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Novel (1*H*-tetrazol-5-yl-*NNO*-azoxy)furazans and their energetic salts: synthesis, characterization and energetic properties

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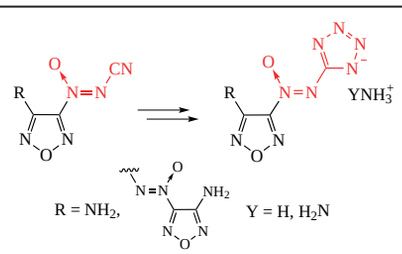
Six novel energetic furazans containing tetrazol-5-yl-*NNO*-azoxy moiety were synthesized using (cyano-*NNO*-azoxy)-furazans as starting compounds. The obtained compounds exhibit high enthalpies of formation (531–792 kcal kg^{-1}), acceptable densities (1.70–1.76 g cm^{-3}), good thermal stability (T_{onset} = 146–199 °C), and, as a result, excellent detonation performance (detonation velocities of 8.61–8.95 km s^{-1} and detonation pressures of 31.6–36.0 GPa).



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

Energetic compounds have found widespread civilian and military applications.[1–3] Some of these compounds are constituents of so-called energetic materials. In order to implement specific practical purposes using energetic materials, components with properties that are optimal for these particular tasks are required.[1,4–6] One of these tasks is the development of solid fuels. Effective components of such fuels are compounds with a high enthalpy of formation (> 500 kcal kg^{-1}), optimal density (⩾1.70 g cm^{-3}) and oxidizer excess coefficient α = 0.2–0.35.[7–9]

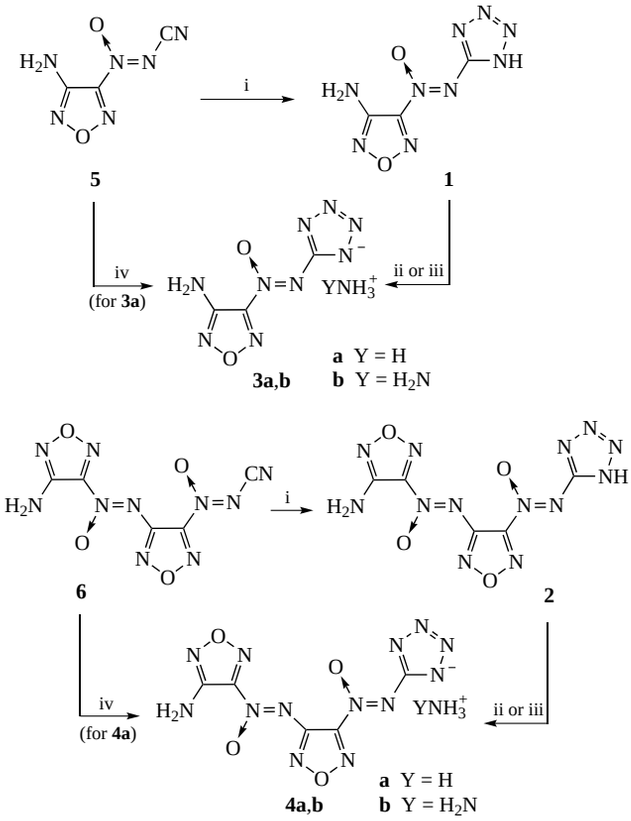
One of the contemporary strategies toward the construction of high energy compounds involves a combination of different high-nitrogen heterocycles into a molecule.[10–12] Due to both high energetic potential and good thermal stability, furazan and tetrazole cycles are in a spotlight of researchers.[13–15] Moreover, tetrazoles owing to the presence of the acidic proton enable to form energetic salts.[16,17] The properties of energetic salts, in turn, can be diversified by combining various cations and anions.[18,19]

The literature describes a number of energetic compounds consisting of furazan and tetrazole cycles linked by C–C bond,[20–26] however, these compounds do not possess sufficient values of enthalpy of formation and density as well as contain too low oxygen. Incorporation of azoxy group into a molecule of energetic compound as a bridge between heterocyclic rings is an effective way to increase the enthalpy of formation and improve the oxygen balance.[27,28] Only one example of 5-[(4-methylfurazan-3-yl)-*ONN*-azoxy]-1*H*-tetrazole is documented[29] where furazan and tetrazole cycles are connected by azoxy bridge, however, that compound cannot be considered energetic because of the presence of methyl substituent.

Herein, we present the synthesis and physicochemical characteristics of novel energetic (1*H*-tetrazol-5-yl-*NNO*-azoxy)-furazans **1**, **2** and their energetic salts **3**, **4** (Scheme 1). The most general method for the synthesis of 5-substituted 1*H*-tetrazoles is the [3 + 2]-cycloaddition of the azide anion to nitriles, particularly the reaction of nitriles with NaN_3 or NH_4N_3,[20–24,30] which we used in this study.

