



5,5'-Dinitrimino-3,3'-methylene-1*H*-1,2,4-bis-triazole – a Metal Free Primary Explosive Combining Excellent Thermal Stability and High Performance

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Abstract: The synthesis of 5,5'-dinitrimino-3,3'-methylene-1*H*-1,2,4-triazole (**1**) and selected nitrogen rich salts are presented. All compounds were fully characterized in terms of sensitivity and energetic properties. Besides a chemical characterization including multinuclear magnetic resonance study (^1H , ^{13}C , ^{14}N) and vibrational analysis (IR, Raman), X-Ray diffraction was performed. Thermal stability was determined using differential scanning calorimetry. Detonation parameters were calculated using the EXPLO5.4 code based on CBS-4M computed heats of formation. The presented compound 5,5'-dinitrimino-3,3'-methylene-1*H*-1,2,4-bis-triazole shows excellent thermal stabilities in combination with high sensitivities and therefore is of interest for possible applications as metal free primary.

Keywords: energetic materials, triazoles, detonation parameter, sensitivities

Introduction

Five-membered nitrogen-containing heterocycles are traditional sources of energetic materials [1]. At present time, triazole derivatives have been intensively investigated as high-energy density materials (HEDMs), due to their high densities, high heats of formation and high thermal stability [2]. One important

issue for the use as an energetic material is the thermal stability of the molecule. Compounds with a decomposition temperature above 200 °C are desired. Methylene-bridged aminotriazole (MBAT) (**1**) is a promising starting material with a very high thermal stability of $T_{\text{dec.}} = 293$ °C [3]. Recently, an improved acid catalyzed synthesis, starting from low cost industrial chemicals in good yields (80%), has been described in literature [4]. By introducing energetic moieties like nitro or nitroamino groups, the oxygen balance, heat of formation and nitrogen content are enhanced [5]. Although the decomposition temperature is effected somewhat by introducing primary nitramines, [1] all compounds presented in this work show an excellent thermal stability with decomposition temperatures above 200 °C. In this work we present the synthesis and energetic characterization of 5,5'-dinitrimino-3,3'-methylene-1*H*-1,2,4-triazole (DNBTM) (**2**) and selected ionic derivatives.

Materials and Methods

General. All chemical reagents were obtained from Sigma-Aldrich Inc. or Acros Organics (analytical grade) and were used as supplied. $^{13}\text{C}\{^1\text{H}\}$, and ^{14}N NMR spectra were recorded on a JEOL Eclipse 400 instrument in DMSO- d_6 at or near 25 °C. The chemical shifts are given relative to tetramethylsilane (^1H , ^{13}C) or nitromethane (^{14}N) as external standards and coupling constants are given in Hertz (Hz). Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum BX FT-IR instrument equipped with an ATR unit at 25 °C. Transmittance values are qualitatively described as “very strong” (vs), “strong” (s), “medium” (m) and “weak” (w). Raman spectra were recorded on a Bruker RAM II spectrometer equipped with a Nd:YAG laser (1064 nm) and a reflection angle of 180°. The intensities are reported as percentages of the most intense peak and are given in parentheses. Elemental analyses were performed with a Netzsch Simultaneous Thermal Analyzer STA 429. Melting points were determined by differential scanning calorimetry (Setaram DSC141 instrument, calibrated with standard pure indium and zinc). Measurements were performed at a heating rate of 5 °C/min in closed aluminum sample pans with a 1 μm hole in the top for gas release under a nitrogen flow of 20 ml/min with an empty identical aluminum sample pan as a reference.

Safety testing: For initial safety testing, the impact and friction sensitivities, as well as the electrostatic sensitivities, were determined. The impact sensitivity tests were carried out according to STANAG 4489 [6], modified according to instruction [7] using a BAM [8] drophammer. The friction sensitivity tests

were carried out according to STANAG 4487 [9] and modified according to instruction [10] using the BAM friction tester. The electrostatic sensitivity tests were accomplished according to STANAG 4490 [11] using an electric spark testing device ESD 2010EN (OZM Research) operating with the “Winspark 1.15 software package”.

X-Ray analysis: The single crystal X-ray diffraction data of **2**, **3** and **4** were collected using an Oxford Xcalibur3 diffractometer equipped with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector. The data collection was undertaken using the CRYSTALIS CCD software [12] while the data reduction was performed with the CRYSTALIS RED software [13]. The structures were solved with SIR-92 [14] and SHELXS-97 and refined with SHELXL-97 [15] implemented in the program package WinGX [16] and finally checked using PLATON [17]. Further information regarding the crystal-structure determination have been deposited with the Cambridge Crystallographic Data Centre [18] filed under CCDC numbers 832616 (**2**) 832614 (**3**) and 832615 (**4**).

Quantum chemical calculations: The heat of formation calculations of the compounds **2**, **3** and **4** was performed using the atomization method based on CBS-4M enthalpies described recently in detail in literature [19].

$$\Delta_f H^\circ_{(g,M,298)} = H_{(Molecule298)} - \sum H^\circ_{(Atoms298)} + \sum \Delta_f H^\circ_{(Atoms298)} \quad (1)$$

All quantum chemical calculations were performed with the Gaussian G03W (revision B.03) program package [20]. The gas phase heat of formation ($\Delta_f H^\circ(g,M)$) was converted into the solid state heat of formation ($\Delta_f H^\circ(s)$) using the Jenkins equations [21].

