crystallographic data are provided in the ESI.†

X-ray powder diffraction studies were performed on a Bruker AXS D8 Advance Vario diffractometer for compound **4** (primary monochromator, CuKα_1, λ = 1.54056 Å, transmission mode) and on a Bruker AXS D8 diffractometer for compounds **5** and **6** (CuKα, λ = 1.534 Å, reflection mode), both equipped with a LynxEye position sensitive detector. Data collection was performed at ambient temperature with a step size of 0.02° and 1 s per step exposure for the 2θ range of 4–60°. Unit cell parameters were refined with a constrained Rietveld method using atomic

coordinates and equivalent isotropic displacement parameters taken from low-temperature single-crystal experiments. In all cases, no phase transition was observed.

Syntheses

1-Amino-4-nitro-1*H*-1,2,4-triazole (8). 3-Nitro-1*H*-1,2,4-triazole (10.00 g, 87.7 mmol) was added in one portion to a stirred solution of NaOH (27.72 g, 693.0 mmol) and KH_2PO_4 (47.72 g, 350.9 mmol) in water (370 mL) at 25 °C. Then *O*-hydroxylamine sulfonic acid (29.73 g, 263.1 mmol) was added. The reaction mixture was stirred at 60 °C for 4 h, cooled to room temperature and then extracted with AcOEt (6 × 80 mL). The combined organic extracts were washed with water (70 mL), brine (70 mL), dried with anhydrous $MgSO_4$ and concentrated under reduced pressure to give triazole **8** (7.55 g, 66%) as colorless crystals, mp 138–139 °C. The compound obtained was identical (^{1}H, ^{13}C NMR, TLC) to triazole **8** prepared according to known procedures.[15,16]

3-Amino-4-[(3-nitro-1*H*-1,2,4-triazol-1-yl)-*NNO*-azoxy]-furazan (4). 1-Amino-3-nitro-1*H*-1,2,4-triazole (**8**) (5.00 g, 38.4 mmol) was added in several portions to a stirred suspension of 2,2,2-trifluoro-*N*-(4-nitrosofurazan-3-yl)acetamide (**9**) (10.10 g, 48.1 mmol) and DBI (14.90 g, 51.9 mmol) in dry MeCN (55 mL) at 0 °C under an argon atmosphere. The reaction mixture was vigorously stirred 0 °C for 2 h. The precipitate of cyanuric acid was then filtered off, washed with CH_2Cl_2 (2 × 15 mL). The combined filtrates were concentrated under reduced pressure. The residue was dissolved in MeOH (40 mL), and the solution of CF_3CO_2H (2.8 mL) in H_2O (14 mL) was added. The resulting reaction mixture was kept at 0 °C for 12 h. The precipitate was collected by filtration, washed with EtOAc (3 × 5 mL) and dried in air to give furazan **4** (5.40 g, 58%) as a yellow solid, mp 200–205 °C. DSC (5 °C min^{-1}): T_{onset} = 200 °C (dec.). ^{1}H NMR (500.1 MHz, acetone-d$_6$): δ 6.60 (br s, 2H, NH_2), 9.97 (s, 1H, H-5′) ppm. ^{13}C NMR (125.8 MHz, acetone-d$_6$): δ 145.5 (C-5′), 150.7 (br s, C-4), 151.7 (br t, C-3, $^1J_{C,N}$ = 5.6 Hz), 160.8 (br, C-3′) ppm. ^{14}N NMR (36.1 MHz, acetone-d$_6$): δ −29 (C–NO_2, $\Delta\nu_{1/2}$ = 80 Hz), −74 [*N*(O)=N, $\Delta\nu_{1/2}$ = 80 Hz], −135 (N-1′ or N-4′, $\Delta\nu_{1/2}$ = 560 Hz), −340 (NH_2, $\Delta\nu_{1/2}$ = 720 Hz) ppm. ^{15}N NMR ([INVGATED], 50.7 MHz, DMSO-d$_6$): δ 27.7, −3.2 (furazan ring), −29.5 (C–NO_2), −57.3 [N(O)=*N*], −74.2 [*N*(O)=N], −91.8 (N-2′), −136.7 (N-1′ or N-4′), −137.8 (N-4′ or N-1′), −333.4 (NH_2) ppm. IR (KBr): ν 3471 (s), 3311 (m), 3157 (m), 1630 (s), 1561 (m), 1519 (s), 1427 (m), 1420 (m), 1383 (w), 1348 (w), 1304 (m), 1230 (w), 1216 (w), 1170 (m) cm^{-1}. HRMS (ESI): *m*/*z* calcd for [$C_4H_3N_9O_4$ + Na^+]: 264.0200; found [M + Na]$^+$: 264.0205.

