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Derivatives of 5-Nitro-1,2,3-2H-triazole – High Performance Energetic Materials

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Abstract: The energetic derivatives of 5-nitro-1,2,3-2H-triazole, which include 2-(methyl or amino)-4-(nitramino, azido, or nitro)-5-nitro-1,2,3-2H-triazoles, were prepared in moderate yields, and confirmed with NMR and IR spectroscopy, and elemental analysis. Their key properties, viz., melting and decomposition temperatures, densities, detonation pressures and velocities, and impact sensitivities, were measured or calculated. Among the new derivatives, 2-amino-4,5-dinitro-1,2,3-2H-triazole exhibits properties (T_m , 94 °C; T_d , 190 °C; ρ , 1.83 gcm⁻³; P, 36.2 Gpa, vD, 8843 ms⁻¹, IS, 24 J), comparable with RDX (T_m , 205 °C; T_d , 230 °C; ρ , 1.80 gcm⁻³; P, 35.0 Gpa, vD, 8762 ms⁻¹, IS, 7.5 J), and may have potential as a high-performance energetic material.

Introduction

The development of new high energy density materials (HEDM) continues to focus on the synthesis of the derivatives of 5-membered nitrogen-containing heterocycles (azoles) which are widely functionalized with energetic groups such as nitro, nitramino, azido, etc, and are reported frequently.¹ In order to achieve better detonation performance, groups which are more energetic are bonded to azole rings, especially the fully C-functionalized azoles such as 5-nitro-tetrazole,² 3,5-dinitro-triazole,³ 4,5-dinitro-triazole,⁴ 2,4,5-trinitro-imidazole,⁵ 3,4,5-trinitro-pyrazole,⁶ and 2,3,4,5-tetranitro-pyrrole.⁷ Many of the resulting azole compounds are very energetic, with high sensitivities (such as the tetrazole derivatives including 5-azido-tetrazole,⁸ 5-nitramino-tetrazole,⁹ and 5-nitro-tetrazole²) and low thermal stabilities (such as pyrrole derivatives, e.g., tetranitro-pyrrole)

which precludes their applications as explosives. Also, the resulting azoles tend to be very acidic as a result of the electron withdrawing effect of the nitro group substitutents on the azole ring upon the N-H group; this enhances the reactivity with metals increasing the sensitivity and accelerating decomposition while concomitantly increasing the cost of storage. Two routes to decrease the acidity include reaction with bases to form energetic salts - a method which have been investigated extensively¹⁰ or the introduction of methyl or amino groups via methylating or aminating reagents to replace the acidic proton.^{5,6} Compared with methylation, amination of energetic azoles is of greater value since while the methyl group has a negative impact on detonation performance, the amino group has a slight positive effect resulting in an increase in detonation performance.

1,2,3-2H-Triazole is a surprisingly stable structure compared to other organic compounds with three contiguous nitrogen atoms. With higher heats of formation, some of the derivatives of 1,2,3-2H-triazole are reported to be more thermally stable than the 1,2,4-1H-triazole isomers, for example, compare 3-amino-5-nitro-1,2,4-1H-triazole (T_{d} , 243 °C) and 4-amino-5-nitro-1,2,3-2H-triazole (T_d , 297 °C).^{3,11} Although the derivatives of 1,2,3-2H-triazole such as 4-amino-5-nitro-1,2,3-2H-triazole and 4,5-dinitro-1,2,3-2Htriazole have been reported.⁴ 1.2.3-2H-triazole-based energetic compounds have been investigated to a lesser extent than the other azoles, such as tetrazole, 1,2,4-1H-triazole, pyrazole, imidazole, and pyrrole. In this paper, a series of derivatives of 5-nitro-1,2,3-2Htriazole including 4-nitramino-5-nitro-1,2,3-2H-triazole and its methyl derivative, 4azido-5-nitro-1,2,3-2H-triazole and its methyl and amino derivatives, and the methyl and amino derivatives of 4,5-dinitro-1,2,3-2H-triazole, were prepared, and fully characterized with ¹H, ¹³C, and ¹⁵ N NMR, and IR spectroscopy, differential scanning calorimetry, elemental analysis, hammer tests, and in some cases with single crystal X-ray structuring. Their heats of formation and detonation properties were calculated by using Gaussian 03 and Explo 5.5, respectively. Some of these compounds show good detonation performances and sensitivities. Considering that the multi-step preparation of derivatives of 5-nitro-1,2,3-2H-triazole is costly, the development of short and efficient method for preparation will be of value.