The reaction of cyano-*NNO*-azoxy compounds **5**[31] or **6**[31] with NaN_3 in water followed by acidification with 10% hydrochloric acid led to corresponding azoxytetrazoles **1**, **2** in yields 88 and 74%, respectively (see Scheme 1). These compounds on treatment with nitrogen bases (25% aqueous ammonia solution or 64% aqueous hydrazine solution) afforded the corresponding ammonium (**3a**,**b**) or hydrazinium (**4a**,**b**) salts in yields 64–79%. Using NH_4N_3, generated *in situ* from $TMSN_3$ and NH_4F in acetonitrile, allows for one-stage transformation of (cyano-*NNO*-azoxy)furazans **5**, **6** into (1*H*-tetrazol-5-yl-*NNO*-azoxy)-furazan ammonium salts **3a** or **4a** in yields 78 and 64%, respectively. It is important to note that tetrazole **1** and ammonium salt **4a** are stable monohydrates.

Synthesized (1*H*-tetrazol-5-yl-*NNO*-azoxy)furazans **1**–**4** were fully characterized by IR, multinuclear NMR spectroscopy, high-resolution mass spectrometry as well as elemental analysis.



Scheme 1 *Reagents and conditions*: i, NaN_3, H_2O, 50 °C, 4 h; ii, NH_3, H_2O, MeOH, 0 °C, 1 h; iii, N_2H_4, H_2O, MeOH, 0 °C, 1 h; iv, $TMSN_3$, NH_4F, MeCN, 25 °C, 24 h (for **3a**, **4a**).

The assignment of signals in the ^{13}C and ^{15}N NMR spectra was performed on the basis of literature data for azoxyfurazans[31] and tetrazolylfurazans[26,32,33] (see Online Supplementary Materials). The structure of ammonium salt monohydrate **3a**·H_2O was unambiguously confirmed by single crystal X-ray diffraction analysis (Figure 1).† The phase purity of bulk sample of water-free salt **3a** was verified by X-ray powder diffraction experiment. The density of water-free salt **3a** is 1.70 g cm^{-3} at 298 K (PXRD data). The density of compounds **2**, **3b** and **4b** was measured with a gas pycnometer at 298 K and found to be 1.73, 1.75 and 1.76 g cm^{-3}, respectively.

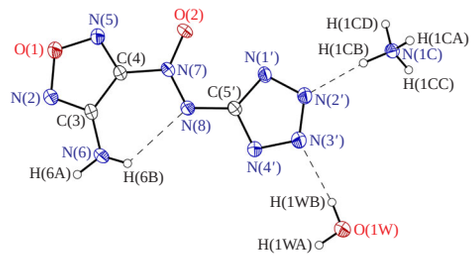


Figure 1 Single-crystal X-ray diffraction data for ammonium salt monohydrate **3a**·H_2O; non-hydrogen atoms are represented by probability ellipsoids of atomic displacements (p = 50%).

The thermal stability of (1*H*-tetrazol-5-yl-*NNO*-azoxy)-furazans **1**–**4** was determined with differential scanning calorimetry (DSC) (Table 1 and Online Supplementary Materials). Tetrazoles **1** and **2** begin to decompose without melting at 147 and 183 °C, respectively. Ammonium salt **3a** (T_{onset} = 199 °C) turned out to be more thermally stable as compared to ammonium salt **4a** (T_{onset} = 146 °C). The same pattern was observed in the case of hydrazinium salts **3b** (T_{onset} = 177 °C) and **4b** (T_{onset} = 149 °C). Installation of the azoxyfurazanyl moiety to (1*H*-tetrazol-5-yl-*NNO*-azoxy)-furazans generally decreased the thermal stability of target energetic materials.

The standard enthalpies of combustion (ΔH_c^0) for energetic salts **3a** and **3b** were determined experimentally by the method of combustion (bomb) calorimetry and the standard enthalpies of formation (ΔH_f^0) were calculated from ΔH_c^0 (see Online Supplementary Materials). The enthalpy of formation of

Table 1 Physical and energetic characteristics of furazans **2**, **3a**,**b** and **4b** in comparison with hexogen (RDX).

Compound	Formula	M_w	T_d[a]/°C	α[b]	d/g cm^{-3}	ΔH_f^0/kcal kg^{-1}	D[g]/km s^{-1}	P_{C-J}[h]/GPa
2	$C_5H_3N_{13}O_4$	309.16	147	0.35	1.73[c]	+792[e]	8.63[i]	32.6[i]
3a	$C_3H_6N_{10}O_2$	214.15	199	0.22	1.70[d]	+531[f]	8.61[i]	31.6[i]
3b	$C_3H_7N_{11}O_2$	229.16	177	0.21	1.75[c]	+623[f]	8.95[i]	36.0[i]
4b	$C_5H_7N_{15}O_4$	341.21	149	0.30	1.76[c]	+710[e]	8.89[i]	35.4[i]
RDX	$C_3H_6N_6O_6$	222.12	204[j]	0.67	1.82[j]	+72[j]	8.96[i] 8.75[j]	36.6[i] 35.0[j]

[a]Decomposition temperature (extrapolated onset temperature at a heating rate of 5 °C min^{-1}). [b]Oxidizer excess coefficient. For a compound with the molecular formula of $C_xH_yN_vO_w$, $\alpha = w/(2x+y/2)$. [c]Density measured with a gas pycnometer at 298 K. [d]Density measured by X-ray powder diffraction at 298 K. [e]Calculated enthalpy of formation. [f]Experimentally measured standard enthalpy of formation. [g]Detonation velocity. [h]Detonation pressure. [i]Calculated with Shock and Detonation (S&D) Version 4.5.[39] [j]Ref. 41.

