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Mendeleev Commun., 2021, **31**, 792–794

Mendeleev Communications

Synthesis and properties of novel energetic (cyano-*NNO*-azoxy)furazans

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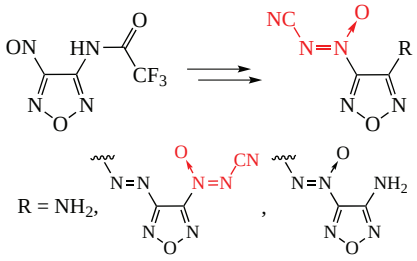
DOI: 10.1016/j.mencom.2021.11.007

Three novel energetic furazans with a cyano-*NNO*-azoxy group were synthesized using cyanamide and 2,2,2-trifluoro-*N*-(4-nitrosofurazan-3-yl)acetamide as the starting compounds. (Cyano-*NNO*-azoxy)furazans obtained display high experimental enthalpies of formation (+742 to +1073 kcal kg^{-1}), good thermal stability (T_{onset} = 193–222 °C) and moderate mechanical sensitivity. These compounds may be of interest as energetic fillers in solid fuels for ramjet engines and in solid composite propellants.



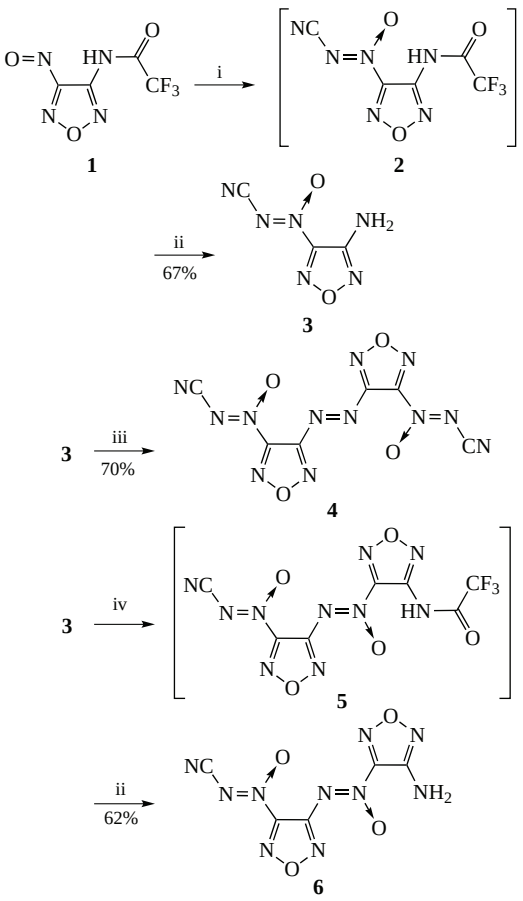
Keywords: azoxy compounds, cyano compounds, furazans, combustion calorimetry, enthalpy of formation, differential scanning calorimetry, X-ray diffraction analysis.

Compounds containing a cyano-*NNO*-azoxy group [N(O)=N–CN] have a wide spectrum of biological activity. The first compound of this type, 4-(cyano-*NNO*-azoxy)-benzoic acid, was isolated from *Calvatia lilacina* fungi and was found to exhibit antimicrobial and fungicidal activity.[1] Several hundred cyano-*NNO*-azoxy compounds have been obtained to date. Some of them are of interest as antibiotics,[2–6] fungicides,[5–7] anti-inflammatory[4] and anticancer substances,[4,8,9] inhibitors of tubulin binding,[10,11] inhibitors of glutathione transferase[12] and ornithine decarboxylase[13] and labels for α_1-adrenergic receptors.[14] At the same time, the cyano-*NNO*-azoxy group is an energetic substituent that allows energetic compounds with a high enthalpy of formation (>700 kcal kg^{-1}) to be created.[15] To our knowledge, only two energetic cyano-*NNO*-azoxy compounds are described, namely, 4,4′-bis(cyano-*NNO*-azoxy)-3,3′-bifurazan[16] and 4,4′-bis(cyano-*NNO*-azoxy)-3,3′-bifuroxan.[15] The enthalpy of formation was experimentally determined for the latter (+894 kcal kg^{-1}). However, the physicochemical characteristics, thermal stability and sensitivity to mechanical stimuli have not been studied for these compounds. Note that polynitrogen compounds with high enthalpies of formation (>700 kcal kg^{-1}) and a low oxygen content (oxidizer excess coefficient α = 0.2–0.35) are efficient components of solid fuels for ramjet engines.[17–19] The methods for the synthesis of cyano-*NNO*-azoxy compounds usually involve the reaction of cyanamide with nitroso compounds in the presence of oxidizing agents such as phenyliodoso diacetate[8,20] or dibromoisocyanuric acid (DBI).[16,21]