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Results and discussion

As the starting material for the series of new compound, 4-amino-5-nitro-1,2,3-2H-triazole (1) was prepared by multi-step reactions from acetic anhydride and nitric acid (100%) according to literature methods (Scheme 1).^{4,12}



Scheme 1. Synthesis of 4-amino-5-nitro-1,2,3-2H-triazole, 1

4-Amino-5-nitro-1,2,3-2H-triazole (1) can be directly nitrated with mixed acid (70% HNO₃/concentrated H₂SO₄) to give 4-nitramino-5-nitro-1,2,3-2H-triazole (2) in 76% yield. Compound 1 has very poor solubility in common organic solvents, and therefore was refluxed with dimethyl sulfate in H₂O for 10 h to obtain 4-amino-2-methyl-5-nitro-2H-triazole (3; yield 51%) (Scheme 2). Mixed acid was used to convert 3 to its 4-nitramino analogue, **4**.



Scheme 2. Synthesis of the 4-nitramino-5-nitro-1,2,3-2H-triazole (2) and its methyl derivative.

4-Azido-5-nitro-1,2,3-2H-triazole (5) was prepared by the diazotation of 1 with sodium nitrite in aqueous sulfuric acid (70%) followed by reaction with sodium azide. It was neutralized with ammonia to form ammonium 4-azido-5-nitro-1,2,3-2H-triazolate which was reacted with methyl iodide or O-picrylhydroxylamine (pic-O-NH₂)¹³ in

acetonitrile to yield 4-azido-2-methyl-5-nitro-1,2,3-2H-triazole (**6**; yield 61%) or 2amino-4-azido-5-nitro-1,2,3-2H-triazole (**7**; yield 75%), respectively (Scheme 3).



Scheme 3. Synthesis of the 4-azido-5-nitro-1,2,3-2H-triazole (5), and its methyl and amino derivatives.

Using the literature method, 4,5-dinitro-1,2,3-2H-triazole (**8**) was prepared by oxidation of **1** with hydrogen peroxide (30%).⁴ With the methodology given in Scheme 3, 2-methyl-4,5-dinitro-1,2,3-2H-triazole (**9**; yield 51%) and 2-amino-4,5-dinitro-1,2,3-2H-triazole (**10**; yield 55%) were obtained by reacting ammonium 4,5-dinitro-1,2,3-2H-triazolate with methyl iodide and pic-O-NH₂, respectively (Scheme 4).



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Scheme 4. Synthesis of the 4,5-dinitro-1,2,3-2H-triazole (8), and its methyl and amino derivatives.

In order to compare the properties of the derivatives of 1,2,3-2H-triazole with the 1,2,4-1H-triazole isomer, N-amino-dinitro-triazole was taken as an example since this is among the most interesting derivatives of the triazole-based energetic compounds. 1-Amino-3,5-dinitro-1,2,4-1H-triazole (**13**; yield, 69%) was prepared by diazotation, neutralization, and amination of 3,5-diamino-1,2,4-1H-triazolate (Scheme 5). While this work was underway, **13** was reported.¹⁴

Scheme 5. Synthesis of 1-amino-3,5-dinitro-1,2,4-1H-triazole, 13

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The structures of the resulting compounds are supported by ¹H, ¹³C, and ¹⁵N NMR, and IR spectroscopy, and elemental analysis. Compounds **2**, **10** and **13** were further confirmed by single-crystal X-ray structuring.

Properties of the compounds

The thermal stabilities of the above compounds were determined by differential scanning calorimetric (DSC) measurements scanning at 5 °C min⁻¹ (Table 1). While compounds **2**, **4**, and **5** decomposed without melting at 130, 112, and 149 °C, respectively, other compounds melted prior to decomposing. Of the four methyl derivatives (**3**, **4**, **6**, and **9**), **3**, **6**, and **9** melt with sharp endothermic peaks. No sharp exothermic peaks which would indicate decomposition are observed which may be a result of the compounds vaporizing before decomposition. Also, in TGA measurements, weight loss occurs after melting for **3**, **6**, and **9** making it very difficult to determine their decomposition points. Among the new compounds, 2-amino-4,5-dinitro-1,2,3-2H-triazole (**10**) shows the highest onset decomposition point at 190 °C.

Densities of these compounds were measured with a gas pycnometer, and found to be in the range between 1.58 (**3**) and 1.87 (**2**) gcm⁻³ at 25 °C. Based on single-crystal X-ray diffraction, the calculated densities of 4-nitramino-5-nitro-1,2,3-2H-triazole and 2amino-4,5-dinitro-1,2,3-2H-triazole (**10**) are 1.919 at 23 °C and 1.868 gcm⁻³ at 20 °C, respectively, while the experimental data as 1.87 and 1.83 gcm⁻³ at 25 °C. Comparison of the nitramino-, azido-, and nitro-based derivatives of 5-nitro-1,2,3-2H-triazole, the nitramino- and nitro-based compounds have similar densities while not surprisingly the corresponding azido-based compounds have the lowest densities.