5,5'-diamino-3,3'-methylene-1H-1,2,4-triazole (DABTM) (1)

According to [4, 22], a suspension of malonic acid (3.8 g, 0.04 mol) and aminoguanidinium bicarbonate (10.0 g, 0.08 mol) in concentrated hydrochloric acid (7.0 ml) was heated to 70 °C. The resulting colorless solution was stirred at 70 °C for 1 h and cooled to room temperature. After addition of sodium hydroxide (17 ml, 6.1N), the mixture was heated to 90 °C for 40 minutes and cooled to 50-60 °C. The precipitate was collected by filtration and recrystallized from hot water to yield 5,5'-diamino-3,3'-methylene-1H-1,2,4-triazole as colorless solid (3.1 g, 17.2 mmol, 47%).

¹H NMR (DMSO-d₆): δ = 3.88 (s, 2H, CH₂) ppm. ¹³C NMR (DMSO-d₆): δ = 158.2 (C-NH₂), 156.6 (C-CH₂), 26.3 (CH₂) ppm. IR: ν (cm⁻¹) (rel. int.) = 3366(m), 3336(m), 3146(m), 2932(m), 1664(vs), 1634(vs), 1594(s), 1582(s), 1570(s), 1374(s), 1338(s), 1256(m), 1190(m), 1098(w), 1000(s), 916(m),

824(m), 754(w), 686(s), 638(m); **Raman** (200 mW): ν (cm⁻¹) (rel. int.) = 3387(7), 3164(22), 2977(23), 2943(63), 1648(18), 1574(21), 1550(98), 1462(25), 1426(33), 1405(34), 1363(26), 1334(14), 1290(8), 1171(13), 1108(16), 1085(32), 1064(100), 1029(13), 923(7), 847(7), 757(23), 690(22), 678(11), 678(11), 628(94), 485(15), 462(15), 397(41), 302(29), 259(6), 233(19); **Elemental analysis** (C₅H₈N₈): calc.: C 62.19, H 4.48, N 62.19; found: C 60.45, H 4.11, N 60.45.

5,5'-dinitrimino-3,3'-methylene-1H-1,2,4-triazole (DNBTM) (2)

5,5'-diamino-3,3'-methylene-1H-1,2,4-triazole (0.5 g, 2.8 mmol) was dissolved in sulfuric acid (conc., 3 ml) and nitric acid (fuming, 1 ml) was added dropwise at 0 °C. The mixture was stirred at room temperature for 1 h and poured on ice. The precipitate was collected by filtration and dried at 60 °C to yield 5,5'-dinitrimino-3,3'-methylene-1H-1,2,4-triazole as colorless solid (0.71 g, 2.6 mmol, 94%).

Sensitivities (grain size: 100-500 μ m): friction: 60 N, impact: 1 J, ESD: 0.2 J; **DSC** (onset, 5 °C min⁻¹): T_{Dec.}: 242 °C; **¹H NMR** (DMSO-d₆): δ = 14.1, 8.1, 4.2 ppm; **¹³C NMR** (DMSO-d₆): δ = 153.4 (C-N-NO₂), 146.5 (C-CH₂), 23.7 (CH₂) ppm; **¹⁴N NMR** (DMSO-d₆): δ = -17 (NO₂) ppm. **IR**: ν (cm⁻¹) (rel. int.) = 3504(w), 3456(w), 3296(w), 3068(w), 2870(w), 1740(m), 1610(vs), 1570(s), 1498(s), 1432(s), 1304(s), 1276(vs), 1260(s), 1244(vs), 1218(s), 1180(m), 1102(m), 996(s), 874(m), 776(w), 716(m), 652(vw); **Raman** (200 mW): ν (cm⁻¹) (rel. int.) = 2977(5), 2942(12), 1628(21), 1566(100), 1494(7), 1438(13), 1368(5), 1305(12), 1295(12), 1272(16), 1241(9), 1182(5), 1143(6), 1108(4), 1092(6), 1008(34), 924(3), 864(7), 810(3), 766(6), 755(21), 738(6), 506(4), 506(4), 471(4), 444(3), 429(5), 334(3), 279(12); **Elemental analysis** (C₅H₆N₁₀O₄): calc.: C 22.23, H 2.24, N 51.84; found: C 22.53, H 2.21, N 51.65.

Bis-guanidinium 5,5'-dinitrimino-3,3'-methylene-1H-1,2,4-triazolate (3)

Guanidinium carbonate (1 eq., 0.11 g, 0.6 mmol) was added to a solution of the neutral compound **2** (0.17 g, 0.63 mmol) in 100 ml of water. Bis-guanidinium 5,5'-dinitrimino-3,3'-methylene-1H-1,2,4-triazolate precipitates as colorless needles while storing the solution at 5 °C. Compound **3** can be dehydrated by heating at 170 °C for 48 h.