This work describes the synthesis and physicochemical characteristics of three new energetic (cyano-*NNO*-azoxy)-furazans (Scheme 1). The reaction of nitrosofurazan **1**[22,23] with cyanamide in the presence of DBI in a CH_2Cl_2–Et_2O mixture gave intermediate (trifluoroacetylamino)furazan **2**, which was subjected to acid hydrolysis to remove the trifluoroacetyl protective group, to give aminofurazan **3** in 67% yield. The use of phenyliodoso diacetate instead of DBI at the first stage was found to be less efficient providing product **3** in only 20% yield.

Treatment of aminofurazan **3** with DBI in CH_2Cl_2 gave azofurazan **4** in 70% yield. The reaction of aminofurazan **3** with nitrosofurazan **1** in the presence of DBI in a MeCN–CH_2Cl_2 mixture resulted in (trifluoroacetylamino)azoxyfurazan **5**, which was deprotected into the corresponding amino azoxyfurazan **6** in 62% yield.

The resulting compounds **3**, **4** and **6** were characterized by IR, multinuclear NMR spectroscopy, and high-resolution mass spectrometry. The signals in the ^{14}N and ^{15}N NMR spectra were assigned by analogy with the known furazan derivatives (see Online Supplementary Materials).[24] Their structures were also confirmed by single crystal X-ray diffraction analysis (Figure 1).[†] The phase purity of bulk samples was confirmed by X-ray powder diffraction method. The density of the crystals was calculated from the unit cell volumes at 120 K (according to single-crystal X-ray diffraction data) and at room temperature



Scheme 1 *Reagents and conditions*: i, H_2NCN, DBI, CH_2Cl_2, Et_2O, 0 °C, 30 min, then 25 °C, 24 h; ii, CF_3CO_2H, H_2O, MeOH, –20 °C, 12 h; iii, DBI, CH_2Cl_2, 25 °C, 24 h; iv, **1**, DBI, CH_2Cl_2, MeCN, 0 °C, 30 min, then 25 °C, 24 h.

(298 K, PXRD data). The calculated densities at 120 and 298 K are, 1.738 and 1.689 g cm^{-3} for compound **3**, 1.768 and 1.722 g cm^{-3} for **4**, respectively, and 1.753 g cm^{-3} for **6** (only at 298 K).

The thermal stability of compounds **3**, **4** and **6** was studied by differential scanning calorimetry (DSC) (see Online Supplementary Materials). Aminofurazan **3** melts at 117 °C and begins to decompose at T_{onset} = 209 °C. Azofurazan **4** has a lower melting point (mp 90 °C) than aminofurazan **3** and has similar thermal stability (T_{onset} = 222 °C). Thus, both compounds have a