The gas phase enthalpies of formation of the above compounds were calculated using the Gaussian 03 (Revision D. 01) suite of programs.¹⁵ The enthalpy of sublimation was estimated according to Trouton's rule.¹⁶ The resulting heats of formation of these compounds vary between 0.87 (**3**) and 3.50 (**7**) kJg⁻¹. Because of the high enthalpy of formation of the azido group (9.86 kJg⁻¹), the azido-based compounds show higher heats of formation than the corresponding nitramino- and nitro- compounds. Moreover, the 2-amino derivatives possess more positive heats of formation than their corresponding

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parents; in contrast the heats of formation of the 2-methyl derivatives are lower than those of their corresponding parents.

With the data for molecular weight, density, and heat of formation in hand, the detonation pressure (P) and velocity (vD) of the resulting compounds were calculated with Explo 5.05.¹⁷ For compounds **10** and **13**, two groups of detonation performance data were obtained by using the measured density and calculated density, respectively. The impact sensitivities were determined by BAM Fallhammer measurements with a 10 kg drop weight. As can be seen in Table 1, the amino derivatives 7 (P, 33.0 Gpa; vD, 8756 ms⁻¹; IS, 3 J) and **10** (P, 36.2 Gpa; vD, 8843 ms⁻¹, IS, 24 J) exhibit higher detonation performance and are more impact sensitive than their corresponding methyl derivatives 6 (P, 26.3 Gpa; vD, 8096 ms⁻¹; IS, 8 J) and 9 (P, 28.5 Gpa; vD, 8126 ms⁻¹; IS, 35 J). Although 4-nitramino-5-nitro-1,2,3-2H-triazole (2, P, 36.9 Gpa, vD, 8876 ms⁻¹), 4-azido-5-nitro-1,2,3-2H-triazole (5, P, 32.9 Gpa; vD, 8669 ms⁻¹) and its amino derivative (7, P, 33.0 Gpa; vD, 8756 ms⁻¹) show good detonation properties, their impact sensitivities are 3.5, 4, and 3 J, respectively, which tends to preclude their further applications. 2-Amino-4,5-dinitro-1,2,3-2H-triazole (10) is competitive with the performance properties of RDX (P. 35.0 Gpa; vD, 8762 ms⁻¹) and it is more than 3X less impact sensitive (24 J). Thus it is the most promising energetic material among the nitramino and nitro derivatives.

The thermal stabilities of 2-amino-4,5-dinitro-1,2,3-2H-triazole (10) and its isomer 1-amino-3,5-dinitro-1,2,4-1H-triazole (13) are shown in Figure 1. It can be seen that 10 with the onset decomposition temperature ($T_{d,onset}$) as 190 °C is more stable thermally than 13 ($T_{d,onset}$, 165 °C). Moreover, with the higher heat of formation (1.58 vs 1.21 kJg⁻¹) and the same experimental densities (1.83 vs 1.83 gcm⁻³), 10 exhibits a somewhat better detonation performance than 13 (P, 36.2 vs 34.9 Gpa; vD, 8843 vs 8725 ms⁻¹) while their impact sensitivities are similar at 24 vs 30 J.

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Comp	$T_{\rm m}^{[a]}$	$T_{d,onset}^{[b]}$	$ ho^{[c]}$	$\Delta H_{\rm f}({\rm g})^{[\rm d]}$	$\Delta H_{\rm sub}^{[e]}$	$\Delta H_{ m f}^{[{ m f}]}$	$P^{[g]}$	$vD^{[h]}$	IS ^[i]
Comp.	[°C]	[°C]	[gcm ⁻³]	[kJmol ⁻¹]	[kJmol ⁻¹]	[kJmol ⁻¹]/[kJg ⁻¹]	[Gpa]	$[ms^{-1}]$	[J]
2	-	130	1.87 (1.919) ^[j]	302.4	75.8	226.6/1.30	36.9	8876	3.5
3	169		1.58	208.2	83.1	125.1/0.87	20.8	7497	> 40
4	-	112	1.74	268.5	72.4	196.1/1.04	30.0	8350	25
5	-	149	1.77	602.4	79.4	523.0/3.37	32.9	8669	4
6	124		1.65	568.6	74.7	493.9/2.92	26.3	8096	8
7	132	141	1.75	670.8	76.2	594.6/3.50	33.0	8756	3
9	79		1.70	240.2	66.2	174.0/1.01	28.5	8126	35
10	94	190	1.83 (1.868) ^[j]	343.6	69.0	274.6/1.58	36.2	8843	24
13	131	165	1.83 (1.855) ^[j]	286.7	76.0	210.7/1.21	34.9	8725	30
RDX	205	230	1.80	192 ^[k]	112 ^[k]	80/0.36	35.0	8762	7.5

Table 1. Properties of the derivatives of 5-nitro-1,2,3-2H-triazole, 1-amino-3.5-diniro-1,2,4-1H-triazole, and RDX.