Sensitivities (grain size: 100-500 μ m): friction: 360 N, impact: 40 J; **DSC** (onset, 5 °C min⁻¹): T_{Dec.}: 239 °C; **¹H NMR** (DMSO-d₆): δ = 12.57, 7.16, 3.72 ppm; **¹³C NMR** (DMSO-d₆): δ = 158.1, 157.1, 156.8, 28.0 ppm; **¹⁴N NMR** (DMSO-d₆): δ = -17 ppm; **IR**: ν (cm⁻¹) (rel. int.) = 3436(m), 3252(s), 3164(s), 2882(w), 1740(w), 1662(s), 1634(s), 1518(m), 1494(m), 1442(m), 1416(m), 1348(vs), 1238(s),

1150(m), 1082(vs), 1038(m), 1008(m), 906(w), 864(w), 758(w), 712(w); **Raman** (200 mW): ν (cm⁻¹) (rel. int.) = 3251(2), 3185(2), 2988(2), 2954(6), 1514(60), 1495(100), 1430(7), 1419(5), 1382(14), 1343(25), 1277(5), 1253(10), 1185(3), 1136(2), 1083(2), 1028(27), 1009(59), 869(11), 840(3), 752(6), 685(2), 520(6), 513(5), 513(5), 443(2), 401(9), 337(3), 313(6), 266(4).

Triaminoguanidinium 5,5'-dinitrimino-3,3'-methylene-1H-1,2,4-triazolate (4)

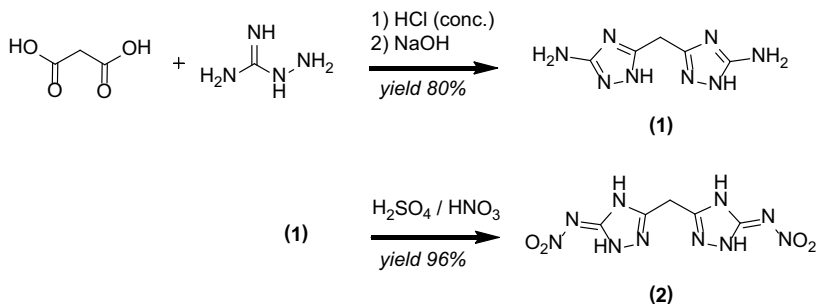
Free base triaminoguanidinium (1 eq., 0.1 g, 0.9 mmol) was added to a solution of the neutral compound **2** (0.25 g, 0.9 mmol) in 100 ml of water. Triaminoguanidinium 5,5'-dinitrimino-3,3'-methylene-1H-1,2,4-triazolate precipitates as colorless needles while storing the solution at 5 °C.

Sensitivities (grain size: 100-500 μ m): friction: 192 N, impact: 40 J. **DSC** (onset, 5 °C min⁻¹): T_{Dec.}: 209 °C; **¹H NMR** (DMSO-d₆): δ = 8.58, 5.09, 2.46 ppm; **¹³C NMR** (DMSO-d₆): δ = 159.1, 155.3, 151.9, 25.7 ppm; **¹⁴N NMR** (DMSO-d₆): δ = -17 ppm. **IR**: ν (cm⁻¹) (rel. int.) = 3531(w), 3423(w), 3353(w), 3201(m), 1689(m), 1612(m), 1563(w), 1516(s), 1494(m), 1452(m), 1296(vs), 1218(m), 1155(m), 1136(s), 1077(m), 996(m), 911(m), 860(m), 776(m), 716(m), 685(m); **Raman** (200 mW): ν (cm⁻¹) (rel. int.) = 3268(3), 2969(4), 2935(5), 1609(6), 1565(28), 1521(100), 1483(13), 1398(8), 1365(5), 1342(5), 1229(5), 1138(4), 1007(48), 867(7), 754(4), 737(4), 522(4), 449(3), 395(4), 374(3), 321(6), 241(12).

Results and Discussion

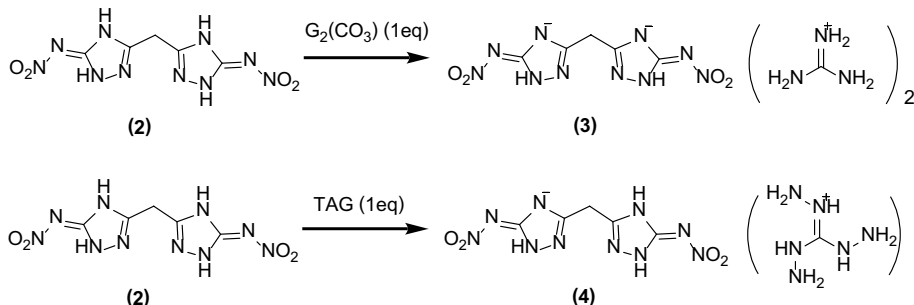
Synthesis

The synthesis of 5,5'-dinitrimino-3,3'-methylene-1H-1,2,4-triazole (**2**) was performed using malonic acid and aminoguanidinium bicarbonate as starting materials as described in literature [4, 22]. Compound **2** is formed via malonic acid diguanylhydrazide as an intermediate product followed by subsequent cyclisation with 6 M sodium hydroxide solution. The yield of the first reaction step is directly dependent on the pH [6]. Hence the reaction is carried out in concentrated hydrochloric acid, without any further solvent. The resulting 5,5'-diamino-3,3'-methylene-1H-1,2,4-bis-triazole (**2**) was nitrated in a mixture of sulfuric acid/nitric acid (3:1) within 1 hour in excellent yields (Scheme 1) and recrystallized from water. This reaction is very straightforward in comparison to the method published by Metelkina *et al.* [23] which reacts malonic acid dihydrazide with nitroguanidine in poor yields.



Scheme 1. Synthetic route towards DNBTM (**2**).

