DOI: 10.1002/ejic.201200221



Insensitive Nitrogen-Rich Energetic Compounds Based on the 5,5'-Dinitro-3,3'bi-1,2,4-triazol-2-ide Anion

Alexander A. Dippold,^[a] Thomas M. Klapötke,^{*[a]} and Nils Winter^[a]

Keywords: Nitrogen heterocycles / Energetic materials / Explosives / Thermodynamics

In this contribution the improvements achieved in the synthesis of the thermally stable energetic heterocycle 5,5'-dinitro-2*H*,2'*H*-3,3'-bi-1,2,4-triazole (DNBT) are described. The main goal was the synthesis of at least equally stable but more powerful energetic compounds based on the DNBT^{2–} anion in combination with nitrogen-rich cations. A complete structural and spectroscopic characterization, including IR, Raman, and multinuclear NMR analyses of the uncharged compound is presented. In addition, X-ray crystallographic measurements on DNBT revealed a very high density of 1.903 g cm⁻³. To increase both performance and stability, highly nitrogen-rich salts of DNBT formed from ammonium, hydroxyammonium, hydrazinium, guanidinium, aminoguanidinium and triaminoguanidinium cations were prepared and fully characterized by vibrational and multinuclear NMR spectroscopy, DSC, and X-ray diffraction measurements. The standard enthalpies of formation were calculated for selected compounds at the CBS-4M level of theory and the detonation parameters were calculated by using the EXPLO5.5 program. In addition, the impact as well as friction sensitivities and sensitivity against electrostatic discharge were determined.

Introduction

The synthesis of energetic materials has attracted interest worldwide over the last decade.^[1] Nitrogen-rich compounds, which mainly generate environmentally friendly molecular nitrogen as an end-product of propulsion or explosion, have been the focus of research into energetic materials across the globe.^[1f,2] Modern heterocyclic energetic compounds derive their energy not only from the oxidation of their backbone but also from ring or cage strain. Owing to the high positive heats of formation resulting from the large number of N–N and C–N bonds^[3] and their high level of environmental compatibility, we have studied these compounds over the last couple of years with growing interest.

Azole-based compounds are a prominent family of novel energetic materials because they are generally highly endothermic with high densities and low sensitivities towards external stimuli. In particular, triazoles show a perfect balance between the thermal stability and high positive heat of formation required for applications as prospective high energy density material (HEDM). Even though the heats of formation are larger for tetrazoles ($\Delta_f H^\circ = +237.2 \text{ kJ mol}^{-1}$)^[4] as well as 1,2,3-triazoles ($\Delta_f H^\circ = +272 \text{ kJ mol}^{-1}$),^[5a] 1,2,4-triazoles ($\Delta_f H^\circ = +109 \text{ kJ mol}^{-1}$)^[5b] are better suited to the development of energetic materials because they have less

Fax: +49-89-2180-77492 E-mail: tmk@cup.uni-muenchen.de

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejic.201200221.

catenated nitrogen atoms in one chain, which generally makes them more stable to external stimuli. Many energetic compounds that combine the triazole backbone with energetic moieties such as nitro groups have been synthesized over the last few decades. Examples of such molecules are 5-amino-3-nitro-1,2,4-triazole (ANTA),^[6] 3-nitro-5-triazolone (NTO),^[7] and azo-bridged compounds like 5,5'-dinitro-3,3'-azo-1,2,4-triazole (DNAT).^[8] The thermal stabilities of these materials are remarkably high with decomposition taking place well above 200 °C and they have low sensitivity values. In particular, the anionic species with nitrogen-rich cations show excellent properties as future high explosives.^[9] In general, the deprotonation of triazole species positively influences their thermal stability as well as their sensitivity. In addition, the nitrogen content and performance are increased by the introduction of nitrogen-rich cations.

5,5'-Dinitro-2*H*,2'*H*-3,3'-bi-1,2,4-triazole as well as its ammonium and guanidinium salts have been described in the literature previously, but they have only been characterized by UV absorption^[10] and IR spectroscopy^[11] (DNBT) or investigated for use in gas-generating propellants (ammonium and guanidinium salts).^[12] The compounds presented in this contribution have not previously been characterized structurally or in terms of their energetic properties.

The focus of this study was on the full structural and spectroscopic characterization of the title compound 5,5'-dinitro-2H,2'H-3,3'-bi-1,2,4-triazole as well as the formation and complete characterization of nitrogen-rich salts formed with ammonium, hydrazinium, hydroxylammo-

3474 WILEY SALARY

 [[]a] Department of Chemistry, Ludwig-Maximilians Universität München, Butenandtstr. 5–13, Haus D, 81377 München, Germany



nium, guanidinium, aminoguanidinium, and triaminoguanidinium as counterions. The potential application of the synthesized compounds as energetic materials will be studied and evaluated by using the experimentally obtained values for thermal decomposition as well as the sensitivity data and the calculated performance characteristics.

Results and Discussion

Synthesis

The starting material 5,5'-diamino-1*H*,1'*H*-3,3'-bi-1,2,4triazole (DABT, 1) was first synthesized in a moderate yield of 56% by Shreve and Charlesworth using oxalic acid and aminoguanidine hydrochloride in water.^[13] We have developed a straightforward synthetic procedure yielding DABT as a pure compound in a yield of up to 70%. The modified procedure starts by reacting oxalic acid with aminoguanidinium bicarbonate in concentrated hydrochloric acid at 70 °C followed by isolation of the intermediate product by filtration. While heating under reflux in basic media, the molecule undergoes cyclization, which leads to the formation of DABT (Scheme 1).



Scheme 1. Synthesis of DNBT (2).

DABT was oxidized by the well-known Sandmeyer reaction by diazotization in sulfuric acid and subsequent reaction with sodium nitrite.^[14] The formation of 5,5'-dinitro-2H,2'H-3,3'-bi-1,2,4-triazole (DNBT, **2**) was first reported by Russian scientists^[11] in a low yield of 31%. We were able to optimize the process by adding a suspension of DABT in 20% sulfuric acid to a solution of sodium nitrite in water at 40 °C, which led to a remarkable increase in the yield to 82%.

The formation of the nitrogen-rich salts 3a-f was straightforward. An ethanolic solution of compound 2 was prepared and 2 equiv. of the corresponding nitrogen-rich bases were added (Scheme 2). Owing to the high solubility



Scheme 2. Synthesis of the nitrogen-rich salts of **2** with the corresponding bases.

of DNBT and the low solubility of compounds 3a-f in ethanol, all ionic compounds could be isolated in excellent yields and with high purity.

All the energetic compounds were fully characterized by IR, Raman, and multinuclear NMR spectroscopy, mass spectrometry, and differential scanning calorimetry (DSC). Selected compounds were additionally characterized by low-temperature single-crystal X-ray spectroscopy.

Molecular Structures

Single-crystal X-ray diffraction studies were undertaken for compounds 2, 3a, 3c, 3e, and 3f. All these compounds were recrystallized from water as colorless plates or blocks. Selected crystallographic data for all the compounds are compiled in Table S1 in the Supporting Information.

During the course of this study we were only able to obtain water-free crystal structures of compound 2 and the nitrogen-rich salts 3c and 3f. In the other cases, even though we used different solvents and crystallization methods, crystals too small for measurement (3b,d) or structures including crystal water (3a,e) were obtained. Selected bond lengths, bond angles, and torsion angles of compounds 2, 3a, 3c, 3e, and 3f are compiled in Table S2 in the Supporting Information.