3-Nitro-4-[(3-nitro-1*H*-1,2,4-triazol-1-yl)-*NNO*-azoxy]-furazan (5). N_2O_5 (15.23 g, 141.0 mmol) was added in one portion to a stirred solution of furazan **4** (3.40 g, 14.1 mmol) in dry MeCN (30 mL) at −20 °C under an argon atmosphere. The reaction mixture was warmed to 0 °C and kept at this temperature for 14 days. Then the reaction mixture was concentrated under reduced pressure. The residue was purified by preparative column chromatography (petroleum ether/ethyl acetate, 3 : 1) to give furazan **5** (2.44 g, 64%) as a white solid, mp 117–118 °C. DSC (5 °C min^{-1}): T_m = 117 °C, T_{onset} = 228 °C (dec.). ^{1}H NMR (600.1 MHz, acetone-d$_6$): δ 10.16 (s, 1H, H-5′) ppm. ^{13}C NMR (150.9 MHz, acetone-d$_6$): δ 145.9 (C-5′), 151.4 (br s, C-4), 155.3 (br t, C-3, $^1J_{C,N}$ = 20.5 Hz), 161.0 (br s, C-3′) ppm. ^{14}N NMR (43.4 MHz, acetone-d$_6$): δ −31 [C–NO_2 (triazole), $\Delta\nu_{1/2}$ = 85 Hz], −41 [C–NO_2 (furazan), $\Delta\nu_{1/2}$ = 10 Hz], −88 [*N*(O)=N, $\Delta\nu_{1/2}$ = 130 Hz] ppm. ^{15}N NMR ([INVGATED], 60.8 MHz, acetone-d$_6$): δ 44.0, 42.3 (furazan ring), −30.1 [C–NO_2 (triazole)], −40.9 [C–NO_2 (furazan)], −48.6 [N(O)=*N*], −87.7 [*N*(O)=N], −91.0 (N-2′), −134.8 (N-1′ or N-4′), −135.3 (N-4′ or N-1′) ppm. IR (KBr): ν 1590 (s), 1557 (s), 1525 (s), 1432 (m), 1386 (w), 1360 (m), 1301 (s), 1243 (w), 1201 (m), 1162 (w) cm^{-1}. HRMS (ESI): *m*/*z* calcd for [$C_4HN_9O_6$ + Na^+]: 293.9942; found [M + Na]$^+$: 293.9930.

3,3′-(*E*)-Diazen-1,2-diylbis{4-[(3-nitro-1*H*-1,2,4-triazol-1-yl)-*NNO*-azoxy]furazan} (6). A solution of $KMnO_4$ (1.19 g, 7.5 mmol) in water (45 mL) was added dropwise to a vigorously stirred suspension of finely powdered furazan **4** (1.5 g, 6.0 mmol) in concentrated HCl (25 mL) at 0 °C. The reaction mixture was warmed to 55 °C and vigorously stirred at this temperature for 4 h. The resulting pale yellow precipitate was collected by filtration, washed with H_2O (15 mL), AcOEt (4 × 6 mL) and dried in air to give furazan **6** (1.4 g, 94%) as a pale yellow solid. DSC (5 °C min^{-1}): T_{onset} = 184 °C (dec.). ^{1}H NMR (600.1 MHz, DMSO-d$_6$): δ 10.16 (s, 1H, H-5′) ppm. ^{13}C NMR (150.9 MHz, DMSO-d$_6$): δ 145.4 (C-5′), 153.5 (br s, C-3 or C-4), 156.8 (br s, C-4 or C-3), 159.5 (C-3′) ppm. ^{14}N NMR (43.4 MHz, DMSO-d$_6$): δ −27 (C–NO_2, $\Delta\nu_{1/2}$ = 580 Hz), −79 [*N*(O)=N, $\nu_{1/2}$ = 500 Hz] ppm. ^{15}N NMR ([INVGATED], 60.8 MHz, DMSO-d$_6$): δ 143.4 (N=N), 35.4, 31.1 (furazan rings), −29.5 (C–NO_2), −50.4 [N(O)=*N*], −81.1 [*N*(O)=N], −91.5 (N-2′), −135.6 (N-1′ or N-4′), −135.9 (N-4′ or N-1′) ppm. IR (KBr): ν 1571 (s), 1523 (s), 1502 (m), 1429 (s), 1381 (w), 1295 (s), 1240 (w), 1213 (w), 1162 (s) cm^{-1}. HRMS (ESI): *m*/*z* calcd for [$C_8H_2N_{18}O_8$ + Na^+]: 501.0195; found [M + Na]$^+$: 501.0189.