As shown in Scheme 2, compound **2** can be deprotonated easily to form the mono- and dianion, respectively. Nitrogen rich salts of 5,5'-dinitrimino-3,3'-methylene-1H-1,2,4-triazole were synthesized by adding free nitrogen rich bases or carbonates to an aqueous solution of the neutral compound **2**. The bis-guanidinium and mono-triaminoguanidinium salts were synthesized and were obtained as colorless crystalline solids from the reaction solution.



Scheme 2. Synthesis of nitrogen rich salts of 5,5'-dinitrimino-3,3'-methylene-1H-1,2,4-triazolate.

Spectroscopic characterization

The ^1H NMR spectra of compound **2** show one sharp signal at 4.26 ppm corresponding to the resonance of the methylene-bridged hydrogen atoms. In the ^{13}C NMR spectra the corresponding carbon atom can be found at 23.7 ppm. Further resonances located at 153.4 ppm and 146.5 ppm could be assigned to the triazol ring. The nitrimino group shows one major signal in the ^{14}N NMR spectra at -17 ppm for all compounds. As shown in Table 1, the NMR signals of the nitrogen rich salts only show slight shifts and are observed in the same range, compared to the neutral compound **2**. Sharp signals of the corresponding

triaminoguanidinium and guanidinium cations can be identified in the ^1H -NMR spectra at 8.58/5.09 ppm and 7.16 ppm, respectively. The corresponding ^{13}C signals can be found at 157.1 ppm for guanidinium and at 159.1 ppm for the triaminoguanidinium cation. The NMR signals of all compounds are summarized in Table 1.

Table 1. Selected characteristic NMR signals of compounds **2-4**

Compound	^1H NMR		$^{13}\text{C}\{\text{H}\}$ NMR			$^{14}\text{N}\{\text{H}\}$ NMR
	CH_2	Cation	CH_2	C-Triazol	C-Cation	N- NO_2
2	4.26		23.7	153.4, 146.5	/	-17
3	3.72	7.16	28	156.8, 158.1	157.1	-17
4	2.46	8.58, 5.09	25.7	151.9, 155.3	159.1	-17

All compounds were characterized using Raman and IR spectroscopy. Dominating stretching modes in the IR spectra of the neutral compound could be observed for the N- NO_2 group at $1620\text{-}1560\text{ cm}^{-1}$ ($\nu_{\text{asym}}(\text{NO}_2)$) and $1300\text{-}1240\text{ cm}^{-1}$ ($\nu_{\text{sym}}(\text{NO}_2)$). Further characteristic bands and peaks of compound **2** are C-H valence vibrations of the methylen bridge at $2800\text{-}3100\text{ cm}^{-1}$. These modes are present in all compounds, since the molecular backbone is not altered. The spectra of the nitrogen rich salts **3** and **4** are accompanied with an additional strong absorptions at $1630\text{-}1680\text{ cm}^{-1}$ and $3350\text{-}3100\text{ cm}^{-1}$ referring to the N-H stretch modes and NH_2 deformation modes, respectively. Further characteristic bands of the triazol ring are observed for both, Raman and IR spectra, in the range between $1300\text{-}1500\text{ cm}^{-1}$ as described in literature [24].

Energetic properties

Although the thermal stability of compound **2** is affected by the introduction of the nitrimino moiety, the substance has an excellent decomposition temperature of $242\text{ }^\circ\text{C}$ (Onset, DSC, $5\text{ }^\circ\text{C min}^{-1}$). Sensitivity measurements of **2** show very high sensitivities towards impact and friction with the impact sensitivity being only 1 J and the friction sensitivity displaying a value of only 60 N. Due to the high sensitivity values, the compound must be classified as very sensitive and therefore could be of potential use as a new high thermally stable metal free primary explosive. The energetic properties were calculated with the EXPLO 5.4 code [25] and summarized in Table 2, together with the sensitivity values. The known values for the widely used primary explosive lead azide are also listed.

Table 2. Energetic properties of compound **2** compared to Pb(N₃)₂

	2	Lead Azide [26]
Formula	C ₅ H ₆ N ₁₀ O ₄	Pb(N ₃) ₂
FW / g mol ⁻¹	270.2	291.3
IS / J	1	2.5-4
FS / N	60	< 1
ESD / J	0.2	0.005
N / %	51.8	28.85
Ω / %	-53.3	-5.5
T _{Dec.} / °C	242 °C	165
ρ / g cm ⁻³	1.864	4.8
Δ _f H _m ^o / kJ mol ⁻¹	358	1637.7
Δ _f U ^o / kJ kg ⁻¹	1417	1663.3
EXPLO 5.04 values:		
-Δ _{Ex} U ^o / kJ kg ⁻¹	4747	-
T _{det} / K	3450	-
P _{CJ} / kbar	309	-
V _{Det.} / m s ⁻¹	8511	-
V _o / L kg ⁻¹	702	-

The bis-guanidinium and mono-triaminoguanidinium salts of 5,5'-dinitrimino-3,3'-methylene-1*H*-1,2,4-triazole were synthesized and were obtained as colorless crystalline solids. Sensitivity measurements of impact and friction demonstrate that the two ionic compounds are nearly insensitive, as shown in Table 3. Quantum chemical calculations for **3** were done for the anhydrous compound assuming the density to remain constant. Detonation parameters are calculated with EXPLO 5.4 [25] code and compared with the most common secondary explosive RDX (Table 3).