Detailed examination of the crystal structure of the uncharged compound showed no difference between the 1,2,4triazole system and other triazole ring systems.^[8,9b,15] The bond lengths in the triazole ring in the molecular structure of 2 all lie between the lengths of formal C-N and N-N single and double bonds (C-N: 1.47, 1.22 Å; N-N: 1.48, 1.20 Å).^[16] 5,5'-Dinitro-2*H*,2'*H*-3,3'-bi-1,2,4-triazole (2) crystallizes in the monoclinic space group $P2_1/n$ with a cell volume of 394.73(8) $Å^3$ and two molecular moieties in the unit cell. The calculated density at 173 K is 1.902 gcm⁻³ and hence much higher than the density of the dihydrate (1.764 gcm⁻³).^[15b] As expected, the molecule shows a completely planar assembly with a torsion angle between the nitro group and the triazole ring of 2.9(2)°. The formula unit of 2 together with the atom labeling is presented in Figure 1.



Figure 1. Crystal structure of **2**. Thermal ellipsoids are shown at the 50% probability level. Symmetry operators: (*i*) -x, 1 - y, 2 - z.

The structure contains only one individual hydrogen bond N1–H1···O1. The D–H···A angle at 171.9(2)° is close to 180° and the D···A length is shorter than the sum of the van der Waals radii $[r_w(O) + r_w(N) = 3.07 \text{ Å}]^{[16a]}$ at 2.902(2) Å (Figure 2, a). The nitrogen atoms of the triazole ring do not participate as acceptor atoms in any hydrogen



Figure 2. a) Hydrogen-bonding scheme in the crystal structure of **2**. b) Wave-like arrangement of the infinite rows in the crystal structure of **2** (layer distance d = 2.96 Å). Thermal ellipsoids are drawn at the 50% probability level. Symmetry operators: (*i*) 1/2 + x, 1/2 - y, 1/2 + z.

bond. As shown in Figure 2, the crystal structure of **3** consists of infinite zig-zag chains along the *b* axis at an angle of 60.5°. The layers are stacked above each other with a layer distance of d = 2.96 Å. The layers are connected by two short contacts: N2···N4(*ii*) and C1···O1(*iii*) [symmetry operators: (*ii*) 3/2 - x, 1/2 + y, 1/2 - z; (*iii*) 3/2 - x, -1/2 + y, 1/2 - z]. Both contacts are shorter than the sum of the van der Waals radii^[16a] with N2···N4 being the shortest [2.922(2) Å] and C1···O1 being the longest [3.051(2) Å]. The stacking of the layers is displayed in Figure 2 (b) together with the distance *d* between the layers.

In the case of the nitrogen-rich salts, only the crystal structures of compounds 3c and 3f will be discussed in detail. Illustrations as well as crystallographic details of the

structures obtained for compounds **3a** and **3e** are presented in the Supporting Information.

Hydroxylammonium 5,5'-dinitro-3,3'-bi-1,2,4-triazol-2ide (**3c**) crystallizes in the monoclinic space group $P2_1/c$ with two molecular moieties in the unit cell and a density of 1.836 g cm⁻³. An illustration of the formula unit is shown in Figure S2 in the Supporting Information. As shown in Figure 3, each DNBT^{2–} anion within the crystal structure is surrounded by six hydroxylammonium cations linked by strong hydrogen bonds to the nitrogen atoms of the triazole ring and the oxygen O2 of the nitro group (Table 1). It is remarkable that all nitrogen atoms of the triazole ring act as acceptor atoms for hydrogen bonds, which is only possible because of the surrounding hydroxylammonium cations. All



Figure 3. Environment of the DNBT²⁻ anion in the crystal structure of **3c**, hydrogen bonds towards hydroxylammonium cations are marked as dotted lines. Thermal ellipsoids are drawn at the 50% probability level. Symmetry operators: (*i*) 1 - x, 1 - y, -z; (*ii*) 1 - x, 1/2 + y, 1/2 - z; (*iii*) 1 + x, 1/2 - y, 1/2 + z; (*iv*) x, 1/2 - y, -1/2 + z; (*v*) -x, 1/2 + y, -1/2 - z.

three contacts are short with a D···A length of 2.706(2), 2.862(3), and 2.880(3) Å, but only the hydrogen bonds O3–H3···N1(*i*) and N5–H5a···N2 are strongly directed with D–H···A angles of 172(3) and 173(3)°, respectively. In addition, the oxygen atom O2 acts as an acceptor in the moderately strong hydrogen bond N5–H5b···O2(*ii*), which has a D···A length of 2.965(3) Å and a relatively small D–H···A angle of 164(3)°. Owing to this strong network of hydrogen bonds, with O1 being the only potential hydrogen-bond acceptor that does not participate in any short contact or other electrostatic interaction, the compound shows a remarkably high density of 1.836 g cm⁻³.

Table 1. Hydrogen bond lengths and angles in 3c.

D–H•••A	d(D–H) [Å]	<i>d</i> (D−H) <i>d</i> (H···A) [Å] [Å]		∠(D–H•••A) [°]	
O3–H3···N1(<i>i</i>)	0.90(4)	1.81(4)	2.706(2)	172(3)	
N5-H5a···N2	1.00(4)	1.87(4)	2.862(3)	173(3)	
N5-H5c···N3(<i>iv</i>)	0.90(3)	2.04(3)	2.880(3)	157(3)	
N5–H5b····O2(<i>ii</i>)	0.92(3)	2.07(3)	2.965(3)	164(3)	
N5–H5c····O3(iii)	0.90(3)	2.55(3)	3.018(2)	113(2)	

Symmetry operators: (i) x, 1/2 - y, 1/2 + z; (ii) -1 + x, 1/2 - y, -1/2 + z; (iii) 1 + x, y, z; (iv) 1 - x, -1/2 + y, 1/2 - z.

The interaction of the DNBT^{2–} anions with hydroxylammonium cations leads to the formation of layers in the *bc* plane (Figure 4). The hydroxylammonium cations build up infinite rows along the *a* axis and the layers are connected by strong hydrogen bonds. This structure of stacked layers is supported by a short contact O1····O2 with a contact distance of 3.030(3) Å.

The triaminoguanidinium salt (**3f**) crystallizes in the triclinic space group $P\bar{1}$ with a density of 1.664 g cm⁻³ and



one formula unit in the unit cell. The molecular structure together with the labeling scheme is presented in Figure 5.



Figure 5. Crystal structure of **3f**. Thermal ellipsoids are drawn at the 50% probability level. Symmetry operators: (i) 1 - x, 1 - y, -z.

As expected for ionic compounds, the structure is constructed of strong hydrogen bonds between the cations and anions. The structure-determining motive are the infinite rows of DNBT^{2–} anions along the *b* axis. The layers of the DNBT^{2–} anions stack with a distance of 3.307 Å and are connected through hydrogen bonds to the TAG molecules (Figure 6).

All the hydrogen-bond lengths lie well within the sum of the van der Waals radii $[r_w(O) + r_w(N) = 3.07 \text{ Å}, r_w(N) + r_w(N) = 3.20 \text{ Å}]^{[16a]}$ with lengths of 3.0443(16) [N5–H5a···O1(*i*)], 3.0652(17) [N6–H6a···N3(*ii*)], and 2.9147(17) Å (N9–H9···N1), but they are not strongly directed, with angles of 147.0(14), 158.3(14), and 143.4(15)°, respectively (Table 2).



Figure 4. Hydrogen-bonding scheme in the crystal structure of **3c** with layers forming in the *bc* plane. Thermal ellipsoids are drawn at the 50% probability level. Symmetry operators: (i) 1 - x, 1 - y, -z; (ii) 1 - x, 1/2 + y, 1/2 - z; (iii) x, 1/2 - y, -1/2 + z.