***N*,*N*′-Bis{4-[(3-nitro-1*H*-1,2,4-triazol-1-yl)-*NNO*-azoxy]-furazanyl}methanediamine (11).** Aqueous 37% formaldehyde (0.15 mL, 5.7 mmol) and 96% H_2SO_4 (0.66 mL, 11.9 mmol) were added dropwise to a vigorously stirred solution of furazan **4** (1.0 g, 4.1 mmol) in 1,4-dioxane (7 mL) at 20 °C. The reaction mixture was vigorously stirred at this temperature for 40 min, then poured into water (20 mL) and extracted with AcOEt (4 × 20 mL). The combined organic extracts were washed with water (50 mL), brine (50 mL), dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was washed with boiling CH_2Cl_2 (3 × 10 mL) and dried in air to give furazan **11** (0.98 g, 96%) as a pale yellow solid, mp 212–214 °C. ^{1}H NMR (500.1 MHz, acetone-d$_6$): δ 5.26 (t, 2H, CH_2, $^1J_{H,H}$ = 5.5 Hz), 7.38 (t, 2H, NH, $^1J_{H,H}$ = 5.5 Hz), 9.96 (s, 1H, H-5′) ppm. ^{1}H NMR (600.1 MHz, DMSO-d$_6$): δ 5.00 (t, 2H, CH_2, $^1J_{H,H}$ = 5.7 Hz), 7.54 (t, 2H, NH, $^1J_{H,H}$ = 5.7 Hz), 10.05 (s, 1H, H-5′) ppm. ^{13}C NMR (125.8 MHz, acetone-d$_6$): δ 54.9 (CH_2), 145.6 (C-5′), 150.5 (br s, C-4), 151.0 (C-3), 160.9 (br s, C-3′) ppm. ^{13}C NMR (150.9 MHz, DMSO-d$_6$): δ 53.8 (CH_2), 145.2 (C-5′), 149.5 (C-4), 150.0 (C-3), 159.4 (C-3′). ^{13}C NMR ([GATED], 150.9 MHz, DMSO-d$_6$): δ 53.8 (t, CH_2, $^1J_{C,H}$ = 153.1 Hz), 145.2 (d, C-5′, $^1J_{C,H}$ = 238.3 Hz), 149.5 (C-4), 150.0 (C-3), 159.4 (d, C-3′, $^3J_{C,H}$ = 14.4 Hz). ^{14}N NMR (36.1 MHz, acetone-d$_6$): δ −29 (C–NO_2, $\Delta\nu_{1/2}$ = 110 Hz), −76 [*N*(O)=N, $\Delta\nu_{1/2}$ = 170 Hz] ppm. ^{15}N NMR ([INVGATED], 60.8 MHz, DMSO-d$_6$): δ 27.7, −4.8 (furazan rings), −29.6 (C–NO_2), −57.1 [N(O)=*N*], −75.8 [*N*(O)=N], −91.9 (N-2′), −136.4 (N-1′ or N-4′),

−137.7 (N-4′ or N-1′), −316.1 (NH) ppm. IR (KBr): ν 3418 (m), 3399 (m), 3169 (w), 1612 (s), 1562 (s), 1534 (m), 1515 (s), 1497 (m), 1421 (s), 1403 (m), 1367 (m), 1301 (s), 1236 (w), 1211 (w), 1174 (s) cm^{-1}. HRMS (ESI): *m*/*z* calcd for $[C_9H_6N_{18}O_8 + Na^+]$: 517.0508; found $[M + Na]^+$: 517.0508.