The thermal stability of **2** is affected by the reaction with guanidinium (compound **3**) and triaminoguanidinium (compound **4**). In general, salts used have higher decomposition temperatures. However, this could not be confirmed in the case of **3** and **4**. Compound **3** shows a decomposition temperature of 239 °C (Onset, DSC, 5 °C min⁻¹) which is in the same range as **2**, while **4** shows a decomposition temperature of only 209 °C (Onset, DSC, 5 °C min⁻¹), which is lowered by more than 30 °C compared with **2**. The detonation velocity of the triaminoguanidinium salt (**4**) is slightly lower than the values calculated for RDX. Compound **4** exhibits a higher heat of formation and a lower detonation temperature but is nearly insensitive towards friction and impact, compared to RDX. Furthermore, it shows a poor solubility in water and other common

solvents, also desired properties for secondary explosives. However, the density is slightly lower as of RDX.

Table 3. Energetic properties of **3** and **4** compared to RDX

	3	4	RDX
Formula	$C_7H_{16}N_{16}O_4$	$C_6H_{14}N_{16}O_4$	$C_3H_6N_6O_7$
FW / g mol ⁻¹	388.3	374.3	222.12
<i>IS</i> / J	40	40	7.5
<i>FS</i> / N	360	192	120
<i>N</i> / %	57.7	59.9	37.8
Ω / %	-74.2	-64.1	-21.6
<i>T</i> _{Dec.} / °C	239	209	210
ρ / g cm ⁻³	1.615	1.733	1.80
$\Delta_f H_m^\circ$ / kJ mol ⁻¹	219	649	70
$\Delta_f U^\circ$ / kJ kg ⁻¹	678	1846	417
EXPLO 5.04 values:			
$-\Delta_{Ex} U^\circ$ / kJ kg ⁻¹	3434	4611	6125
<i>T</i> _{det} / K	2510	3123	4236
<i>P</i> _{CJ} / kbar	206	284	349
<i>V</i> _{Det.} / m s ⁻¹	7527	8468	8748
<i>V</i> _o / L kg ⁻¹	772	781	739

Electrostatic Potential Calculations for compound **2**

The electrostatic potential of DNBTM was computed at the fully optimized B3LYP/cc-pVTZ level of theory using the program package Gaussian [20]. Figure 1 shows the 0.001 electron bohr⁻³ 3D isosurface of electron density for DNBTM with an electrostatic potential contour value of 0.05 hartree. The red regions represent extremely electron-rich regions ($V(r) < -0.05$ hartree) and the blue regions extremely electron-deficient regions ($V(r) > 0.05$ hartree). In general, the calculated electrostatic potentials of the surface of molecules can be related to the impact sensitivities as described in literature [27]. Molecules with inhomogenous charge distribution often show an increased impact sensitivity, as it is the case for 5,5'-Dinitrimino-3,3'-methylene-1H-1,2,4-bistriazole (**2**).

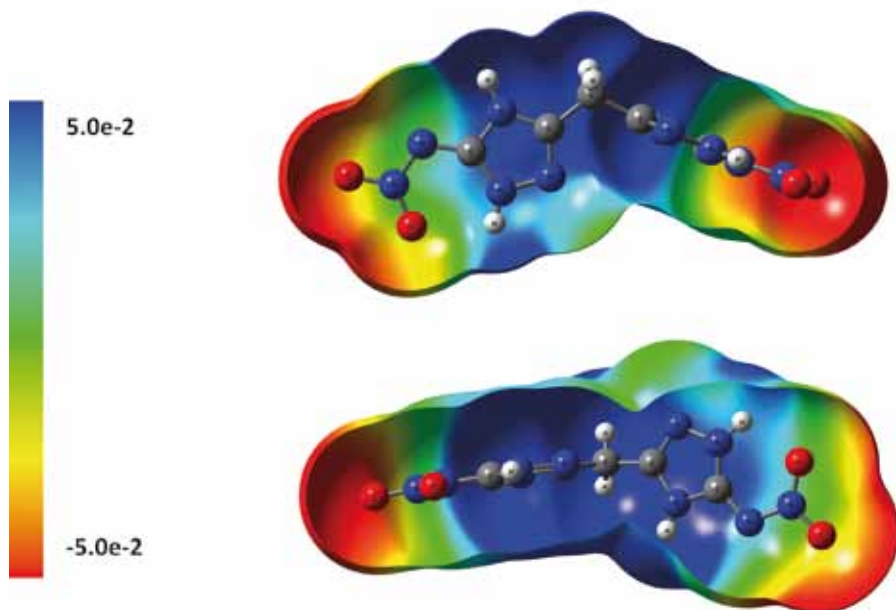


Figure 1. Electrostatic potential of DNBTM (values given in Hartree).

Selected crystallographic data

Crystals of 5,5'-dinitrimino-3,3'-methylene-1*H*-1,2,4-triazole (**2**), mono triaminoguanidinium 5,5'-dinitrimino-3,3'-methylene-1*H*-1,2,4-triazolate (**3**) and bis(guanidinium) 5,5'-di-nitrimino-3,3'-methylene-1*H*-1,2,4-triazolate (**4**) were obtained by recrystallization from water. All of the presented structures contain the DNBTM moiety. The DNBTM moieties have nearly the same bond angles and bond lengths within the three described structures below. The bond lengths and angles are all as expected for this kind of compounds, showing a planar triazole ring with the nitrimino moiety lying exactly in the same plane, supported by the formation of hydrogen bonds building up stable six-membered ring systems (Table 4).