Figure 6. Hydrogen-bonding scheme in the crystal structure of **3f** showing the connection of the infinite rows of DNBT anions by TAG cations. Thermal ellipsoids are drawn at the 50% probability level. Symmetry operators: (*i*) 1 - x, 2 - y, 1 - z; (*ii*) x, y, 1 + z; (*iii*) 1 - x, 1 - y, -z; (*iv*) 1 - x, 1 - y, 1 - z; (*v*) x, 1 + y, z; (*vi*) x, -1 + y, -1 + z; (*vii*) 1 - x, 1 - y, -1 - z; (*vii*) x, y, -1 + z; (*vi*) 1 - x, 2 - y, -1 - z; (*vi*) 1 - x, 2 - y, -z.

Table 2. Hydrogen bond lengths and angles in 3f.

D–H•••A	d(D–H) [Å]	d(H•••A) [Å]	d(D−H•••A) [Å]	∠(D–H···A) [°]	
N5–H5a····O1(<i>i</i>)	0.851(16)	2.295(16)	3.0443(16)	147.0(14)	
N9–H9•••N1	0.890(10)	2.223(15)	2.9147(17)	143.4(15)	

Symmetry operators: (*i*) 1 - x, 2 - y, 1 - z; (*ii*) x, y, 1 + z.

Spectroscopic Data

Vibrational Spectroscopy

IR and Raman spectra were recorded for all the compounds and the frequencies assigned according to the literature.^[17] The Raman spectrum of compound 1 is dominated by the deformation mode of the amino groups at 1579 cm^{-1} . The valence stretching mode of the N-H bond is observed at 3116 (IR) and 3107 cm⁻¹ (Raman). After oxidation of the amino groups, the deformation modes of the amine groups disappear. Instead, the symmetric and asymmetric stretching modes of the nitro groups of compound 2 are observed. The vibrational frequencies of the v_{as} stretching mode of the nitro groups are observed at 1551 (IR) and 1546 cm⁻¹ (Raman), and the v_s stretching modes are located at a lower energy at 1410 (IR) and 1393 cm⁻¹ (Raman). The valence stretching mode of the N-H bond can be observed at 3189 (IR) and 3191 cm⁻¹ (Raman). In addition, as for any heterocyclic compound, many combined stretching, deformation, and torsion stretching modes can be observed in the fingerprint region between 1200 and 600 cm⁻¹.^[17b]

The nitrogen-rich salts of **2** also show absorption bands in the region between 3100 and 3500 cm⁻¹ for the N–H valence stretching modes of the cations (ammonium, hydrazinium, and guanidines). The v_{as} stretching modes of the nitro groups are shifted to higher energy compared with **2** and are observed between 1582 and 1562 cm⁻¹ in the Raman spectra and between 1521 and 1508 cm⁻¹ in the IR spectra, respectively. The symmetric stretching modes of the nitro groups are in the same range as for the uncharged compound and can be found at 1410-1380 (IR) and 1407-1383 cm⁻¹ (Raman). The combined stretching and deformation modes as well as torsion modes for the triazole rings are again observed between 1200 and 600 cm⁻¹ for the nitrogen-rich salts.

Multinuclear NMR Spectroscopy

All the compounds were investigated by ¹H, ¹³C, and ¹⁴N NMR spectroscopy. In addition, ¹⁵N NMR spectra were recorded for compounds **2** and **3e**. The two signals of the uncharged compounds **1** and **2** differ only slightly in the ¹³C{¹H} NMR spectra and are in the expected range.^[8,9c] One singlet arising from the bridging carbon atoms appears at $\delta = 149.3$ ppm for DABT (**1**) and at $\delta = 145.6$ ppm for DNBT (**2**). The oxidation of the amino group leads to a downfield shift of the signal of the other carbon atoms from 157.3 ppm for **1** to 162.7 ppm for **2**. The protons in the triazole rings of DNBT can be observed at $\delta = 9.68$ ppm. In the ¹⁴N{¹H} NMR spectra, the nitro groups of compound **2** appear as a broad singlet at $\delta = -26$ ppm. The NMR signals of all energetic the compounds are summarized in Table 3.

Table 3. NMR signals of compounds 2, 3a-f.

	δ [ppm]					
	DNBT	2–[a]	Cation			
	$^{13}C\{^{1}H\}$	$^{14}N\{^{1}H\}$	$^{1}\mathrm{H}$	$^{14}N\{^1H\}$		
2	162.7, 145.6	-26	_	_		
3a	165.5, 157.4	-18	7.16	-359		
3b	165.0, 156.5	-22	7.24	-359		
3c	165.1, 155.5	-14	5.52	_		
				$^{13}C\{^{1}H\}$		
3d	165.2, 156.6	-23	7.57	158.2		
3e	165.4, 157.1	-17	7.60, 4.73	157.8		
3f	165.6, 157.8	-16	7.61, 4.56	159.0		

[a] DNBT in the case of 2.

As described in previous publications on triazole compounds,^[9b,18] the deprotonation of DNBT with nitrogenrich bases shifts the signals in the ¹³C{¹H} NMR spectra downfield. The carbon atoms connecting the two triazole rings can be found in the range 155.5–157.8 ppm and the carbon atoms connected to the nitro groups are in the range of 165.0–165.6 ppm. A trend in the shift of the nitro group signal in the ¹⁴N{¹H} NMR spectra could not be observed; all the signals are found in the range of –18 to –23 ppm. The ¹⁴N{¹H} NMR spectra of **3a** and **3b** also show the signal of the corresponding cation at $\delta = -359$ ppm. The signals of all the nitrogen-rich cations in the ¹H NMR spectra are found in the expected range and have been assigned on the basis of similar countercations of triazolide anions.^[9c]

Four well-resolved resonances for the four nitrogen atoms of compounds **2** and **3f** are observed in the ¹⁵N NMR spectra (Figure 7). In addition, two signals from the triaminoguanidinium cation are observed for compound **3f**. The signals have been assigned by comparison with literature values.^[17a,19]



Figure 7. ¹⁵N NMR spectra of 5,5'-dinitro-2*H*,2'*H*-3,3'-bi-1,2,4-triazole (**2**, top) and bis(triaminoguanidinium) 5,5'-dinitro-3,3'-bi-1,2,4-triazol-2-ide (**3e**, bottom); the *x* axis represents the chemical shift δ in ppm.

As expected, the nitrogen atoms N1, N2, and N4 are shifted to a lower field upon deprotonation. The largest effect can be observed for the nitrogen atom N1, which is found at $\delta = -55.3$ ppm ($\delta = -156.1$ ppm for **2**).

ra Theoretical Calculations, Performance Characteristics, and le Stabilities

All calculations of energies of formation were carried out by using the Gaussian G09W program package.^[20] Because very detailed descriptions of the calculation process have been published earlier^[9c] and can be found in specialized books,^[1b] only a short summary of the computational methods will be given here. The enthalpies (H) and Gibbs free energies (G) were calculated by using the complete basis set method (CBS) of Petersson and co-workers to obtain very accurate energies. In this contribution, we used the modified CBS-4M method with M referring to the use of minimal population localization, which is a reparametrized version of the original CBS-4 computational method and also includes additional empirical calculations.^[21] The enthalpies of formation for the gas-phase species were computed by the atomization energy method using NIST^[22] values as standardized values for the standard heats of formation ($\Delta_{\rm f} H^{\circ}$) according to Equation (1).^[23]

$$\Delta_{\rm f} H^{\circ}_{\rm (g,Molecule,298)} = H_{\rm (Molecule)} - \Sigma H^{\circ}_{\rm (Atoms)} + \Sigma \Delta_{\rm f} H^{\circ}_{\rm (Atoms,NIST)}(1)$$

The solid-state enthalpies of formation for uncharged compounds were estimated from the computational results using Troutons rule ^[24] [Equation (2), in which $T_{\rm m}$ is the decomposition temperature].