^[a] Melting temperature. ^[b] Decomposition temperature (onset). ^[c] Density (25 °C) ^[d] Gas phase enthalpy of formation. ^[e] Enthalpy of sublimation according to Trouton's rule. ^[f] Heat of formation. ^[g] Detonation pressure. ^[h] Detonation velocity. ^[i] Impact sensitivity. ^[j] Calculated density from singlecrystal X-ray diffraction. ^[k] Data from NIST Chemistry WebBook



Figure 1. The DSC curves of 2-amino-4,5-dinitro-1,2,3-2H-triazole (**10**) and 1-amino-3,5-dinitro-1,2,4-1H-triazole (**13**).

X-ray Crystallography:

Crystals of **2**, **10** and **13**, suitable for single-crystal X-ray diffraction, were obtained by slow evaporation of ethyl acetate/benzene, ethyl acetate/benzene, and ethanol solutions, respectively. Their structures are shown in Figures 2, 3, and 4, and

2b

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Figure 2. 2a) Thermal ellipsoid plot (50%) and labeling scheme for 4-nitramino-5-nitro-1,2,3-2H-triazole (2). Hydrogen atoms are included but are unlabeled for clarity. 2b) Ball and stick packing diagram of 2 viewed down the b axis. Dashed lines indicate strong hydrogen bonding.



Figure 3. 3a) Thermal ellipsoid plot (50%) and labeling scheme for 2-amino-4,5-dinitro-1,2,3-2H-triazole (10). Hydrogen atoms are included but are unlabeled for clarity. 3b) Ball and stick packing diagram of 10 viewed down the b axis. Dashed lines indicate strong hydrogen bonding.

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Figure 4. 4a) Thermal ellipsoid plot (50%) and labeling scheme for 2-amino-3,5-dinitro-1,2,4-1H-triazole (**13**). Hydrogen atoms are included but are unlabeled for clarity. 4b) Ball and stick packing diagram of **13** viewed down the b axis. Dashed lines indicate strong hydrogen bonding.

crystallographic data are summarized in Table 2. Crystals 2 and 10 crystallize in the monoclinic $P2_1/c$ space group, while 13 crystallizes in the triclinic P1 space group. For 2, the nitro group is twisted out of the triazole ring plane with torsion angles of N(1)-C(5)-N(10)-O(11), 6.1(4); C(4)-C(5)-N(10)-O(11), -174.5(3); N(1)-C(5)-N(10)-O(12), -173.1(2); C(4)-C(5)-N(10)-O(12), 6.3(4). There are two groups of intermolecular hydrogen bonds N(2)-H(2)...N(3) and N(6)-H(6)...O(12). For crystals 10 and 13, the big differences between the two isomers are their torsion angles of the nitro groups out of the triazole ring plane. For crystal 10, the twisted angles of the two nitro groups are as follows: N(5)-C(1)-N(6)-O(8), 145.88°; C(2)-C(1)-N(6)-O(8), -25.3°; N(5)-C(1)-N(6)-O(7), -31.6°; C(2)-C(1)-N(6)-O(7), 157.26°; N(3)-C(2)-N(9)-O(11), 149.86°; C(1)-C(2)-N(9)-O(11), -26.9°; N(3)-C(2)-N(9)-O(10), -29.5°; C(1)-C(2)-N(9)-O(10), 153.8°, while those of crystal 13 are as follows: N(1A)-C(5A)-N(10A)-O(11A), 169.5°; N(1B)-C(5B)-N(10B)-O(11B), 153.1°; N(4A)-C(5A)-N(10A)-O(12A), 165.7°; N(4B)-C(5B)-N(10B)-O(12B), 155.4°; N(2A)-C(3A)-N(7A)-O(9A), -178.1°; N(2B)-C(3B)-N(7B)-O(9B), -176.4°; N(4A)-C(3A)-N(7A)-O(8A), -177.1°; N(4B)-C(3B)-N(7B)-O(8B), - 177.0° . From Figures 2b and 3b, it can be clearly seen that the intermolecular hydrogen bonds are formed in the triazole-based energetic compounds, such as N(12)-

H(12A)...N(12) for **10**, and N(6A)-HAA...O(9A) for **13**. The extensive hydrogen bonding interactions contribute to an increase in density and decrease in sensitivity of the two compounds. Further details are provided in the ESI.