Compound **2** crystallizes in the monoclinic spacegroup $P2_1/n$ with four formula units per unit cell and a density of 1.864 g cm^{-3} . The asymmetric unit is shown in Figure 2.

Table 4. Intermolecular hydrogen bonds present in the crystal structure of **2**, **3** and **4**

Compound	Atoms	Dist. D–H [Å]	Dist. H–A [Å]	Dist. D–A [Å]	Angle D–H–A [°]
2	N1 – H1 – O1	0.826(19)	2.174(17)	2.5847(17)	110.8(15)
	N8 – H8 – O3	0.853(18)	2.192(19)	2.6277(17)	111.5(15)
3	N1 – H1 – O1	0.826(19)	2.174(17)	2.5847(17)	110.8(15)
4	N1 – H1 – O1	0.837(18)	2.173(18)	2.6093(18)	112.4(14)
	N8 – H8 – O3	0.767(18)	2.193(18)	2.6007(19)	114.0(16)

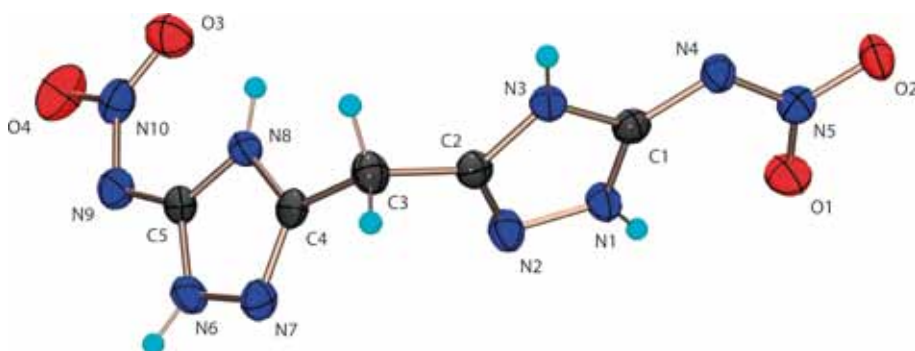


Figure 2. Asymmetric unit of compound **2**. Thermal ellipsoids represent the 50% probability level; Selected bond lengths (Å): N3 C1 1.3543(18), N3 C2 1.3554(18), N3 H3 0.851(18), N7 C4 1.2939(18), N7 N6 1.3663(16), N5 O1 1.2377(16), N5 O2 1.2411(15), N5 N4 1.3465(17), N4 C1 1.3492(19), N1 C1 1.3338(18), N1 N2 1.3776(17), N1 H1 0.82(2), N2 C2 1.3105(19), C2 C3 1.493(2), Selected bond angles (°): C1 N3 C2 107.31(12), C1 N3 H3 123.2(12), C2 N3 H3 129.4(12), C4 N7 N6 103.87(12), O1 N5 O2 123.18(12), O1 N5 N4 121.84(12), O2 N5 N4 114.98(12), N5 N4 C1 115.83(12), C1 N1 N2 111.95(12), C1 N1 H1 127.2(13), N2 N1 H1 120.8(13), C5 N8 C4 106.81(12), C5 N8 H8 126.1(12), C4 N8 H8 127.1(12), C2 N2 N1 103.51(11), N1 C1 N4 135.31(13), N1 C1 N3 105.38(13), N4 C1 N3 119.28(13); Selected torsion angles (°): N5 N4 C1 N1 -1.9(2), C1 N1 N2 C2 0.12(15).

The protons are located at the nitrogen atoms N1, N3, N6 and N8, therefore the compound can be classified as nitrimino-triazole. Both nitrimino-triazoles show a different conformation of the nitrimino moiety due to the formation of hydrogen bonds. This results in the formation of six-membered rings including

the hydrogen bonds $N1-H1\cdots O1$ and $N8-H8\cdots O3$.

Compound **3** crystallizes in the monoclinic spacegroup $C2c$ with four formula units per unit cell and a density of 1.615 g cm^{-3} . The deprotonation takes place at the nitrogen atom N3 since this is apparently the most acidic proton of the system. The crystal structure of compound **3** is shown in Figure 3. In the case of the dianion, both nitrimino moieties show the same conformation due to the formation of six-membered rings including the hydrogen bonds $N1-H1\cdots O1$ and $N1(i)-H1(i)\cdots O1(i)$.