$$\Delta H_{\rm m} = \Delta_{\rm f} H^{\circ}_{(g,\text{Molecule},298)} - \Delta H_{\rm sub} = \Delta_{\rm f} H^{\circ}_{(g,\text{Molecule},298)} - (188 \,[\text{J}\,\text{mol}^{-1}\,\text{K}^{-1}] \times T_{\rm m})$$
(2)

The solid-state enthalpies of formation for the ionic compounds were derived from the calculation of the corresponding lattice energies $(U_{\rm L})$ and enthalpies $(H_{\rm L})$, calculated from the corresponding molecular volumes using the equations provided by Jenkins and co-workers.^[25] The molar standard enthalpies of formation determined for the solid state $(\Delta H_{\rm m})$ were used to calculate the solid-state energies of formation $(\Delta U_{\rm m})$ according to Equation (3) with Δn being the change in the number of moles of gaseous components.^[1b]

$$\Delta U_{\rm m} = \Delta H_{\rm m} - \Delta n R T \tag{3}$$

The calculated standard energies of formation were used to predict the detonation parameters with the program package EXPLO5.5.^[26] The program is based on the chemical equilibrium, steady-state model of detonation. It uses the Becker-Kistiakowsky-Wilson equation of state (BKW EOS) for gaseous detonation products together with the Cowan-Fickett equation of state for solid carbon.^[27] The equilibrium composition of the detonation products was calculated by using the modified free-energy minimization technique of White, Johnson, and Dantzig. The program was designed to enable calculations of the detonation parameter at the Chapman-Jouguet point. The BKW equation (4) as implemented in the EXPLO5.5 program was used with the BKW-G set of parameters $(a, \beta, \kappa, \theta)$ given below Equation (4) in which X_i is the mol fraction of the i^{th} gaseous detonation product and k_i is the molar co-volume of the *i*th gaseous detonation product.^[26,27]

FULL PAPER

$pV/RT = 1 + xe^{\beta x}$	with	$x = (\kappa \Sigma X_{i}k_{i}) / [V(T+\theta)]^{\alpha}$	
α = 0.5, β =	0.096,	$\kappa = 17.56, \ \theta = 4950$	(4)

The results of the detonation runs, together with the calculated energies of formation and the corresponding sensitivities are compiled in Table 4.

Compound **2** shows a remarkably high thermal stability up to 251 °C together with an insensitivity towards friction and a moderate sensitivity towards impact (10 J). In comparison, 5,5'-dinitrimino-4,4',5,5'-tetrahydro-1*H*,1'*H*-3,3'bi-1,2,4-triazole, recently reported by Shreeve and coworkers, decomposes at 165 °C.^[29] The beneficial detonation parameters of DNBT with $V_{det.} = 8413 \text{ ms}^{-1}$ mainly stem from the high positive heat of formation (285 kJ mol⁻¹) and the remarkably high density of 1.902 g cm⁻³ (X-ray measurement).

Because salts of energetic compounds tend to be more stable than the uncharged compound, the nitrogen-rich salts of DNBT are expected to show improved stability. The decomposition temperatures of the ammonium (3a) and aminoguanidinium (3e) salts are similar to that of the uncharged compound, whereas the decomposition temperature of the guanidinium compound (3d) is higher (335 °C). As shown in Figure 8, the decomposition temperature decreases along the series **3a–c** with the ammonium salt **3a** showing the highest value of 252 °C and the hydroxylammonium salt 3c showing decomposition onset at 204 °C. The same trend can be observed for the guanidinium derivatives 3e,f. The guanidinium salt 3d shows the highest decomposition temperature with 335 °C, followed by the amminoguanidinium salt 3e at 253 °C, and the triaminoguanidinium salt 3f with a decomposition onset at 201 °C. Nearly all the compounds are insensitive towards friction, impact,



Figure 8. DSC plots of DNBT (2), $(NH_4^+)_2DNBT^{2-}(3a)$, $(N_2H_5^+)_{2^-}DNBT^2(3b)$, $(NH_3OH^+)_2DNBT^{2-}(3c)$, $(G^+)_2DNBT^{2-}(3d)$, $(AG^+)_{2^-}DNBT^{2-}(3e)$, and $(TAG^+)_2DNBT^{2-}(3f)$. DSC plots were recorded at a heating rate of 5 °C min⁻¹.

and electrostatic discharge; only the hydrazinium salt is moderately sensitive towards impact (15 J).

	2	3a	3b	3c	3d	3e	3f	RDX ^[0]
Formula	C ₄ H ₂ N ₈ O ₄	C ₄ H ₈ N ₁₀ O ₄	C ₄ H ₁₀ N ₁₂ O ₄	C ₄ H ₈ N ₁₀ O ₆	C ₆ H ₁₂ N ₁₄ O ₄	C ₆ H ₁₄ N ₁₆ O ₄	C ₆ H ₁₈ N ₂₀ O ₄	C ₃ H ₆ N ₆ O ₆
Molecular mass [gmol ⁻¹]	226.1	261.0	290.2	292.1	344.2	374.2	434.3	222.1
Impact sensitivity [J] ^[a]	10	40	15	40	40	40	40	7
Friction sensitivity [N] ^[b]	360	360	360	360	360	360	360	120
ESD test [J]	0.1	0.5	0.15	0.5	0.75	1.0	0.5	_
N [%] ^[c]	49.45	53.84	57.92	47.94	56.96	59.88	64.50	37.8
$\Omega [\%]^{[d]}$	-35.4	-49.2	-49.6	-49.2	-65.1	-64.1	-62.6	-21.6
$T_{\rm dec.} [^{\circ}C]^{[e]}$	251	252	237	204	335	253	201	210
$\rho [\text{g cm}^{-3}]^{[\text{f}]}$	1.902	1.7 ^[n]	1.7 ^[n]	1.836	1.7 ^[n]	1.7 ^[n]	1.664	1.80
$\Delta_{\rm f} H_{\rm m}^{\circ} [\rm kJ mol^{-1}]^{[g]}$	285	109	412	189	125	355	828	70
$\Delta_{\rm f} U^{\circ} [\rm kJ kg^{-1}]^{[\rm h]}$	1338	522	1530	617	470	1060	2027	417
EXPLO5 values, v. 5.05								
$-\Delta_{\rm E} U^{\circ} [\rm kJ kg^{-1}]^{[i]}$	4888	4176	4914	4277	3419	3839	4538	6125
$T_{\rm E} [\rm K]^{[j]}$	3890	3121	3399	3111	2596	2782	3045	4236
p_{C-I} [kbar] ^[k]	320	248	281	299	225	248	271	349
$V_{\rm det} [{\rm ms^{-1}}]^{[1]}$	8413	7938	8400	8477	7699	8020	8365	8748
Gas volume [Lkg ⁻¹] ^[m]	642	771	798	771	760	780	811	739

Table 4. Physicochemical properties of compounds 2 and 3a-f in comparison with hexogen (RDX).

[a] BAM drop hammer. [b] BAM friction tester. [c] Nitrogen content. [d] Oxygen balance. [e] Temperature of decomposition by DSC (β = 5 °C, onset values). [f] Derived from the X-ray structure. [g] Molar enthalpy of formation. [h] Energy of formation. [i] Energy of explosion. [j] Explosion temperature. [k] Detonation pressure. [l] Detonation velocity. [m] Assumes only gaseous products. [n] Density values of **3a**, **3b**, **3d**, and **3e** were estimated based on additional pycnometer measurements and in relation to **3f** and trends in the triazolide salts (see ref.^[9c]). [o] Values based on ref.^[28] and the EXPLO5.5 database.

