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New heterocyclic furazano[3,4-*d*][1,2,3]triazine system as a platform for energetic compound engineering

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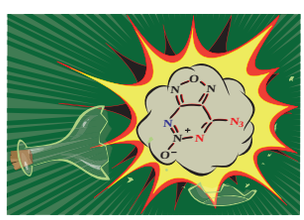
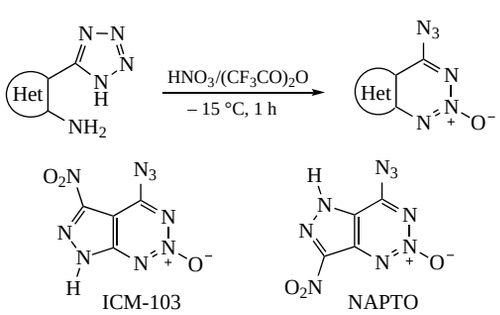
Novel 7-azidofurazano[3,4-*d*][1,2,3]triazine 5-oxide was synthesized from 3-amino-4-(tetrazol-5-yl)furazan and nitronium salt. Its characterization including energetic properties is described.



Keywords: furazans, tetrazoles, [1,2,3]triazine 5-oxide, azido group, cascade nitration/ring-closure/ring-opening reaction, nitronium salts.

The azido group is a privileged explosophoric group[1] and is found in numerous energetic materials.[2–5] The diverse applications of azidoazoles and azidoazines have aroused interest in their synthesis.[6–8] Recently, Zhang *et al*. showed that 3,4-fused 4-azido-1,2,3-triazine 2-oxide can be constructed from amino heterocycles bearing a tetrazolyl substituent in the *ortho* position through an unusual nitration cyclization process (Scheme 1)[9–11] with the use of fuming HNO_3/98% H_2SO_4 and $HNO_3/(CF_3CO)_2O$. While various benzene, azole, and azine precursors have been investigated, only pyridine and pyrazole precursors have been found to be compatible with this chemistry. Isomeric ICM-103[9] and NAPTO[10] (see Scheme 1) are the novel energetic compounds with remarkably high energy content.

These reports prompted us to disclose our own investigation of cascade nitration/ring closure reactions aiming to readily access polycyclic heterocyclic architectures from available starting compounds. Our continuing interest in furazan (1,2,5-oxadiazole) derivatives[12–16] has resulted in a novel bicyclic system, namely, [1,2,5]oxadiazolo[3,4-*d*][1,2,3]triazine.

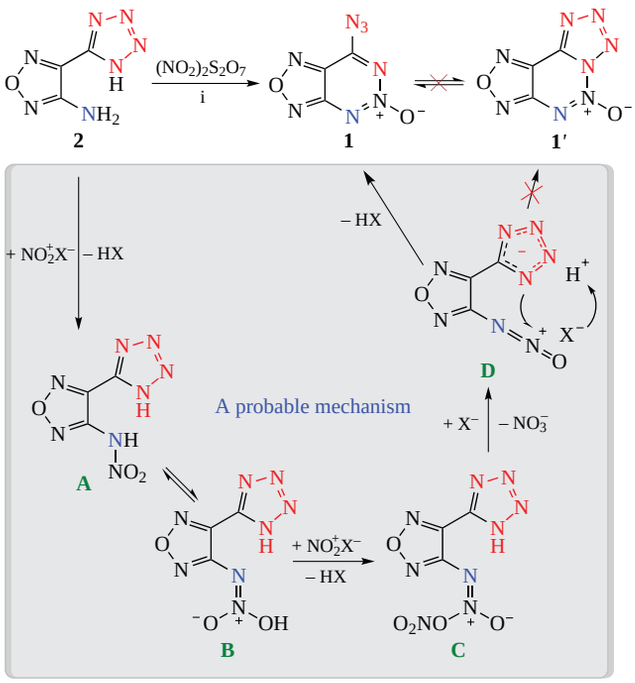


Scheme 1

Herein, we report a cascade nitration/ring-closure/ring-opening reaction sequence affording 7-azidofurazano[3,4-*d*][1,2,3]-triazine 5-oxide **1**, starting from 3-amino-4-(tetrazol-5-yl)-furazan **2** and a nitronium salt (see Scheme 1). Under conditions similar to those used to prepare ICM-103 and NAPTO (HNO_3/H_2SO_4 or $HNO_3/(CF_3CO)_2O$ at –15 to 0 °C),[9–11] reactions of compound **2** with the same nitrating mixtures failed to give the corresponding 1,2,3-triazine due to decomposition of the substrate. This is not surprising, since the use of aminofurazans is often difficult due to their sometimes low basicity and specific reactivity.[17–19]

Our current strategy was based on our previous observation,[20,21] as well as on related studies,[22] that the reactions of poorly basic (het)aromatic amines with nitronium salts, *via* a nitramine and a diazonio oxide intermediate, can lead to cyclization with a suitable adjacent substituent. Those reactions were empoyed for the synthesis of 1,2,3,4-tetrazine 1,3-dioxides.[23] Our interest in the use of nitronium salts as nitrating/ring closure agents for furazanamines stemmed from a protocol we developed for the preparation of furazano[3,4-*e*]-[1,2,3,4]tetrazine 4,6-dioxide from 4-(*tert*-butyl-*NNO*-azoxy)-furazanamine using salts $(NO_2)_2S_2O_7$ or NO_2HSO_4.[21]