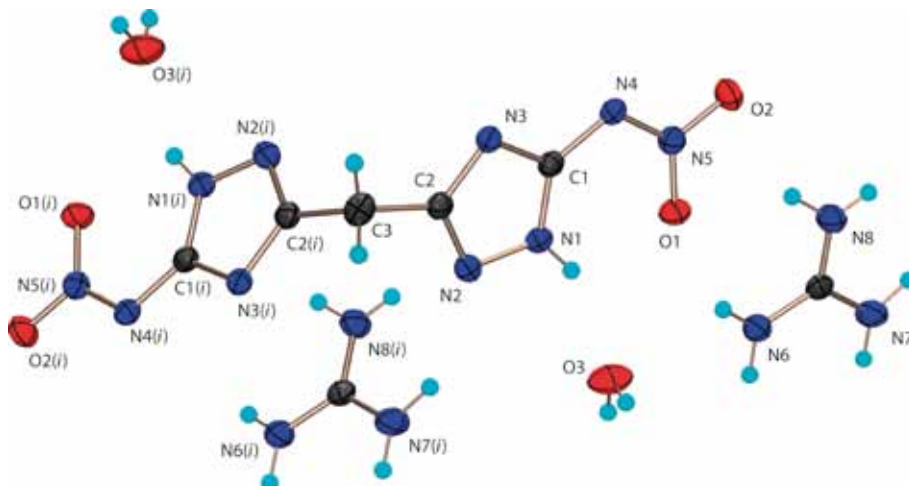


Figure 3. Crystal structure of bis(guanidinium) 5,5'-dinitrimino-3,3'-methylene-1H-1,2,4-triazolate (**3**). Thermal ellipsoids represent the 50% probability level. Symmetric code: (i): $-x, y, -z+1/2$; Selected bond lengths (Å): N4 N5 1.2970(19), N4 C1 1.384(2), O1 N5 1.2694(17), O2 N5 1.2677(19), N1 C1 1.337(2), N1 N2 1.363(2), N1 H1 0.88(2), N3 C1 1.338(2), N3 C2 1.355(2), N2 C2 1.321(2), N8 C4 1.320(2), N7 C4 1.326(2), C2 C3 1.493(2); Selected bond angles (°): N5 N4 C1 116.97(14), C1 N1 N2 109.96(15), C1 N1 H1 127.3(15), N2 N1 H1 122.5(15), O2 N5 O1 118.18(15), O2 N5 N4 118.45(14), O1 N5 N4 123.37(16), C1 N3 C2 103.64(13), C2 N2 N1 103.01(15), N8 C4 N6 120.45(19), N8 C4 N7 120.32(18), N6 C4 N7 119.22(19), N1 C1 N3 109.31(16), N1 C1 N4 130.71(17), N3 C1 N4 119.98(14), N2 C2 N3 114.08(16), N2 C2 C3 121.66(15), N3 C2 C3 124.26(13); Selected torsion angles (°): N5 N4 C1 N1 $-4.4(3)$, C1 N1 N2 C2 $-0.27(18)$.

Compound **4** crystallizes in the monoclinic spacegroup $P2_1/n$ with four formula units per unit cell and a density of 1.733 g cm^{-3} . The asymmetric unit of compound **4** is shown in Figure 4. The crystallographic data of all compounds are summarized in Table 5.

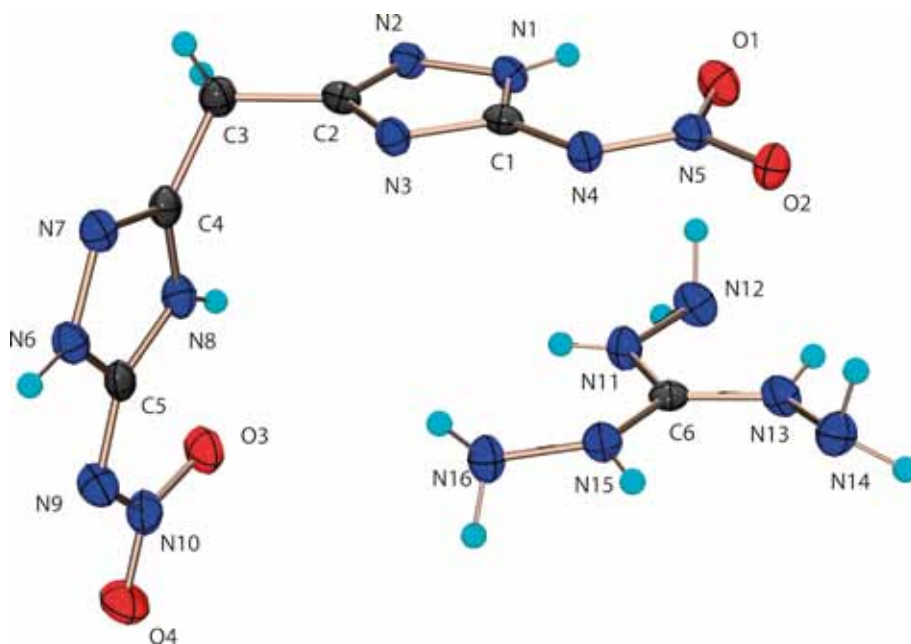


Figure 4. Crystal structure of triaminoguanidinium 5,5'-dinitrimino-3,3'-methylene-1*H*-1,2,4-triazolate (**4**). Thermal ellipsoids represent the 50% probability level; Selected bond lengths (Å): O1 N5 1.2611(16), O2 N5 1.2618(16), N3 C1 1.3376(19), N3 C2 1.3564(19), N4 N5 1.3082(17), N4 C1 1.370(2), N1 C1 1.3371(19), N1 N2 1.3683(18), N1 H1 0.837(18), N2 C2 1.3087(19), C3 C2 1.495(2); Selected bond angles (°): C1 N3 C2 103.90(12), N5 N4 C1 117.19(13), O1 N5 O2 119.57(13), O1 N5 N4 123.87(14), O2 N5 N4 116.56(13), C1 N1 N2 110.56(13), C1 N1 H1 126.9(12), N2 N1 H1 122.5(12), C4 C3 C2 112.63(13), C2 N2 N1 102.51(12), N1 C1 N3 108.49(14), N1 C1 N4 132.89(14), N3 C1 N4 118.61(13), N2 C2 N3 114.53(13), N2 C2 C3 122.49(14), N3 C2 C3 122.96(14); Selected torsion angles (°): N5 N4 C1 N1 1.7(2), C1 N1 N2 C2 -0.03(15).