The nitrogen-rich salts of DNBT all exhibit highly positive heats and energies of formation in the range of the similar ionic nitrimino compound.^[29] The detonation velocities were calculated to be in the range of 7699 (**3d**) to 8477 m s⁻¹ (**3b**). The best performances were calculated for the hydrazinium salt (**3b**), which has a detonation velocity of 8400 m s⁻¹, and the hydroxylammonium salt **3c**, which has a detonation velocity of 8477 m s⁻¹ and is around 4% lower than that of RDX.

Because the focus of this study was the evaluation of potential replacements for commonly used secondary explosives, only three compounds show suitable values regarding detonation parameters, sensitivities, and thermal stabilities. The best compounds for replacing RDX, taking into account the performance values and sensitivities, would be the triaminoguanidinium and hydroxylammonium salts. Compound 3c displays the best performance with a calculated detonation velocity of 8477 m s⁻¹, a detonation pressure of 299 kbar, and a decomposition temperature of 204 °C. The triaminoguanidinium compound exhibits energetic properties in the same range with a detonation velocity of 8365 m s⁻¹, a detonation pressure of 271 kbar, and a decomposition temperature of 201 °C. In addition, both compounds are, in contrast to RDX, insensitive towards friction and impact.

The performance characteristics of the hydrazinium compound **3b** are even better than those of **3f** with a calculated detonation velocity of 8400 m s⁻¹ and a detonation pressure of 281 kbar. Unfortunately, the compound is sensitive towards impact (15 J). Although the guanidinium salt **3d** shows lower performance values ($V_{det.} = 7699 \text{ m s}^{-1}$, $p_{C-J} =$ 225 kbar) than **3c** and **3f**, it has an excellent decomposition temperature of 335 °C together with an insensitivity towards friction and impact and therefore it could be a potential replacement for hexanitrostilbene (HNS). Although not all the compounds perform better than RDX by calculations, they can probably find use in certain applications in civilian use or as burn-rate modifiers in military applications.

Conclusions

The starting material DABT (1) has been synthesized following a modified literature procedure^[13] resulting in an increase in the yield from 56 to 70%. Optimization of the reaction conditions for the oxidation of the amine to 5,5'dinitro-2H,2'H-3,3'-bi-1,2,4-triazole (DNBT, 2)[11] resulted in an improvement in the yield from 31 to 82%. Compound 2 can therefore be considered as a low-cost starting material for new energetic materials and it has been fully characterized by IR, Raman, and multinuclear NMR spectroscopy, mass spectrometry, and DSC. The uncharged compound 2 shows thermal stability up to 251 °C together with an insensitivity towards friction and a moderate sensitivity towards impact (10 J). As a result of the calculated positive heat of formation (285 kJ mol⁻¹), the detonation parameters ($V_{det.} = 8413 \text{ m s}^{-1}$) are in the range of those of RDX.



Energetic ionic compounds were synthesized from 2 by using nitrogen-rich cations. All the reactions were carried out with the free bases or their corresponding carbonates. The energetic ionic compounds 3a-f were characterized by the same techniques as used for the uncharged compounds. Crystal structures were obtained for selected compounds and have been discussed in detail for compounds 2, 3c, and 3f. All the ionic compounds have positive heats of formation in the range of 109 (3a) to 828 kJ mol⁻¹ (3f). The most interesting compounds with regard to energetic properties are the hydroxylammonium (3c), triaminoguanidinium (3f), and hydrazinium (3b) salts. All of these compounds exhibit decomposition temperatures above 200 °C and performance values in the range of RDX [8477 m s⁻¹ (3c), 8365 m s⁻¹ (3f)]. Worth mentioning is the guanidinium salt 3d, which has a remarkably high decomposition temperature of 335 °C and an insensitivity towards friction and impact. These compounds could find applications because they are easy to obtain, safe to handle, and show performance characteristics in the range of modern secondary explosives.^[2e]

Experimental Section

Caution: Although all the nitroazoles are rather stable against external stimuli, proper safety precautions should be taken when handling the dry materials. All the derivatives of DNBT are energetic materials and tend to explode under the influence of heat, impact, or friction. Laboratory personnel and equipment should be properly grounded and protective equipment such as earthed shoes, leather coat, Kevlar[®] gloves, ear protection, and face shield is recommended.

General: All chemical reagents and solvents were obtained from Sigma-Aldrich or Acros Organics (analytical grade) and were used as supplied without further purification. ¹H, ¹³C{¹H}, ¹⁴N{¹H}, and ¹⁵N NMR spectra were recorded with a JEOL Eclipse 400 instrument in [D₆]DMSO at 25 °C. The chemical shifts are given relative to tetramethylsilane (¹H, ¹³C) or nitromethane (¹⁴N, ¹⁵N) as external standards and coupling constants are given in Hz. IR spectra were recorded with a Perkin-Elmer Spectrum BX FT-IR spectrometer equipped with an ATR unit at 25 °C. Transmittance values are qualitatively described as "very strong" (vs), "strong" (s), "medium" (m), "weak" (w), and "very weak" (vw). Raman spectra were recorded with a Bruker RAM II spectrometer equipped with a Nd:YAG laser (200 mW) operating at 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 (CHNO) were performed with a Netzsch Simultaneous Thermal Analyzer STA 429 instrument. Melting and decomposition points were determined by differential scanning calorimetry (Linseis PT 10 DSC, calibrated with standard pure indium and zinc). Measurements were made at a heating rate of 5 °C min⁻¹ in closed aluminium sample pans with a 1 µm hole in the lid for gas release to avoid an unsafe increase in pressure under a flow of nitrogen (20 mL min⁻¹) with an empty identical aluminium sample pan as reference.

For the initial safety testing, the impact and friction sensitivities, and the electrostatic sensitivities were determined. The impact sensitivity tests were carried out according to STANAG 4489,^[30] modified according to WIWEB instruction 4-5.1.02^[31] using a BAM^[32] drop hammer. The friction sensitivity tests were carried out accord-

FULL PAPER

ing to STANAG 4487^[33] and modified according to WIWEB instruction 4-5.1.03^[34] using the BAM^[32] friction tester. The electrostatic sensitivity tests were accomplished according to STANAG 4490^[35] using an electric spark testing device ESD 2010EN (OZM Research) operating with the "Winspark 1.15 software package".

Crystallographic Measurements: Single-crystal X-ray diffraction data for **2**, **3a**, **3e**, and **3f** were collected with an Oxford Xcalibur3 diffractometer equipped with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD detector. Data collection was undertaken by using the CrysAlis CCD software^[36] and the data reduction with the CrysAlis Red software.^[37] Crystals of compound **3c** were investigated with a Bruker Nonius–Kappa CCD diffractometer equipped with a rotating molybdenum anode and Montel-graded multilayered X-ray optics. The structures were solved with Sir-92^[38] or SHELXS-97^[39] and refined with SHELXL-97^[40] implemented in the program package WinGX^[41] and finally checked by using Platon.^[42]

CCDC-864398 (for 2), -864400 (for 3a), -864399 (for 3c), -864397 (for 3e), and -864401 (for 3f) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

