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Novel energetic aminofurazans with a nitro-*NNO*-azoxy group

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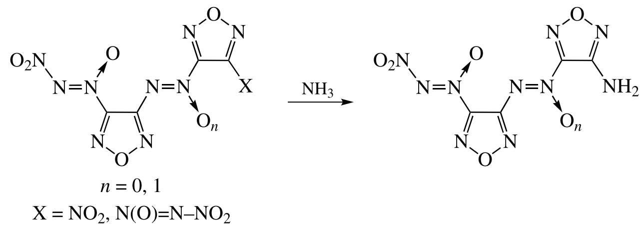
Novel energetic azoxy- and azofurazans bearing nitro-*NNO*-azoxy and amino groups were synthesized using the ammonolysis of some known (nitro-*NNO*-azoxy)furazans. 3-Amino-4-{[4′-(nitro-*NNO*-azoxy)furazan-3′-yl]-*NNO*-azoxy}furazan displays the highest melting point (114 °C, decomp.) among the known (nitro-*NNO*-azoxy)furazans, optimal density (1.80 g cm^{-3}), high experimental enthalpy of formation (639 kcal kg^{-1}) and mechanical sensitivity on the level of PETN. In terms of the specific impulse level, the model solid composite propellant formulations based on this compound outperform similar formulations based on RDX, HMX or CL-20 by 7–12 s.



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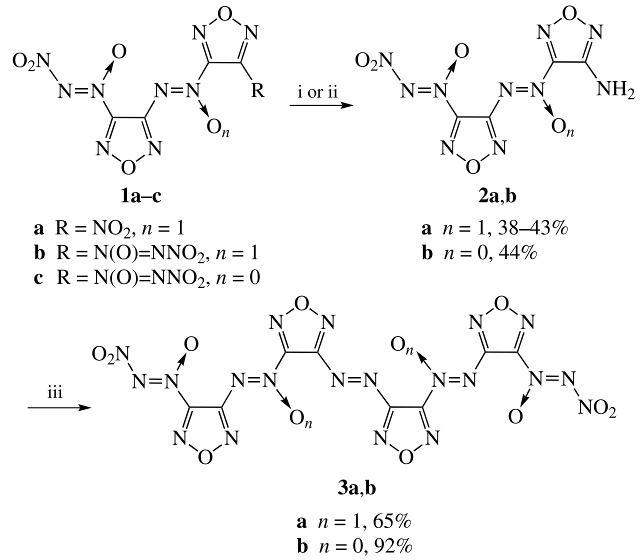
One of the most difficult problems of the modern chemistry of high-energy compounds involves the synthesis of energetic fillers required for solid composite propellants with high specific impulses.[1,2] Compounds of this kind should combine a high enthalpy of formation (>500 kcal kg^{-1}), high density (⩾1.80 g cm^{-3}), optimal oxygen content (oxidizer excess coefficient $\alpha \geqslant 0.6$), acceptable thermal stability, and sufficiently high melting point required to formulate solid composite propellants.[3–6] It is also desirable that hydrogen atoms be present in the molecule of an energetic filler in order to increase the specific impulse of the solid composite propellant.[1] One of the ways to solve this problem is to design compounds that comprise a polynitrogen heterocyclic core along with various energetic functional groups (NO_2, N–NO_2, N_3, *etc*.) and hydrogen-containing substituents (NH_2, *etc*.).[3,7]

The nitro-*NNO*-azoxy moiety [N(O)=N–NO_2, N_3O_3] is a new poorly studied explosophorous group that attracted attention only recently.[8–13] Incorporation of this group into a molecule of an energetic compound should improve the oxygen balance and increase the enthalpy of formation of the latter.[9,14–19] Previously documented energy-rich furazans with nitro-*NNO*-azoxy group appeared as liquids or low-melting compounds[8,10,11,14] whose thermal decomposition began in the liquid phase at temperatures below 100 °C.[14] At the same time, the decomposition of high-melting heterocycles containing a nitro-*NNO*-azoxy group occurred in the solid phase at temperatures near 150 °C.[16] Thus, high-melting (nitro-*NNO*-azoxy)furazans are anticipated for having improved thermal stability. One of the ways to increase the melting point is to incorporate an amino group that forms intra- and intermolecular hydrogen bonds with polar substituents into a molecule.[7,20,21]