	2	10	13
formula	$C_2H_2N_6O_4$	$C_2H_2N_6O_4$	$C_2H_2N_6O_4$
CCDC number	897415	879779	879777
$M_{ m r}$	174.10	174.10	174.10
Crystal size [mm ³]	0.11 x 0.07 x 0.06	0.18 x 0.16 x 0.05	0.50 x 0.37 x 0.20
crystal system	Monoclinic	Monoclinic	Triclinic
space group	$P2_1/c$	$P2_1/c$	P1
a [Å]	11.430(7)	8.044(4)	8.3290(10)
<i>b</i> [Å]	5.989(4)	16.110(6)	11.4808(15)
<i>c</i> [Å]	8.915(5)	4.998(2)	13.6457(17)
α [°]	90	90	78.002(4)
β[°]	99.043(8)	107.119(5)	77.916(4)
γ[°]	90	90	89.974(4)
$V[Å^3]$	602.6(6)	619.0(5)	1246.8(3)
Ζ	4	4	8
<i>T</i> [K]	296(2)	293(2) K	293(2)
$\rho_{\rm calcd} [{ m Mg/m}^3]$	1.919	1.868	1.855
μ [mm ⁻¹]	0.180	0.176	0.174
<i>F</i> (000)	352	352	704
θ [°]	1.80 to 26.47	2.53 to 26.25	1.56 to 26.48
index ranges	-14<=h<=14,	-9<=h<=9,	-10<=h<=10,
	-7<=k<=6,	-19<=k<=0,	-14<=k<=14,
	-11<=1<=11	-6<=l<=6	-17<=l<=17
reflections collected	5068	2355	12125
independent reflections	$1242 [R_{int} = 0.0692]$	$1218 [R_{int} = 0.0393]$	8734 [0.0145]
$(R_{\rm int})$			
data / restraints /	1242 / 0 / 109	1218 / 2 / 115	8734 / 19 / 913
parameters			
GOF on F^2	1.007	1.086	1.063
$R_1 (I > 2\delta (I))^{[a]}$	0.0551	0.0376	0.0339
$wR_2 (I > 2\delta (I))^{[b]}$	0.1402	0.0889	0.0773
R_1 (all data)	0.0841	0.0587	0.0403
wR_2 (all data)	0.1600	0.1015	0.0821
Largest diff. peak and	0.325 and -0.339	0.159 and -0.237	0.159 and -0.202
hole [e.Å ⁻³]			
$\begin{bmatrix} a \end{bmatrix}$ $R = \sum \ E\ - \ E\ / \sum \ E\ $	$\begin{bmatrix} b \end{bmatrix}$, $\begin{bmatrix} b \end{bmatrix} = \begin{bmatrix} \sum w (E^2 - E^2)^2 / \sum e^{-2} \end{bmatrix}$	$(F^2)^2$ /2	
$\mathbf{n}_1 - \mathbf{\Delta} \ \mathbf{r}_o\ - \ \mathbf{r}_c\ / \mathbf{\Delta} \ \mathbf{r}_o\ $	$wR_2 = [\angle w(r_o - r_c) / \angle v]$	(r_o)	

Table 2. Crystallographic data for 2, 10, and 13.

Conclusion

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The energetic 5-nitro-1,2,3-2H-triazole-based compounds, including 4-nitramino-5-nitro-1,2,3-2H-triazole (**2**) and its methyl derivative (**4**), 4-azido-5-nitro-1,2,3-2H-triazole (**5**) and its methyl (**6**) and amino (**7**) derivatives, and the methyl (**9**) and amino (**10**) derivatives of 4,5-dinitro-1,2,3-2H-triazole, were synthesized, and fully characterized with 1 H, 13 C, and 15 N NMR, and IR spectroscopy, differential scanning calorimetry,

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elemental analysis, and hammer tests. The heats of formation and detonation properties of the resulting compounds were calculated by Gaussian 03 and Explo 5.05 programs, respectively. The amino derivatives exhibit higher detonation performances and are more impact sensitive than the corresponding methyl derivatives. Although 4-azido-5-nitro-1,2,3-2H-triazole (**5**) and its methyl (**6**) and amino (**7**) derivatives show excellent detonation performances, their high impact sensitivities discourage their actual applications. Among the 4-nitramino and 4-nitro-5-nitro-1,2,3-2H-triazole-based products, 4-nitramino-5-nitro-1,2,3-2H-triazole (**2**) and 2-amino-4,5-dinitro-1,2,3-2Htriazole (**10**) exhibit identical detonation performances, viz., *P*, 36.9 Gpa; *vD*, 8876 ms⁻¹ and *P*, 36.2 Gpa; *vD*, 8843 ms⁻¹, respectively, which are comparable with RDX (*P*, 35.0 Gpa; *vD*, 8762 ms⁻¹). Compound **10** with good thermal stability ($T_{d,onset}$, 190 °C) and impact insensitivity (24 J) is the most promising high-performance energetic material prepared in this work.

Experimental Part:

Cautions: Although none of the compounds described herein exploded or detonated in the course of this research, these materials should be handled with care using the best safety practices.