We initiated our studies by evaluating the reaction of 3-amino-4-(tetrazol-5-yl)furazan **2**[24,25] with nitronium salts, $NO_2^+X^-$, to give product **1**, under a variety of conditions. The presumed course of events in this cascade reaction (Scheme 2) involves the attack of NO_2^+ on the amino group, a shift of the proton of primary nitramine **A** to the oxygen atom, the O-nitration of tautomer **B**, the ionic dissociation of intermediate **C** promoted by the anion X^-. Finally, the diazonio oxide intermediate **D** would undergo reorganization through an electrophilic attack of the tetrazole ring with its synchronous opening, accompanied by

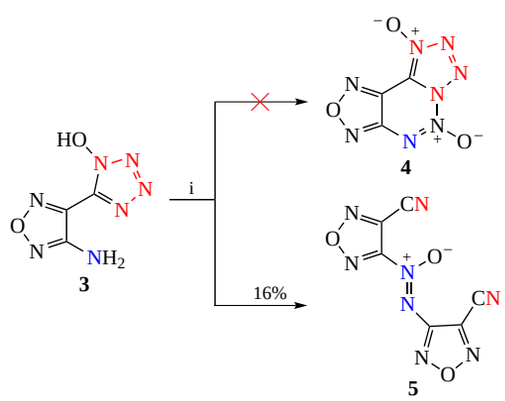


Scheme 2 *Reagents and conditions*: i, $(NO_2)_2S_2O_7$ (3 equiv.), MeCN, room temperature, 4 h.

an expulsion of HX. Azido-tetrazole isomerism plays an important role in tetrazole chemistry.[26]

Gratifyingly, an efficient procedure for the formation of compound **1** was rapidly identified. While a number of nitronium salts[27–29] such as NO_2BF_4, $(NO_2)(CF_3CO)SO_4$ and NO_2ClO_4 were viable reagents, $(NO_2)_2S_2O_7$ provided the best results. Accordingly, the treatment of amine **2** with $(NO_2)_2S_2O_7$ in MeCN under anhydrous conditions provided azide **1** in 68% yield. Three equivalents of this nitronium salt were required to achieve full conversion of starting amine **2**. Interestingly, the azido tautomer **1** was obtained directly. The putative intermediate **1′** was not detected, presumably because the tetrazole ring in this tricycle should be destabilized by the electron-withdrawing effect of neighboring fragments.

N-Hydroxytetrazoles are very accessible compounds.[30,31] We were curious if *N*-hydroxy compound **3**[32,33] could be cyclized using the above method (Scheme 3). *N*-Oxide moiety stabilizes high nitrogen compounds,[34,35] which gives reason to hope for the stabilization of the fused tetrazole ring in the target product **4**. To test this, we subjected *N*-hydroxytetrazole **3** to the same conditions as simple tetrazole **2**. The reaction did not produce the expected *N*,*N*′-dioxide **4**. Instead, a complex mixture, probably due to the destructive nitration of the hydroxytetrazole fragment, resulted. Only a small amount of dinitrile **5** was isolated (see Scheme 3).



Scheme 3 *Reagents and conditions*: i, $(NO_2)_2S_2O_7$, MeCN, 5 °C, then room temperature, 2 h.

Compounds of this study were characterized by IR, ^{13}C and ^{15}N NMR spectroscopy, HRMS, as well as by microanalysis. The characteristic IR absorption band of N_3 group in compound **1** was observed as sharp peak at 2170 cm^{-1}, and in the ^{14}N NMR spectrum two signals for positively charged nitrogen atoms appear at –47 (N→O) and –135 (N_3) ppm (relative to $MeNO_2$). This spectral pattern is typical for azido tautomer.[36] The structure of compound **1** was confirmed unequivocally by X-ray crystallographic analysis.† Compound **1** crystallizes in the orthorhombic space group $P2_12_12_1$ with four molecules per unit cell (Figure 1).

The molecule of compound **1** adopts nearly planar geometry, as recently observed in related nitropyrazole fused azido[1,2,3]-triazine 5-oxides ICM-103[9] and NAPTO.[10] However, ICM-103 was obtained in the form of hydrate, and, therefore, the features of its crystal packaging cannot be used in a comparative analysis of the structure–property relationship. On the other hand, NAPTO is suitable for comparison with compound **1**. While NAPTO formed a layered crystal structure through a combination of N–H···O(N) hydrogen bonds and weak π···π interactions, the main intermolecular interactions in crystal of **1** are of the O(N)···π type. According to a thorough comparison of the crystal packing of compound **1** and NAPTO, based on the inspection of the Hirshfeld surfaces and pair interaction energies[37,38] (see Online Supplementary Materials), the molecular environment in compound **1** is significantly more isotropic than in NAPTO. As a result, it has higher packing coefficient (73.9 *vs.* 73.3% for NAPTO), but is more sensitive to external mechanical stimuli (Table 1).