This work describes the synthesis and physicochemical characteristics of two novel energetic furazans containing nitro-*NNO*-azoxy and amino groups (Scheme 1). Selective replacement of nitro- or nitro-*NNO*-azoxy group with ammonia in a previously obtained[14] (nitro-*NNO*-azoxy)furazans **1a** and **1b** gave aminofurazan **2a**. We studied two procedures of this reaction (see Online Supplementary Materials, Table S1). In the first case, a solution of dry ammonia in CH_2Cl_2 was added to a solution of furazans in CH_2Cl_2 (*cf*. ref. 22). In the second case, a 25% aqueous ammonia solution was added to a solution of furazans in CH_2Cl_2 (*cf*. ref. 23). The reaction was completed in 30 min at 25 °C. The second version was found to be more efficient, and compound **2a** was obtained in 38% yield from furazan **1a** and in 43% yield from furazan **1b**.

Bis(nitro-*NNO*-azoxy)azofurazan **1c** was analogously transformed into aminoazofurazan **2b** (see Scheme 1). The treatment with dry ammonia in CH_2Cl_2 at 15 °C for 1 min turned out to be the most efficient way for selective replacement of one (nitro-*NNO*-azoxy) group to produce aminoazofurazan **2b** in 44% yield (the conversion of **1c** was 62%). Further treatment of



Scheme 1 *Reagents and conditions*: i, NH_3, H_2O, CH_2Cl_2, 25 °C, 30 min (for **1a**,**b**); ii, NH_3, CH_2Cl_2, 15 °C, 1 min (for **1c**); iii, DBI, CH_2Cl_2, 25 °C, 12 h.

aminofurazans **2a** and **2b** with dibromoisocyanuric acid (DBI) in CH_2Cl_2 at 25 °C for 12 h gave the corresponding azofurazans **3a** and **3b** in 65 and 92% yields, respectively.

The resulting compounds **2a**,**b** and **3a**,**b** were characterized by multinuclear NMR spectroscopy, IR 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] The structures of aminofurazans **2a** and **2b** were ultimately determined by single crystal X-ray diffraction analysis (Figures 1 and 2).† The phase purity of bulk samples was confirmed by X-ray powder diffraction experiments. The density of crystals was calculated from the unit cell volumes at 120 K (according to single-crystal X-ray diffraction data) and at room temperature (about 298 K, PXRD data). The calculated densities at 298 and 120 K are 1.796 and 1.865 g cm^{-3} for aminofurazan **2a** and 1.758 and 1.815 g cm^{-3} for aminofurazan **2b**, respectively.

In the crystals of both aminofurazans, one of the hydrogen atoms of the amino group, H(3A), participates in the intramolecular hydrogen bond with the N(7) nitrogen atom (see Figures 1 and 2). The geometry of the hydrogen bond is similar in both structures [the N(3)···N(7) distance is 2.8152(17) and 2.8920(17) Å in **2a** and **2b**, while the N(3)–H(3A)···N(7) angles are 119.7 and 116.6°, respectively, if the N–H length is set to 1.015 Å]. Moreover, a weaker intramolecular hydrogen bond with the O(2′) atom is formed in structure **2a** [the N(3)···O(2′) distance is 3.1739(17) Å and the N(3)–H(3A)···O(2′) angle is 151.9°], while the conformation of the molecule of compound **2b** prevents the formation of this bond. The existence of an additional intramolecular hydrogen bond makes the conformation of aminofurazan **2a** more compact, which can in principle affect its melting point. The second hydrogen atom H(3B) in the amino group of both structures participates in the intermolecular hydrogen bonds with the N(2) atom of the neighboring molecules, thus binding them into centrosymmetric dimers (see Figures 1 and 2).