General methods: ¹H, and ¹³C spectra were recorded on a 300 MHz (Bruker AVANCE 300) nuclear magnetic resonance spectrometer operating at 300.13, and 75.48 MHz, and a 500 MHz (Bruker AVANCE 500) nuclear magnetic resonance spectrometer operating at 50.69 MHz for ¹⁵N spectra, respectively, using [D₆]DMSO as a locking solvent unless otherwise stated. Chemical shifts in ¹³C and ¹⁵N NMR spectra were reported relative to Me₄Si and MeNO₂, respectively. The melting and decomposition points were recorded on a differential scanning calorimeter (DSC, TA Instruments Q10) at a scan rate of 5 °C min⁻¹ in closed aluminum containers with a small hole in the lids. IR spectra were recorded by using KBr pellets. Densities were measured at room temperature using a Micromeritics Accupyc 1330 gas pycnometer. Elemental analyses were obtained on a CE-440 elemental analyzer (EAI Exeter Analytical).

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X-ray crystallography:

An irregular colorless crystal of dimensions 0.11 x 0.07 x 0.06 mm² (2), an orange plate crystal of dimensions 0.18 x 0.16 x 0.05 mm² (10), and an irregular colorless crystal of dimensions 0.50 x 0.37 x 0.20 mm² (13) were mounted on a MiteGen MicroMesh using a small amount of Cargille Immersion Oil. Data were collected on a Bruker threecircle platform diffractometer equipped with a SMART APEX II CCD detector. The crystals were irradiated using graphite monochromated MoK_{α} radiation ($\lambda = 0.71073$). An Oxford Cobra low temperature device was used to keep the crystals at a constant 293(2)°K during data collection.

Data collection was performed and the unit cell was initially refined using *APEX2* [v2010.3-0].¹⁸ Data Reduction was performed using *SAINT* [v7.60A]¹⁹ and *XPREP* [v2008/2].²⁰ Corrections were applied for Lorentz, polarization, and absorption effects using *TWINABS* [v2008/2].²¹ The structure was solved and refined with the aid of the programs in the *SHELXTL-plus* [v2008/4] system of programs.²² The crystal of **10** was a two-component twin and all refinements were performed on the only the major twin component. The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included using a riding model.

Theoretical study: Calculations were performed with the Gaussian 03 (Revision D.01) suite of programs.¹⁵ The geometric optimization of the structures based on single-crystal structures, where available, and frequency analyses were carried out using the B3LYP functional with 6-31+G** basis set,²³ and single energy points were calculated at the MP2/6–311++G** level. All of the optimized structures were characterized to be true local energy minima on the potential energy surface without imaginary frequencies.

The gas phase enthalpies of formation of the resulting compounds were computed by using the method of isodesmic reactions. The enthalpy of reaction $(\Delta H_{r298}^{\circ})$ is obtained by combining the MP2/6-311++G** energy difference for the reaction, the scaled zero point energies, and other thermal factors. Thus, the gas phase enthalpy $[\Delta H_{f}(g)]$ of the species being investigated can be readily extracted. The enthalpy of sublimation (ΔH_{sub}) was estimated by using Troutons rule.¹⁶ The heat of formation (ΔH_{f}) Downloaded by Linkopings universitetsbibliotek on 25 October 2012 "ublished on 23 October 2012 on http://pubs.rsc.org | doi:10.1039/C2TA00136E

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of the resulting compounds were calculated with Equation (1), in which T_m is the melting temperature.

$$\Delta H_f = \Delta H_f(g) - \Delta H_{sub} = \Delta H_f(g) - (188[Jmol^{-1}K^{-1}] \times T_m)$$
⁽¹⁾

With values of the heats of formation and densities, the detonation pressure (*P*) and velocity (*vD*), and specific impulse (I_{sp}) were calculated based on the traditional Chapman-Jouget thermodynamic detonation theory using Explo 5.5.

4-Amino-5-nitro-1,2,3-2H-triazole (1): Prepared according to the reference method.⁴

4-Nitramino-5-nitro-1,2,3-2H-triazole (2): 4-Amino-5-nitro-1,2,3-2H-triazole (645 mg, 5 mmol) was added in portions to a mixture of HNO₃ (70%; 5 mL) and concentrated H₂SO₄ (5 mL) under stirring and cooling at 0 °C. The mixture was stirred for 2 h and then warmed slowly to room temperature. After stirring for additional 2 h, the reaction mixture was poured into ice water (80 mL), and extracted with ethyl ether (4 × 25 mL). The combined organic phase was dried over anhydrous Na₂SO₄ and filtered. After removing the solvent, the crude product was recrystallized from ethyl acetate and hexane (1/4) to get orange solid (661 mg, 76%). ¹H NMR: δ = 14.18 ppm (s, 2H; NH); ¹³C NMR: δ = 144.7, 136.2 ppm; ¹⁵N NMR: δ = -25.8, -29.7, -49.4, -76.1, -107.4, -197.8 ppm; IR(KBr pellet):3430, 3292, 3211, 2940, 1615, 1570, 1449, 1348, 1317, 1295, 1198, 1140, 982, 814, 763, 567 cm⁻¹; elemental analysis (%) calcd for C₂H₂N₆O₄ (174.08): C, 13.80; H, 1.16; N, 48.28; found: C, 13.80; H, 1.10; N, 47.75.