5,5'-Diamino-1H,1'H-3,3'-bi-1,2,4-triazole (DABT, 1): According to a modified literature procedure,^[13] hydrochloric acid (60 mL) was added to a stirred mixture of oxalic acid (20.0 g, 159 mmol) and aminoguanidinium bicarbonate (45.4 g, 332 mmol). The reaction mixture was stirred at 70 °C for 1 h and the precipitate was collected by filtration. The colorless solid was dissolved in water (240 mL), which was made alkaline with sodium hydroxide to pH = 14. The reaction mixture was heated at reflux for 1 h and subsequently acidified with acetic acid to pH = 4. The resulting precipitate was collected by filtration, washed with water (ca. 200 mL), and dried in air to yield 5,5'-diamino-1H,1'H-3,3'-bi-1,2,4-triazole (1; 18.6 g, 112 mmol, 70%) as a colorless solid. ¹H NMR ($[D_6]$ -DMSO): $\delta = 6.46$ (s, 2 H, NH₂) ppm. ¹³C NMR ([D₆]DMSO): $\delta =$ 157.3, 149.3 ppm. IR: $\tilde{v} = 3325$ (m), 3116 (m), 2863 (m), 2784 (m), 1706 (s), 1668 (s), 1654 (s), 1618 (m), 1606 (m), 1484 (m), 1457 (m), 1267 (m), 1104 (vs), 1061 (s), 987 (w), 956 (w), 769 (w), 721 (s) cm⁻¹. Raman (200 mW): $\tilde{v} = 1636$ (62), 1614 (100), 1591 (67), 1575 (57), 1495 (13), 1439 (21), 1432 (21), 1361 (9), 1152 (24), 1143 (23), 1059 (23), 1042 (34), 1022 (22), 980 (27), 772 (18), 554 (7), 413 (11), 328 (12), 249 (16) cm⁻¹. MS (DEI+): $m/z = 166.1 [C_4H_7N_8]^+$. C₄H₆N₁₀ (194.16): calcd. C 28.92, H 3.64, N 67.44; found C 28.72, H 3.58, N 66.11.

5,5'-Dinitro-2H,2'H-3,3'-bi-1,2,4-triazole (DNBT, 2): A solution of 5,5'-diamino-1H,1'H-3,3'-bi-1,2,4-triazole (1; 11.9 g, 72 mmol) in 20% sulfuric acid (140 mL) was added dropwise to a solution of sodium nitrite (10 equiv., 98.8 g, 1.4 mol) in water (140 mL) at 40 °C. The mixture was stirred at 50 °C for 1 h. After cooling to room temperature the mixture was acidified with sulfuric acid (20%) until no evolution of nitrogen dioxide could be observed. The precipitate was collected by filtration and dissolved in boiling water. The hot solution was filtered and allowed to cool to room temperature. Collection of the pale-green precipitate afforded 5,5'dinitro-2H,2'H-3,3'-bi-1,2,4-triazole dihydrate (15.5 g, 59 mmol, 82%) as a crystalline solid. ¹H NMR ([D₆]DMSO): δ = 9.68 (s, 2 H, H_{Triazole}) ppm. ¹³C NMR ([D₆]DMSO): δ = 162.7, 145.6 ppm. ¹⁴N NMR ([D₆]DMSO): $\delta = -26$ (NO₂) ppm. ¹⁵N NMR ([D₆]-DMSO): $\delta = -27.8$ (N4), -88.8 (N2), -141.7 (N3), -156.1 (N1) ppm. IR: $\tilde{v} = 3599$ (m), 3499 (m), 3052 (w), 2849 (w), 2747 (w), 2670 (m), 2621 (m), 2574 (m), 2530 (m), 2488 (m), 2419 (m), 1844 (w), 1609 (m), 1532 (vs), 1466 (w), 1416 (vs), 1314 (vs), 1245 (m), 1183 (m), 1024 (m), 953 (s), 837 (s), 690 (w), 690 (w) cm⁻¹. Raman (200 mW): $\tilde{v} = 3192$ (3), 1641 (100), 1546 (28), 1519 (5), 1485 (75), 1468 (43), 1458 (95), 1413 (18), 1393 (97), 1365 (6), 1362 (6), 1345 (13), 1325 (27), 1306 (35), 1172 (58), 1062 (67), 1015 (31), 855 (4), 774 (8), 744 (5), 619 (4), 511 (4), 452 (5), 452 (5), 399 (9), 297 (9), 203 (6) cm⁻¹. MS (FAB–): m/z = 225.1 [C₄HN₈O₄]⁻. C₄H₂N₈O₄ (226.11): calcd. C 21.25, H 0.89, N 49.56; found C 21.44, H 0.95, N 49.19. Sensitivities (grain size: <100 µm): friction: 360 N, impact: 10 J, ESD: 0.1 J; DSC (onset, 5 °C min⁻¹): $T_{Dec.} = 251$ °C.

Ammonium 5,5'-Dinitro-3,3'-bi-1,2,4-triazol-2-ide (3a): 5,5'-Dinitro-2H,2'H-3,3'-bi-1,2,4-triazole (2; 250 mg, 1.1 mmol) was dissolved in ethanol (50 mL). Ammonia was passed through the solution for 5 min. Collection of the precipitate by filtration afforded ammonium 5,5'-dinitro-3,3'-bi-1,2,4-triazol-2-ide (3a; 374 mg, 1.0 mmol, 91%) as a yellow solid. ¹H NMR ([D₆]DMSO): δ = 7.16 (s, 8 H, NH_4^+) ppm. ¹³C NMR ([D₆]DMSO): δ = 165.4, 159.1 $(CH_7N_4^+)$, 157.1 ppm. ¹⁴N NMR ([D₆]DMSO): $\delta = -18$ (NO₂), $-359 (NH_4^+)$ ppm. ¹⁵N NMR ([D₆]DMSO): $\delta = -20.0$ (N4), -58.6(N1), -59.2 (N2), -147.3 (N3), -358.5 (NH_4^+) ppm. IR: $\tilde{v} = 3265$ (m), 2999 (m), 2890 (m), 2852 (m), 2786 (m), 1704 (w), 1671 (m), 1521 (s), 1457 (s), 1438 (s), 1408 (s), 1390 (vs), 1306 (s), 1244 (s), 1090 (s), 1036 (m), 984 (m), 841 (s), 714 (m), 661 (m) cm⁻¹. Raman (200 mW): $\tilde{v} = 1572 (58), 1555 (7), 1541 (1), 1523 (7), 1480 (10),$ 1472 (24), 1427 (3), 1405 (39), 1399 (51), 1352 (45), 1314 (1), 1300 (3), 1109 (76), 1101 (100), 1072 (6), 1032 (9), 850 (13), 779 (2), 765 (2), 521 (1), 472 (2), 420 (2), 298 (2), 298 (2), 206 (2) cm⁻¹. C₄H₈N₁₀O₄ (260.17): calcd. C 18.47, H 3.10, N 53.84; found C 18.79, H 3.04, N 53.28. MS (FAB+): $m/z = 18 [NH_4]^+$. MS (FAB-): m/z = 225.1 [C₄HN₈O₄]⁻. Sensitivities (grain size: <100 µm): friction: 360 N, impact: 40 J, ESD: 0.5 J; DSC (onset, 5 °C min⁻¹): $T_{dec.} = 252$ °C.