The thermal stability of compounds **2a**,**b** and **3a**,**b** was studied by differential scanning calorimetry (DSC, see Online Supplementary Materials). Aminofurazan **2a** melts with decomposition at 114 °C and is the highest-melting compound among the currently known (nitro-*NNO*-azoxy)furazans. Aminofurazan **2b** is a low-melting crystalline compound (mp 62 °C), which begins to decompose at $T_{onset} = 103$ °C. Azofurazans **3a** and **3b** are liquid at room temperature and decompose at $T_{onset} = 114$ and 111 °C, respectively and hence cannot be considered as energetic fillers for solid composite propellants.

The standard enthalpy of combustion (ΔH°_{c}) of compound **2a** was experimentally determined by the combustion calorimetry (bomb calorimetry) method. The standard enthalpy of formation (ΔH°_{f}) calculated from ΔH°_{c} (see Online Supplementary Materials) amounts to +639 kcal kg^{-1}. The enthalpy of formation of compound **2b** in the solid phase (+735 kcal kg^{-1}) was calculated by the additive method using the values of the

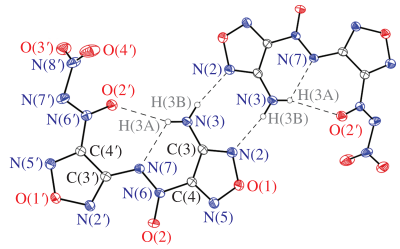


Figure 1 A centrosymmetric dimer with a hydrogen bond in the crystal of aminofurazan **2a** [N(3)···N(2), 3.0074(18) Å; N(3)–H(3B)···N(2), 165.5° if the N–H length is set to 1.015 Å]. Non-hydrogen atoms are represented by atomic displacement ellipsoids (p = 50%).

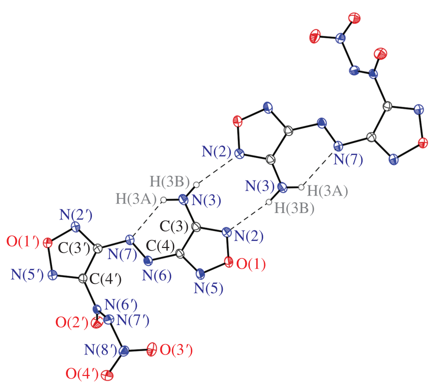


Figure 2 A centrosymmetric dimer with a hydrogen bond in the crystal of aminofurazan **2b** [N(3)···N(2), 3.0250(17) Å; N(3)–H(3B)···N(2), 156.3° if the N–H length is set to 1.015 Å]. Non-hydrogen atoms are represented by atomic displacement ellipsoids (p = 50%).

† *Crystal data for* **2a**. $C_4H_2N_{10}O_6$ (M = 286.16) at 120 K: monoclinic, space group $P2_1/n$, a = 11.6644(16), b = 5.1526(7) and c = 17.160(2) Å, β = 98.890(3)°, V = 1019.0(2) Å^3, Z = 4, Z' = 1, d_{calc} = 1.865 g cm^{-3}. The intensities of 2970 independent reflections (R_{int} = 0.0549) out of 16868 collected ($2\theta_{max}$ = 60° for MoKα radiation) were used in the refinement that converged to R_1 = 0.0384 [for 2257 reflections with $I > 2\sigma(I)$], wR_2 = 0.0955 and GOF = 1.030. Residual electron density, 0.274/0.446 e Å^{-3} (ρ_{max}/ρ_{min}).

Crystal data for **2b**. $C_4H_2N_{10}O_5$ (M = 270.16) at 120 K: monoclinic, space group $C2/c$, a = 15.3881(9), b = 7.3037(4) and c = 17.7330(11) Å, β = 97.2030(14)°, V = 1977.3(2) Å^3, Z = 8, Z' = 1, d_{calc} = 1.815 g cm^{-3}. The intensities of 2875 independent reflections (R_{int} = 0.0379) out of 10593 collected ($2\theta_{max}$ = 60° for MoKα radiation) were used in the refinement that converged to R_1 = 0.0372 [for 2140 reflections with $I > 2\sigma(I)$], wR_2 = 0.0931 and GOF = 1.031. Residual electron density, –0.300/0.421 e Å^{-3} (ρ_{max}/ρ_{min}).