† *Crystal data for* **3a**·H_2O. $C_3H_8N_{10}O_3$ (M = 232.19) at 120 K, monoclinic, space group $P2_1/n$, a = 12.2912(18), b = 12.7236(19) and c = 13.115(2) Å, β = 109.104(4)°, V = 1938.0(5) Å^3, Z = 8, Z' = 2, d_{calc} = 1.592 g cm^{-3}. Intensities of 5648 independent reflections (R_{int} = 0.0609) out of 24176 collected ($2\theta_{max}$ = 60° for MoKα radiation) were used in refinement that converged to R_1 = 0.0416 [for 3952 reflections with $I > 2\sigma(I)$], wR_2 = 0.1083 and GOF = 1.021; residual electron density –0.247/0.409 e Å^{-3}(ρ_{max}/ρ_{min}).

Powder diffraction crystal data for **3**. $C_3H_6N_{10}O_2$ (M = 214.18) at room temperature (*ca.* 298 K): monoclinic, space group $P2_1/c$, a = 6.9973(3), b = 10.1103(4) and c = 11.9008(6) Å, β = 96.4751(19)°, V = 836.56(6) Å^3, Z = 4, Z' = 1, d_{calc} = 1.700 g cm^{-3}. The restrained Rietveld refinement converged to R_{bragg} = 0.0099 and R_{wp} = 0.0450 for diffraction data with 2θ < 90° (CuKα radiation).

Single crystal X-ray diffraction data were collected on a Bruker Apex II diffractometer equipped with PHOTON 2 detector using graphite-monochromated MoKα radiation (λ = 0.71073 Å). The structure was solved by dual-space method using SHELXT,[34] and was refined in anisotropic approximation against F^2 using SHELXL.[34] 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 **3a** were determined by singular value decomposition index algorithm[35] implemented in the Bruker TOPAS 5.0 software,[36] the space group was determined by the analysis of systematic absences. The structure was solved using the parallel tempering approach implemented in FOX program.[37] The restrained Rietveld refinement was carried out in TOPAS 5.0.

CCDC 2204819 (for **3a**) and 2204820 (for **3a**·H_2O) 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.

ammonium salt **3a** is 531 kcal kg^{-1}. Hydrazinium salt **3b** has ΔH_f^0 = 623 kcal kg^{-1}. The enthalpy of formation of compounds **2** and **4b** in the solid phase (792 and 710 kcal kg^{-1}, respectively) was calculated by the additive method using the values of the contributions of functional groups to the enthalpy of formation (see Online Supplementary Materials). In terms of enthalpy of formation novel compounds **2**, **3a**,**b** and **4b** significantly exceed the commonly used energetic materials (TNT, RDX, HMX) and hexanitrohexaazaisowurtzitane (CL-20) (ΔH_f^0 = 205 kcal kg^{-1}).[38]

The detonation parameters of compounds **2**, **3a**,**b** and **4b** (see Table 1) were calculated using the Shock and Detonation (S&D) software package, version 4.5.[39] Salts **3a** and **3b** have the following calculated characteristics: detonation velocities are 8.61 and 8.95 km s^{-1} and the detonation pressures are 31.6 and 36.0 GPa, respectively. The corresponding values for tetrazole **2** and its hydrazinium salt **4b** are 8.63 and 8.89 km s^{-1} and 32.6 and 35.4 GPa, respectively. Thus, the detonation parameters of hydrazinium salts **3b** and **4b** are comparable to those of hexogen (RDX) (8.96 km s^{-1} and 36.6 GPa). These values for tetrazole **2** and ammonium salt **3a** are slightly lower. Ammonium salt **3a** is sensitive to impact at the level of octogen (HMX)[40] (IS = 6 J) and has a low sensitivity to friction (FS = 230 N). Hydrazinium salt **3b** (IS = 4 J, FS = 130 N) is more sensitive to mechanical stimuli than salt **3a**, and is impact sensitive as CL-20,[40] while its friction sensitivity is at the level of HMX.[40]

In summary, methods for the synthesis of novel energetic compounds, (1*H*-tetrazol-5-yl-*NNO*-azoxy)furazans, have been developed. These energetic compounds were fully characterized by IR and multinuclear NMR (^{1}H, ^{13}C, ^{14}N, ^{15}N) spectroscopy as well as high-resolution mass spectrometry and elemental analysis. Tetrazole **2** and hydrazinium salts **3b** and **4b** have high energy performance and may be of interest as potential components of energetic materials.

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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.2022.11.002.

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