Hydrazinium 5,5'-Dinitro-3,3'-bi-1,2,4-triazol-2-ide (3b): 5,5'-Dinitro-2H,2'H-3,3'-bi-1,2,4-triazole (2; 250 mg, 1.1 mmol) was dissolved in ethanol (50 mL) and hydrazine hydrate (0.11 mL, 2.2 mmol) was then added. Collection of the precipitate by filtration afforded hydrazinium 5,5'-dinitro-3,3'-bi-1,2,4-triazol-2-ide (3b; 263 mg, 0.9 mmol, 83%) as a yellow solid. ¹H NMR ([D₆]-DMSO): $\delta = 7.24$ (s, N₂H₅⁺) ppm. ¹³C NMR ([D₆]DMSO): $\delta =$ 165.0, 156.5 ppm. ¹⁴N NMR ([D₆]DMSO): $\delta = -22$ (NO₂), -359 $(N_2H_5^+)$ ppm. IR: $\tilde{v} = 3346$ (w), 3258 (w), 2648 (m), 1642 (w), 1586 (w), 1509 (s), 1455 (vs), 1392 (vs), 1306 (s), 1263 (s), 1135 (m), 1110 (s), 1104 (s), 1043 (m), 990 (m), 968 (s), 836 (vs), 709 (m), 652 (m) cm⁻¹. Raman (200 mW): $\tilde{v} = 1575$ (30), 1554 (3), 1525 (4), 1516 (5), 1485 (16), 1400 (61), 1355 (44), 1305 (4), 1113 (100), 1032 (6), 970 (2), 845 (12), 778 (2), 765 (3), 473 (2), 408 (2), 293 (1), 210 (4) cm⁻¹. C₄H₁₀N₁₂O₄ (290.20): calcd. C 16.56, H 3.47, N 57.92; found C 16.89, H 3.44, N 57.28. Sensitivities (grain size: <100 µm): friction: 360 N, impact: 15 J, ESD: 0.15 J; DSC (onset, 5 °Cmin⁻¹): $T_{\rm dec.} = 237 \,^{\circ}{\rm C}.$

Hydroxylammonium 5,5'-Dinitro-3,3'-bi-1,2,4-triazol-2-ide (3c): 5,5'-Dinitro-2*H*,2'*H*-3,3'-bi-1,2,4-triazole (2; 250 mg, 1.1 mmol) was dissolved in ethanol (50 mL) and hydroxylamine (50% in H₂O, 145 mg, 2.2 mmol) was then added. The mixture was heated at reflux for 30 min and allowed to cool to room temperature. Collection of the precipitate by filtration afforded hydroxylammonium 5,5'-dinitro-3,3'-bi-1,2,4-triazol-2-ide (3c; 273 mg, 0.9 mmol, 93%) as a yellow solid. ¹H NMR ([D₆]DMSO): δ = 5.52 (s, NH₃OH⁺) ppm. ¹³C NMR ([D₆]DMSO): δ = 165.1, 155.5 ppm. ¹⁴N NMR ([D₆]DMSO): δ = -14 (*N*O₂) ppm. ¹⁵N NMR ([D₆]-DMSO): δ = -22.5 (N4), -64.0 (N1), -75.3 (N2), -155.8 (N3), -296.9 (*N*H₄OH⁺) ppm. IR: \tilde{v} = 3174 (w), 2915 (w), 2668 (w), 2510 (w), 1614 (w), 1537 (w), 1508 (m), 1483 (w), 1473 (w), 1454 (s), 1401 (vs), 1310 (s), 1266 (m), 1248 (m), 1218 (w), 1119 (s), 1050 (w), 998 (m), 843 (s), 801 (m), 766 (w), 710 (w), 656 (w), 656 (w) cm⁻¹. Raman (200 mW): $\tilde{v} = 1582$ (37), 1526 (5), 1480 (14), 1408 (58), 1363 (43), 1311 (2), 1117 (100), 1041 (5), 1003 (3), 851 (7) cm⁻¹. MS (FAB+): m/z = 126.1 [Matrix + NH₃O]⁺. MS (FAB-): m/z = 224.9 [C₄HN₈O₄]⁻. C₄H₈N₁₀O₆ (292.17): calcd. C 16.44, H 2.76, N 47.94; found C 17.03, H 2.74, N 47.90. Sensitivities (grain size: <100 µm): friction: 360 N, impact: 40 J, ESD: 0.5 J; DSC (onset, 5 °Cmin⁻¹): $T_{dec.} = 204$ °C.

Guanidinium 5,5'-Dinitro-3,3'-bi-1,2,4-triazol-2-ide (3d): 5,5'-Dinitro-2H,2'H-3,3'-bi-1,2,4-triazole (2; 250 mg, 1.1 mmol) was dissolved in ethanol (50 mL) and guanidinium carbonate (198 mg, 1.1 mmol) was then added. The mixture was heated at reflux for 30 min and the precipitate was collected by filtration to afford guanidinium 5,5'-dinitro-3,3'-bi-1,2,4-triazol-2-ide (3d; 331 mg, 1.0 mmol, 87%) as a yellow solid. ¹H NMR ([D₆]DMSO): δ = 7.57 (s, 12 H, $CH_6N_3^+$) ppm. ¹³C NMR ([D₆]DMSO): δ = 165.2, 158.2 $(CH_6N_3^+)$, 156.6 ppm. ¹⁴N NMR ([D₆]DMSO): $\delta = -23$ (NO_2) ppm. IR: $\tilde{v} = 3467$ (m), 3357 (w), 3143 (m), 1663 (s), 1560 (w), 1510 (s), 1447 (s), 1387 (vs), 1302 (s), 1246 (m), 1105 (s), 1036 (w), 990 (w), 843 (s), 716 (m), 689 (w), 655 (w) cm⁻¹. Raman $(200 \text{ mW}): \tilde{v} = 1568 (44), 1554 (8), 1540 (3), 1525 (5), 1516 (7),$ 1470 (25), 1401 (56), 1389 (43), 1348 (71), 1298 (4), 1099 (100), 1088 (77), 1065 (14), 1060 (20), 1029 (12), 1008 (28), 849 (16), 778 (2), 764 (3), 536 (7), 472 (5), 419 (3), 207 (3) cm⁻¹. MS (FAB+): *m*/*z* = 60.1 $[CH_6N_3]^+$. MS (FAB-): $m/z = 225 [C_4HN_8O_4]^-$. $C_6H_{12}N_{14}O_4$ (344.25): calcd. C 20.93, H 3.51, N 56.96; found C 19.88, H 4.95, N 47.06. Sensitivities (grain size: <100 µm): friction: 360 N, impact: 40 J, ESD: 0.75 J; DSC (onset, 5 °C min⁻¹): $T_{dec.} = 335$ °C.

Aminoguanidinium 5,5'-Dinitro-3,3'-bi-1,2,4-triazol-2-ide (3e): 5,5'-Dinitro-2H,2'H-3,3'-bi-1,2,4-triazole (2; 250 mg, 1.1 mmol) was dissolved in ethanol (50 mL) and aminoguanidinium hydrogen carbonate (299 mg, 2.2 mmol) was then added. The mixture was heated at reflux for 30 min and allowed to cool to room temperature. Collection of the precipitate by filtration afforded aminoguanidinium 5,5'-dinitro-3,3'-bi-1,2,4-triazol-2-ide (3e; 374 mg, 1.0 mmol, 91%) as a yellow solid. ¹H NMR ([D₆]DMSO): δ = 9.38 (s, 2 H, AG⁺), 7.60 (s, 4 H, CH₇N₄⁺), 4.73 (s, 8 H, CH₇N₄⁺) ppm. ¹³C NMR ([D₆]DMSO): δ = 165.4, 159.1 (CH₇N₄⁺), 157.1 ppm. ¹⁴N NMR ([D₆]DMSO): $\delta = -17$ (NO₂) ppm. IR: $\tilde{v} = 3265$ (m), 2999 (m), 2890 (m), 2852 (m), 2786 (m), 1704 (w), 1671 (m), 1521 (s), 1457 (s), 1438 (s), 1408 (s), 1390 (vs), 1306 (s), 1244 (s), 1090 (s), 1036 (m), 984 (m), 841 (s), 714 (m), 661 (m) cm⁻¹. Raman (200 mW): $\tilde{v} = 1572 (58), 1555 (7), 1541 (1), 1523 (7), 1480 (10),$ 1472 (24), 1427 (3), 1405 (39), 1399 (51), 1352 (45), 1314 (1), 1300 (3), 1109 (76), 1101 (100), 1072 (6), 1032 (9), 850 (13), 779 (2), 765 (2), 521 (1), 472 (2), 420 (2), 298 (2), 298 (2), 206 (2) cm⁻¹. MS (FAB+): $m/z = 75.1 [CH_7N_3]^+$. MS (FAB-): m/z = 225.1[C₄HN₈O₄]⁻. C₆H₁₄N₁₆O₄ (374.28): calcd. C 19.25, H 3.77, N 59.88; found C 18.17, H 3.81, N 46.95. Sensitivities (grain size: <100 µm): friction: 360 N, impact: 40 J, ESD: 1.0 J; DSC (onset, 5 °C min⁻¹): $T_{dec.} = 253$ °C.