4-Amino-2-methyl-5-nitro-1,2,3-2H-triazole (3): 4-Amino-5-nitro-1,2,3-2H-triazole (1.548 g, 12 mmol) was added to 15 mL aqueous NaOH (0.96 g, 24 mmol). After stirring for 5 min at room temperature, dimethyl sulfate (1.513 g, 12 mmol) was added drop wise, and the reaction mixture was stirred at reflux for 10 h. The reaction mixture was slowly cooled to room temperature. The resulting yellow needles (0.876 g, 51% yield) were filtered, washed with a small amount of cold H₂O, and dried. The needles can be recrystallized with hot water. ¹H NMR: $\delta = 6.72$ (s, 2H; NH₂), 4.05 ppm (s, 3H; CH₃); ¹³C NMR: $\delta = 149.2$, 137.4, 42.9 ppm; IR(KBr pellet): 3442, 3316, 1639, 1576, 1474,

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1451, 1354, 1300, 1211, 1111, 868, 784, 642 cm⁻¹; elemental analysis (%) calcd for C₃H₅N₅O₂ (143.10): C, 25.18; H, 3.52; N, 48.94; found: C, 25.21; H, 3.46; N, 48.54.

2-Methyl-4-nitramino-5-nitro-1,2,3-2H-triazole (4): After using the same procedure as for **2**, the crude product was purified via chromatography with ethyl acetate/hexane (2/5) to obtain a yellow solid (564 mg, 60%), which can be recrystallized from ethyl acetate/hexane (1/3). ¹H NMR: $\delta = 11.90$ (s, 1H; NH), 4.32 ppm (s, 3H; CH₃); ¹³C NMR: $\delta = 145.5$, 135.3 44.0 ppm; ¹⁵N NMR: $\delta = -27.6$, -33.1, -49.8, -137.8, -208.0 ppm; IR(KBr pellet): 3428, 3285, 1602, 1578, 1511, 1485, 1375, 1336, 1292, 1160, 927, 812, 759 cm⁻¹; elemental analysis (%) calcd for C₃H₄N₆O₄ (188.10): C, 19.16; H, 2.14; N, 44.68; found: C, 19.46; H, 2.22; N, 43.93.

4-Azido-5-nitro-1,2,3-2H-triazole (5): 4-Amino-5-nitro-2H-triazole (1.032 g, 8 mmol) was dissolved in H₂SO₄ (70%, 20 mL) at room temperature. The solution was cooled in an ice-bath and NaNO₂ (0.607 g, 8.8 mmol) was added in small portions with stirring. After addition, the reaction mixture was stirred in room temperature for 50 min and placed in an ice-bath again and diluted with 80 mL H₂O. A small portion of urea was added, and then NaN₃ (0.650 g, 10 mmol) in small portions. After stirring for 1 h, the reaction mixture was extracted with ethyl ether (4 × 30 mL), and the collected ether phase was dried with anhydrous Na₂SO₄. The ethyl ether solution was evaporated under air to obtain a white solid (1.005 g, 81%), which was recrystallized with hexane/ethyl acetate (2/1) to yield colorless plates. ¹H NMR: δ = 11.8 ppm (s, 1H; NH); ¹³C NMR: δ = 142.4, 139.8 ppm; ¹⁵N NMR: δ = -25.8, -51.2, -75.0, -120.8, -144.4, -145.7, -298.8 ppm; IR(KBr pellet): 3172, 2995, 2928, 2149, 1578, 1518, 1434, 1339, 1260, 1219, 1173, 991, 847, 785 cm⁻¹; elemental analysis (%) calcd for C₂HN₇O₂ (155.08): C, 15.49; H, 0.65; N, 63.23; found: C, 15.51; H, 0.66; N, 62.82.