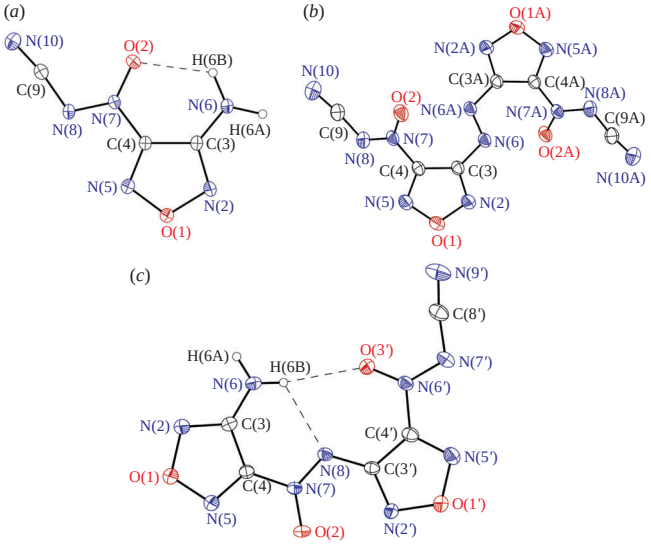


Figure 1 Single-crystal X-ray diffraction data for (*a*) compound **3**, (*b*) compound **4** and (*c*) acetone solvate **6** (acetone molecule and minor disordered component of the cyano-*NNO*-azoxy fragment are omitted for clarity). Thermal ellipsoids are given with 50% probability.

broad range where a stable melt exists. In this case, the melting point values fall within the range of temperatures recommended for castable energetic materials (80–120 °C).[28] Azoxyfurazan **6** melts at 124 °C and begins to decompose at T_{onset} = 193 °C.

The standard enthalpies of combustion (ΔH_c^o) of (cyano-*NNO*-azoxy)furazans **3**, **4** and **6** were experimentally determined by the combustion calorimetry (bomb calorimetry) method. The standard enthalpies of formation (ΔH_f^o) were calculated from ΔH_c^o (see Online Supplementary Materials for details). Azofurazan **4** has the highest enthalpy of formation (+1073 kcal kg^{-1}). The enthalpy of formation of azoxyfurazan **6** is +803 kcal kg^{-1}. Aminofurazan **3** has ΔH_f^o = +742 kcal kg^{-1}. The enthalpies of formation of the new compounds **3**, **4** and **6** are several times higher than those of standard explosives (TNT, RDX, HMX) and hexanitrohexaazaisowurtzitane (CL-20) (ΔH_f^o = +205 kcal kg^{-1}).[29]

The detonation parameters of compounds **3**, **4** and **6** were calculated using the Pepekin–Lebedev method.[30] Furazans **4** and **6** possess similar calculated characteristics, namely, the detonation velocities are 8.71 and 8.51 km s^{-1} and the detonation pressures are 33.1 and 32.3 GPa, respectively. The corresponding values for furazan **3** are 8.13 km s^{-1} and 28.9 GPa, respectively.

† *Crystal data for* **3**. $C_3H_2N_6O_2$ (M = 154.11) at 120 K: orthorhombic, space group *Pnma*, a = 12.6958(8), b = 5.8719(4) and c = 7.9002(5) Å, V = 588.95(7) Å^3, Z = 4, Z' = 0.5, d_{calc} = 1.738 g cm^{-3}. The intensities of 973 independent reflections (R_{int} = 0.0304) out of the 7780 collected ones ($2\theta_{max}$ = 60° for MoKα radiation) were used in the refinement that converged to R_1 = 0.0295 [for 762 reflections with $I > 2\sigma(I)$], wR_2 = 0.0784 and GOF = 0.982; residual electron density –0.228/0.404 e Å^{-3} (ρ_{max}/ρ_{min}).

Crystal data for **4**. $C_6N_{12}O_4$ (M = 304.18) at 120 K: monoclinic, space group $P2_1/n$, a = 8.8356(6), b = 6.1919(4) and c = 11.2137(8) Å, β = 111.354(3)°, V = 571.38(7) Å^3, Z = 2, Z' = 0.5, d_{calc} = 1.768 g cm^{-3}. The intensities of 1675 independent reflections (R_{int} = 0.0470) out of the 9359 collected ones ($2\theta_{max}$ = 60° for MoKα radiation) were used in the refinement that converged to R_1 = 0.0387 [for 1393 reflections with $I > 2\sigma(I)$], wR_2 = 0.1033 and GOF = 1.012; residual electron density −0.258/0.286 e Å^{-3} (ρ_{max}/ρ_{min}).