Table 5. Crystallographic data of compound **2** as well as the corresponding guanidinium (**3**) and aminoguanidinium (**4**) salt

Compound	2	3	4
Formula	C ₅ H ₆ N ₁₀ O ₄	C ₇ H ₂₀ N ₁₆ O ₆	C ₆ H ₁₄ N ₁₆ O ₄
FW [g mol ⁻¹]	270.2	424.3	374.3
Crystal system	monoclinic	monoclinic	monoclinic
Space Group	<i>P</i> 2 ₁ / <i>n</i>	C2c	<i>P</i> 2 ₁ / <i>n</i>
Color / Habit	Colourless block	Colourless needle	Colourless needle
Size [mm]	0.31 x 0.09.0.08	0.4 x 0.35 x 0.02	0.35 x 0.21 x 0.02
<i>a</i> [Å]	8.356(2)	13.519(2)	8.184(1)
<i>b</i> [Å]	4.914 (1)	7.798(2)	19.914(2)
<i>c</i> [Å]	23.689(2)	16.64(2)	9.280(1)
α [°]	90	90	90
β [°]	98.232(7)	96.156(1)	108.488(4)
γ [°]	90	90	90
<i>V</i> [Å ³]	962.77(12)	1745.2(4)	1434.42(16)
Z	4	4	4
ρ_{calc} [g cm ⁻³]	1.863	1.615	1.733
μ [mm ⁻¹]	0.161	0.138	0.145
<i>F</i> (000)	551	888	776
$\lambda_{\text{MoK}\alpha}$ [Å]	0.71073	0.71073	0.71073
<i>T</i> [K]	173	173	173
Theta Min-Max [°]	4.2-24.6	4.65-32.53	4.14-26.00
Dataset h	-9; 10	-18; 19	-9; 10
Dataset k	-4; 6	-5; 11	-24; 23
Dataset l	-29; 28	-20; 24	-10; 11
Reflections collected	4910	5401	7405
Independent reflections	1988	2855	2808
Observed reflections	1549	1150	2021
No. parameters	196	172	291
<i>R</i> _{int}	0.020	0.040	0.027
<i>R</i> ₁ , w <i>R</i> ₂ (I > σ I ₀)	0.0298; 0.0764	0.0369; 0.0790	0.0330; 0.0849
<i>R</i> ₁ , w <i>R</i> ₂ (all data)	0.0406; 0.0793	0.0622; 0.0841	0.0495; 0.905
S	0.968	0.620	0.740
Resd. Dens. [e Å ⁻³]	-0.224, 0.233	-0.207, 0.222	-0.0204, 0.270
Device type	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD	Oxford Xcalibur3 CCD
Solution	Sir-92	Shelxs-97	Sir-92
Refinement	Shelxl-97	Shelxl-97	Shelxl-97
Absorption correction	multi-scan	multi-scan	multi-scan
CCDC	832616	832614	832615

Conclusions

From this combined theoretical and experimental study the following conclusions can be drawn:

- 1) The neutral compound **2** shows a very high sensitivity towards impact and a moderate sensitivity towards friction paired with a high thermal stability and could therefore be of use as a potential metal free primary explosive.
- 2) The starting material 5,5'-diamino-3,3'-methylene-1H-1,2,4-triazole can be synthesized easily in good yields starting from low cost industrial chemicals.
- 3) Nitrogen rich salts **2** and **3** were synthesized by direct acid-base reactions adding free nitrogen rich bases or carbonates to an aqueous solution of the neutral compound **2** resulting in crystals suitable for X-Ray analysis.
- 4) Complete characterization of all compounds was performed using IR and RAMAN spectroscopy, NMR spectroscopy, as well as differential scanning calorimetry and single crystal X-ray diffraction measurements.
- 5) High detonation parameters were calculated for the triaminoguanidinium salt ($D = 8468 \text{ m s}^{-1}$, $p_{C-J} = 284 \text{ kbar}$, $T_{\text{ex}} = 3123 \text{ K}$ (**4**)) indicating a possible use as a high thermally stable insensitive secondary explosive.

Acknowledgements

Financial support of this work by the Ludwig-Maximilian University of Munich (LMU), the U.S. Army Research Laboratory (ARL), the Armament Research, Development and Engineering Center (ARDEC), the Strategic Environmental Research and Development Program (SERDP) and the Office of Naval Research (ONR Global, title: "Synthesis and Characterization of New High Energy Dense Oxidizers (HEDO) – NICOP Effort") under contract Nos. W911NF-09-2-0018 (ARL), W911NF-09-1-0120 (ARDEC), W011NF-09-1-0056 (ARDEC) and 10 WPSEED01-002 / WP-1765 (SERDP) is gratefully acknowledged. The authors acknowledge collaborations with Dr. Mila Krupka (OZM Research, Czech Republic) in the development of new testing and evaluation methods for energetic materials and with Dr. Muhamed Sućesca (Brodarski Institute, Croatia) in the development of new computational codes to predict the detonation and propulsion parameters of novel explosives. We are indebted to and thank Drs. Betsy M. Rice and Brad Forch (ARL, Aberdeen, Proving Ground, MD) and Mr. Gary Chen (ARDEC, Picatinny Arsenal, NJ) for many helpful and inspired discussions and support of our work.

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