To evaluate the possibility of compound **1** as a suitable green primary explosive candidate, the thermal stability, sensitivity towards impact and friction were investigated (see Table 1). Using a calculated enthalpy of formation and measured density, the detonation pressure (P_{C-J}) and velocity (D) for all compounds were calculated using the PILEM program.[39] Among the analogues, compound **1** has the highest total nitrogen and oxygen content. Compound **1** melts at 129 °C, followed by an onset of decomposition at 130 °C, while ICM-103 and NAPTO

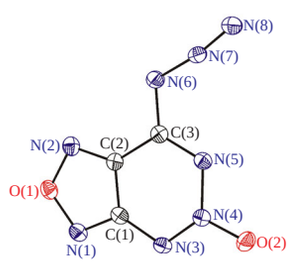


Figure 1 General view of 7-azidofurazano[3,4-*d*][1,2,3]triazine 5-oxide **1**. Thermal ellipsoids are drawn at 50% probability level.

† *Crystal data for* **1**. $C_3N_8O_2$, M = 180.11, orthorhombic at 100 K, space group $P2_12_12_1$, a = 5.8386(3), b = 9.3082(5) and c = 11.7264(6) Å, V = 637.29(6) Å^3, Z = 4, d_{cryst} = 1.877 g cm^{-3}, $F(000)$ = 360. Total 8933 reflections were measured and 1391 independent reflections (R_{int} = 0.0453) were used in a further refinement. The refinement converged to wR_2 = 0.0608 calculated on F^2_{hkl} for all 1391 independent reflections with $2\theta < 54.1°$ [GOF = 1.066, R = 0.0235 calculated on F_{hkl} for 1329 reflections with $I > 2\sigma(I)$]. The measurements were made on a Bruker Apex II CCD diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å). The structure was solved by the direct methods and refined by the full-matrix least-squares procedure against F^2 in anisotropic approximation. The refinement was carried out with the SHELXL program.

CCDC 2172459 contains 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 energetic properties of compound **1** and related analogues.

Compound	ICM-103[9]	NAPTO[10]	**1**
Formula	$C_4HN_9O_3$	$C_4HN_9O_3$	$C_3N_8O_2$
M_W	223.11	223.11	180.09
[N] (%)[a]	56.50	56.50	62.22
[N] + [O] (%)[b]	78.01	78.01	79.99
$\Omega(CO_2)$ (%)[c]	–35.85	–35.85	–35.54
α[d]	0.353	0.353	0.333
ρ^{20}/g mol^{-3} [e]	1.86	1.85	1.81
T_m/°C [f]	–	–	129
T_{dec}/°C [g]	160	203	130
IS/J[h]	4	18	1.8
FS/N[i]	60	325	< 5
$\Delta_f H^o$ (*s*)/kJ mol^{-1} (kJ g^{-1}) [j]	744 (3.33)	774 (3.47)	838 (4.65)
D/m s^{-1} [k]	8.8	8.9	9.1
P_{C-J}/GPa[l]	37	37	37

[a] Nitrogen content. [b] Total nitrogen and oxygen content. [c] Oxygen balance; for $C_xH_yN_wO_z$, Ω (%) = 1600 $[(z-2x-y/2)/M_w]$. [d] Oxygen coefficient; for $C_xH_yN_wO_z$, $\alpha = z/(2x+y/2)$; a compound with $\alpha > 1$ is an oxidizer. [e] Density from X-ray analysis at room temperature. [f] Melting point. [g] Decomposition temperature (an onset temperature) measured at a heating rate of 5 °C min^{-1}. [h] Impact sensitivity (STANAG 4489). [i] Friction sensitivity (STANAG 4487). [j] Calculated enthalpy of the formation for solid state. [k] Detonation velocity at maximal density. [l] Detonation pressure.

decompose (onset temperature) without melting. Thermal stability and mechanical safety of compounds follow similar trends increasing from **1** to NAPTO. In terms of impact and friction sensitivity, compound **1** can be classified as a primary explosive. Due to the increase in the enthalpy of formation of compound **1**, its detonation characteristics are much superior to those of ICM-103 and NAPTO.

In summary, we have designed and synthesized a new green energetic material, 7-azidofurazano[3,4-*d*][1,2,3]triazine 5-oxide **1**, comprising fused furazan and [1,2,3]triazine moieties, an azido group, and *N*-oxide as an oxygen carrier. This promising bicyclic compound can be prepared in a straightforward manner from an available precursor. Compound **1** exhibits excellent for primary explosive detonation performance, and sensitivity to external stimuli with an impact sensitivity of 1.8 J and a friction sensitivity of <5 N (for comparison, pentaerythrityl tetranitrate: *IS* = 3.5 J, *FS* = 70 N). It is important to note that compound **1** is 80% composed of nitrogen and oxygen atoms.

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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.2022.11.003.

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