X-ray diffraction data were collected on an Apex DUO CCD diffractometer using graphite-monochromated MoKα radiation (λ = 0.71073 Å). All structures were solved by dual-space method using SHELXT,[25] and were refined in anisotropic approximation against F^2 using SHELXL.[25]

CCDC 1852709 and 1852710 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.

Table 1 Physical and calculated energy characteristics of aminofurazans **2a** and **2b** in comparison with hexogen (RDX).

Compound	M_w	T_m[a]/ °C	T_d[b]/ °C	α[c]	d/ g cm^{-3}	ΔH_f^0/ kcal kg^{-1}	D[d]/ m s^{-1}	P_{C-J}^e/ GPa
2a $C_4H_2N_{10}O_6$	286.11	114	114	0.67	1.80[f]	+639[g]	8.96[h]	37.4[h]
2b $C_4H_2N_{10}O_5$	270.12	62	103	0.56	1.76[f]	+730[i]	8.82[h]	35.2[h]
RDX $C_3H_6N_6O_6$	222.12	204[j]	204[j]	0.67	1.82[j]	+72[j]	8.96[h] 8.75[j]	36.6[h] 35.0[j]

[a] Melting temperature (DSC). [b] Decomposition temperature (extrapolated onset temperature at a heating rate of 5 °C min^{-1}). [c] Oxidizer excess coefficient. For a compound with molecular formula $C_xH_yN_vO_w$, $\alpha = w/(2x + y/2)$. [d] Detonation velocity. [e] Detonation pressure. [f] Density measured by powder diffraction at 298 K. [g] Experimentally measured standard enthalpy of formation. [h] Calculated with Shock and Detonation (S&D) Version 4.5. [i] Calculated enthalpy of formation. [j] Ref. 28.

'contributions' of functional groups to the enthalpy of combustion. In terms of the enthalpy of formation, compounds **2a**,**b** significantly exceed the standard explosives such as TNT, hexogen (RDX), octogen (HMX) and hexanitrohexaazaisowurtzitane (CL-20) (ΔH_f^0 = +205 kcal kg^{-1}).[26]

The detonation parameters of aminofurazans **2a**,**b** were calculated using the Shock and Detonation (S&D) software package, version 4.5.[27] Compound **2a** has a calculated detonation velocity of 8.96 km s^{-1} and a detonation pressure of 37.4 GPa. Similar values for furazan **2b** are 8.82 km s^{-1} and 35.2 GPa, respectively. Thus, the detonation parameters of compounds **2a**,**b** are at the level of the calculated values for hexogen (RDX) (8.96 km s^{-1} and 36.6 GPa) (Table 1). The impact sensitivity (IS) of compound **2a** is 2 J, and the friction sensitivity (FS) is 96 N. These values are at the level of the values for pentaerythritol tetranitrate (PETN, IS = 3 J, FS = 60 N).[28]

The efficiency of using aminofurazans **2a**,**b** as energetic fillers for solid composite propellants in comparison with standard components of such propellants as RDX, HMX and CL-20 was calculated (see Online Supplementary Materials). It was shown that replacing RDX, HMX and CL-20 with compound **2a** or **2b** made it possible to increase the specific impulse of model compositions of solid composite propellants by 7–12 or 5–10 s, respectively.

To conclude, novel high-energy furazans **2a**,**b** and **3a**,**b** containing a nitro-*NNO*-azoxy group were synthesized. Their thermal stability was explored and it was demonstrated that compound **2a** was the highest-melting compound among the known (nitro-*NNO*-azoxy)furazans. The enthalpy of formation and sensitivity to mechanical stress were experimentally determined for this compound. Aminofurazan **2a** may be of interest as energetic filler for solid composite propellants due to a combination of a high enthalpy of formation and an optimal oxygen balance.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.11.006.

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