4-Azido-2-methyl-5-nitro-1,2,3-2H-triazole (6): 4-Azido-5-nitro-1,2,3-2H-triazole (310 mg, 2 mmol) was neutralized with excess aqueous ammonia. After removing the volatile materials, the resulting ammonium 4-azido-5-nitro-2H-triaozolate was dried in vacuo. The dried 4-azido-5-nitro-2H-triaozolate was suspended in CH₃CN (25 mL) at room

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temperature and excess methyl iodide (853 mg, 6 mmol) was added. After stirring for 4 h at 40 °C, the precipitate was filtered, and the solvent was removed. The crude product was purified by chromatography with ethyl acetate/hexane (1/3) to obtain the white solid (206 mg, 61%), which was crystallized from ethyl acetate/hexane (1/3) to yield very thin white plates. ¹H NMR: δ = 4.2 ppm (s, 3H; CH₃); ¹³C NMR: δ = 141.5, 140.6, 43.6 ppm; ¹⁵N NMR: δ = -27.1, -49.7, -63.0, -141.6, -144.4, -145.3, -298.2 ppm; IR(KBr pellet): 3443, 2144, 1566, 1445, 1337, 1222, 1080, 872, 797, 761, 617cm⁻¹; elemental analysis (%) calcd for C₃H₃N₇O₂ (169.10): C, 21.31; H, 1.79; N, 57.98; found: C, 21.65; H, 1.85; N, 57.34.

2-Amino-4-azido-5-nitro-1,2,3-2H-triazole (7): 4-Azido-5-nitro-1,2,3-2H-triazole (310 mg, 2 mmol) was neutralized with excess aqueous ammonia. After removing the volatile materials, the resulting ammonium 4-azido-5-nitro-2H-triazolate was dried in vacuo. The dried 4-azido-5-nitro-2H-triazolate was suspended in CH₃CN (25 mL) at room temperature and Pic-O-NH₂ (488 mg, 2 mmol) was added. After stirring for 8h at room temperature, the yellow precipitate (ammonium picrate) was filtered off, and the solvent was removed. The crude product was purified by chromatography with ethyl acetate/hexane (1/3) to obtain a yellow solid (255 mg, 75%), which was crystallized from ethyl acetate/hexane (1/3) to yield thin yellow plates. ¹H NMR: δ = 7.92 ppm (s, 2H; NH₂); ¹³C NMR: δ = 138.8, 137.9 ppm; ¹⁵N NMR: δ = -27.3, -66.0, -74.3, -124.3, -144.3, -144.8, -274.4, -297.8 ppm; IR(KBr pellet): 3448, 3348, 3273, 2147, 1564, 1506, 1406, 1339, 1223, 924, 795 cm⁻¹; elemental analysis (%) calcd for C₂H₂N₈O₂ (170.09): C, 14.12; H, 1.19; N, 65.88; found: C, 14.17; H, 1.13; N, 65.37.

4,5-Dinitro-1,2,3-2H-triazole (8): Prepared according to the reference method.⁴

2-Methyl-4,5-dinitro-1,2,3-2H-triazole (9): After using the same procedure as for **6,9** was purified by chromatography with ethyl acetate/hexane (1/4) to yield a white solid (176 mg, 51%). ¹H NMR: δ = 4.41 ppm (s, 2H; NH₂); ¹³C NMR: δ = 143.6, 44.5 ppm; ¹⁵N NMR: δ = -32.2, -48.6, -138.8 ppm; IR(KBr pellet): 3447, 1629, 1560, 1437, 1362,

2-Amino-4,5-dinitro-1,2,3-2H-triazole (10): After using the same procedure as for **7, 10** was purified by chromatography with ethyl acetate/hexane (1/3) to yield an amber solid (191 mg, 55%). ¹H NMR (CD₃CN): δ = 7.13 ppm (s, 2H; NH₂); ¹³C NMR (CD₃CN): δ = 142.7 ppm; ¹⁵N NMR (CD₃CN): δ = -32.60, -57.78, -127.62, -278.1 ppm; IR(KBr pellet): 3328, 3141, 1625, 1559, 1535, 1456, 1366, 1325, 1142, 997, 872, 814, 752, 669 cm⁻¹; elemental analysis (%) calcd for C₂H₂N₆O₄ (174.08): C, 13.80; H, 1.16; N, 48.28; found: C,14.00; H, 1.11; N, 47.80.

3,5-Dinitro-1,2,4-1H-triazole (12): Prepared according to the reference method.³

1-Amino-3,5-dinitro-1,2,4-1H-triazole (13): After using the same procedure as for **7**, **13** was purified by chromatography with ethyl acetate/hexane (1/3) to yield a white or pale yellow solid (240 mg, 69%); ¹H NMR (CD₃CN): δ = 7.05 ppm (s, 2H; NH₂); ¹³C NMR (CD₃CN): δ = 154.9, 147.4 ppm; ¹⁵N NMR (CD₃CN): δ = -30.39, -35.53, -81.05, -144.45, -155.41, -286.13 ppm; IR(KBr pellet): 3336, 3280, 1566, 1516, 1342, 1323, 1132, 937, 860, 827, 648 cm⁻¹; elemental analysis (%) calcd for C₂H₂N₆O₄ (174.08): C, 13.80; H, 1.16; N, 48.28; found: C,13.88; H, 1.14; N, 47.88.

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