***N*,*N*′-Dinitro-*N*,*N*′-bis{4-[(3-nitro-1*H*-1,2,4-triazol-1-yl)-*NNO*-azoxy]-furazanyl}methanediamine (7).** N_2O_5 (0.44 g, 4.1 mmol) was added in one portion to a stirred solution of furazan **11** (1.0 g, 2.0 mmol) in dry MeCN (15 mL) at −20 °C under an argon atmosphere. The reaction mixture was warmed to 0 °C and stirred at this temperature for 1 h. Then the reaction mixture was concentrated under reduced pressure. The residue was purified by preparative column chromatography (petroleum ether/ethyl acetate, 2 : 1 to 1.5 : 1) to give furazan **7** (700 mg, 59%) as a pale yellow solid. DSC (5 °C min^{-1}): T_{onset} = 147 °C (dec.). ^{1}H NMR (600.1 MHz, acetone-d_6): δ 6.99 (s, 2H, CH_2), 10.06 (s, 1H, H-5′) ppm. ^{1}H NMR (500.1 MHz, DMSO-d_6): δ 6.84 (s, 2H, CH_2), 10.16 (s, 1H, H-5′) ppm. ^{13}C NMR (125.8 MHz, DMSO-d_6): δ 64.9 (CH_2), 145.3 (C-3), 145.5 (C-5′), 153.9 (C-4), 159.6 (C-3′) ppm. ^{13}C NMR ([GATED], 125.8 MHz, DMSO-d_6): δ 64.9 (t, CH_2, $^1J_{C,H}$ = 165.1 Hz), 145.3 (C-3), 145.5 (d, C-5′, $^1J_{C,H}$ = 240.4 Hz), 154.0 (C-4), 159.6 (d, C-3′, $^3J_{C,H}$ = 14.4 Hz). ^{14}N NMR (43.4 MHz, acetone-d_6): δ −31 (C–NO_2, $\Delta\nu_{1/2}$ = 120 Hz); −44 (N–NO_2, $\Delta\nu_{1/2}$ = 100 Hz), −83 [*N*(O)═N, $\Delta\nu_{1/2}$ = 260 Hz] ppm. ^{15}N NMR ([INVGATED], 50.7 MHz, DMSO-d_6): δ 40.9, 36.4 (furazan rings), −30.1 (C–NO_2), −42.7 (N–NO_2), −53.4 [N(O)═*N*], −82.3 [*N*(O)═N], −92.0 (N-2′), −135.4 (N-1′ or N-4′), −137.0 (N-4′ or N-1′), −208.2 (*N*–NO_2) ppm. IR (KBr): ν 3178 (w), 1609 (s), 1566 (s), 1520 (m), 1425 (m), 1376 (w), 1285 (s), 1245 (w), 1179 (w) cm^{-1}. HRMS (ESI): *m*/*z* calcd for $[C_9H_4N_{20}O_{12} + NH_4^+]$: 602.0656; found $[M + NH_4]^+$: 602.0654.

Conflicts of interest

There are no conflicts to declare.

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1.029; for compound **5**: sp. gr. $P2_1$, $a = 6.2831(10)$, $b = 6.0046(10)$, $c = 13.003(2)$ Å, $\beta = 91.560(3)^\circ$, $V = 490.38(14)$ Å^3, $Z = 2$ ($Z' = 1$), $R_1 = 0.0511$ (for 2016 reflns with $I > 2\sigma(I)$), w$R_2 = 0.1175$, GOF = 0.987; for compound **6**: sp. gr. *Pbcn*, $a = 17.283(8)$, $b = 7.552(2)$, $c = 13.411(6)$ Å, $V = 1750.3(12)$ Å^3, $Z = 4$ ($Z' = 0.5$), $R_1 = 0.0393$ (for 1843 reflns with $I > 2\sigma(I)$), w$R_2 = 0.0942$, GOF = 1.022.

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