Crystal data for **6**·$(CH_3)_2CO$. $C_8H_8N_{10}O_5$ (M = 324.24) at 120 K: monoclinic, space group $P2_1/c$, a = 12.2155(3), b = 6.3751(2) and c = 17.4126(5) Å, β = 90.4490(10)°, V = 1355.97(7) Å^3, Z = 4, Z' = 1, d_{calc} = 1.588 g cm^{-3}. The intensities of 3941 independent reflections (R_{int} = 0.0304) out of the 19659 collected ones ($2\theta_{max}$ = 60° for MoKα radiation) were used in the refinement that converged to R_1 = 0.0352 [for 3564 reflections with $I > 2\sigma(I)$], wR_2 = 0.0972 and GOF = 1.011; residual electron density −0.243/0.457 e Å^{-3} (ρ_{max}/ρ_{min}).

Powder diffraction crystal data for **6**. $C_5H_2N_{10}O_4$ (M = 266.14) at room temperature (*ca.* 298 K): monoclinic, space group $P2_1/n$, a = 10.6759(14), b = 5.6105(8) and c = 16.872(2) Å, β = 93.683(4)°, V = 1008.5(2) Å^3, Z = 4, Z' = 1, d_{calc} = 1.753 g cm^{-3}, R_{wp} = 4.03.

Single crystal X-ray diffraction data were collected on a Bruker Apex II diffractometer equipped with a PHOTON 2 detector using graphite-monochromated MoKα radiation (λ = 0.71073 Å). Structures were solved by the dual-space method using SHELXT[25] and were refined in anisotropic approximation against F^2 using SHELXL.[25] X-ray powder diffraction measurements were performed on a Bruker AXS D8 diffractometer (CuKα, λ = 1.534 Å, reflection mode) equipped with a LynxEye position sensitive detector. Unit cell parameters from the PXRD pattern for **6** were determined by the singular value decomposition index algorithm[26] implemented in Bruker TOPAS 5.0 software.[27] The space group was determined by analysis of systematic absences.

CCDC 2100752 (**3**), 2100753 (**4**) and 2102989 [**6**·$(CH_3)_2CO$] contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

Thus, the detonation parameters of compounds **4** and **6** are somewhat lower than the calculated values for hexogen (8.87 km s^{-1} and 35.5 GPa).

Apparently due to the planar geometry of its molecule, aminofurazan **3** has a low sensitivity to impact (IS = 22 J) and is sensitive to friction at the level of hexogen (RDX)[31] (FS = 130 N). The impact sensitivity of azofurazan **4** is 4.4 J and its friction sensitivity is 29 N. Azoxyfurazan **6** (IS = 5.5 J, FS = 160 N) is less sensitive than compound **4**.

The efficiency of (cyano-*NNO*-azoxy)furazans **3**, **4** and **6** as energetic fillers of solid fuels for ramjet engines and in solid composite propellants in comparison with the most efficient standard fuel component, octogen (HMX), was computed (see Online Supplementary Materials). According to the calculations, the ramjet fuel formulations containing compounds **3**, **4** and **6** are significantly more efficient than a similar formulation based on HMX and are superior to the latter by 16–23% in the lowest volumetric specific heat of combustion. It has also been shown that replacement of RDX or HMX with compound **4** makes it possible to increase the specific impulse of model formulations of solid composite propellants by 5–7 s, while the content of compound **4** in the composition is at a safe level (40–50%).

In summary, three novel energetic (cyano-*NNO*-azoxy)-furazans **3**, **4** and **6** have been synthesized and their physicochemical and special properties have been examined. Compounds **3**, **4** and **6** may be of interest as energetic fillers of solid fuels for ramjet engines and in solid composite propellants due to high enthalpies of formation and combustion.

This study was supported by The Ministry of Science and Higher Education of the Russian Federation (agreement with N. D. Zelinsky Institute of Organic Chemistry RAS no. 075-15-2020-803). The contribution of the Center for molecule composition studies of INEOS RAS is gratefully acknowledged.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.11.007.

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Received: 23rd August 2021; Com. 21/6655