Triaminoguanidinium 5,5'-Dinitro-3,3'-bi-1,2,4-triazol-2-ide (3f): 5,5'-Dinitro-2*H*,2'*H*-3,3'-bi-1,2,4-triazole (2; 250 mg, 1.1 mmol) was dissolved in ethanol (50 mL) and triaminoguanidine (230 mg, 2.2 mmol) was then added. The mixture was heated at reflux for 30 min and allowed to cool to room temperature. Collection of the precipitate by filtration afforded triaminoguanidinium 5,5'-dinitro-3,3'-bi-1,2,4-triazol-2-ide (3f; 292 mg, 0.7 mmol, 61%) as a yellow solid. ¹H NMR ([D₆]DMSO): δ = 8.69 (s, 3 H, CH₉N₆⁺), 4.56 (s, 6 H, TAG⁺) ppm. ¹³C NMR ([D₆]DMSO): δ = 165.6, 159.0



(CH₉N₆⁺), 157.8 ppm. ¹⁴N NMR ([D₆]DMSO): $\delta = -16$ (*N*O₂) ppm. ¹⁵N NMR ([D₆]DMSO): $\delta = -19.4$ (N4), -55.3 (N1), -56.3 (N2), -145.7 (N3), -289.4 (CH₉N₆⁺, *N*H), -329.8 (CH₉N₆⁺, *N*H₂) ppm. IR: $\tilde{v} = 3343$ (m), 3308 (s), 3184 (m), 1671 (vs), 1585 (m), 1520 (s), 1446 (s), 1380 (s), 1347 (m), 1295 (s), 1236 (s), 1194 (m), 1132 (s), 1088 (s), 1034 (s), 978 (vs), 962 (s), 838 (s), 739 (w), 714 (m) cm⁻¹. Raman (200 mW): $\tilde{v} = 1573$ (10), 1563 (49), 1555 (31), 1542 (4), 1514 (16), 1461 (26), 1384 (67), 1340 (41), 1293 (4), 1083 (100), 1018 (6), 990 (2), 894 (2), 841 (2), 765 (2), 464 (3), 412 (2) cm⁻¹. MS (FAB+): *m*/*z* = 105.1 [CH₉N₆]⁺. MS (FAB-): *m*/*z* = 225.1 [C₄HN₈O₄]⁻.C₆H₁₈N₂₀O₄ (434.34): calcd. C 16.59, H 4.18, N 64.50; found C 17.58, H 3.98, N 63.30. Sensitivities (grain size: <100 µm): friction: 360 N, impact: 40 J, ESD: 0.5 J; DSC (onset, 5 °C min⁻¹): *T*_{dec.} = 201 °C.

Supporting Information (see footnote on the first page of this article): Additional crystallographic data and parameters as well as selected bond lengths, bond angles and torsion angles of compounds 2 and 3a–f.

Acknowledgments

Financial support of this work by the Ludwig-Maximilians University (LMU) of Munich, 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 numbers W911NF-09-2-0018 (ARL), W911NF-09-1-0120 (AR-DEC), W011NF-09-1-0056 (ARDEC) and 10 WPSEED01-002/W-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 Sucesca (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 Dr. Betsy M. Rice and Dr. 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. We are also indebted to and thank Stefan Huber for measuring all sensitivity values and Dr. Burkhard Krumm for assistance in ¹⁵N NMR spectroscopy. The authors would like to thank one reviewer for stimulating criticism concerning thermodynamic approximations.

a) T. M. Klapötke, Chemistry of high-energy materials, De Gruyter, Berlin, 2011; b) T. M. Klapötke, Chemie der hochenergetischen Materialien, de Gruyter, Berlin, 2009; c) P. F. Pagoria, G. S. Lee, A. R. Mitchell, R. D. Schmidt, Thermochim. Acta 2002, 384, 187–204; d) R. P. Singh, R. D. Verma, D. T. Meshri, J. M. Shreeve, Angew. Chem. 2006, 118, 3664; Angew. Chem. Int. Ed. 2006, 45, 3584–3601; e) C. M. Sabate, T. M. Klapötke, Proceedings of the 12th Seminar, New Trends in Research of Energetic Materials, University of Pardubice, Czech Republic, Apr. 1–3, 2009, 172–194; f) S. Yang, S. Xu, H. Huang, W. Zhang, X. Zhang, Huaxue Jinzhan 2008, 20, 526–537; g) M. B. Talawar, R. Sivabalan, T. Mukundan, H. Muthurajan, A. K. Sikder, B. R. Gandhe, A. S. Rao, J. Hazard. Mater. 2009, 161, 589–607.

^[2] a) T. M. Klapötke, J. Stierstorfer, A. U. Wallek, *Chem. Mater.* 2008, 20, 4519–4530; b) T. M. Klapötke, C. M. Sabate, *Chem. Mater.* 2008, 20, 3629–3637; c) D. E. Chavez, M. A. Hiskey, D. L. Naud, *Prop. Explos. Pyrot.* 2004, 29, 209–215; d) Y. Huang, H. Gao, B. Twamley, J. M. Shreeve, *Eur. J. Inorg. Chem.*

FULL PAPER

2008, 2560–2568; e) H. Gao, J. M. Shreeve, *Chem. Rev.* **2011**, *111*, 7377–7436.

- [3] T. M. Klapötke, in: *Structure and Bonding* (Ed.: D. M. P. Mingos), Springer, Berlin, Heidelberg, 2007.
- [4] V. A. Ostrovskii, M. S. Pevzner, T. P. Kofman, I. V. Tselinskii, *Targets Heterocycl. Syst.* 1999, 3, 467–526.
- [5] a) J. B. Pedley, *Thermodynamic Research Center Data Series*, vol. 1, Texas A&M University, College Station, Texas, **1994**; b)
 P. Jiminez, M. V. Roux, C. J. Turrion, *J. Chem. Thermodyn.* **1989**, 21, 759–764.
- [6] K. Y. Lee, C. B. Storm, M. A. Hiskey, M. D. Coburn, J. Energ. Mater. 1991, 9, 415–428.
- [7] a) S. L. Collignon, R. E. Farncomb, K. L. Wagaman, U.S. Pat.
 861 H 19901204, 1990; b) J. Schmidt, H. Gehlen, Z. Chem.
 1965, 5, 304.
- [8] D. L. Naud, M. A. Hiskey, H. H. Harry, J. Energ. Mater. 2003, 21, 57–62.
- [9] a) L. Y. Lee, M. M. Stinecipher, **1993**, U.S. Pat. 450788; b) D. E. Chavez, B. C. Tappan, B. A. Mason, D. Parrish, *Prop. Explos. Pyrot.* **2009**, *34*, 475–479; c) A. Dippold, T. M. Klapötke, F. A. Martin, *Z. Anorg. Allg. Chem.* **2011**, *637*, 1181–1193.
- [10] Y. V. Serov, M. S. Pevzner, T. P. Kofman, I. V. Tselinskii, J. Org. Chem. USSR (Engl. Transl.) 1990, 26, 773–777.
- [11] L. I. Bagal, M. S. Pevzner, A. N. Frolov, N. I. Sheludyakova, *Chem. Heterocycl. Compd.* **1970**, *6*, 240–244.
- [12] a) G. K. Williams, S. P. Burns, I. B. Mishra, Automotive Systems Laboratory, Inc., patent WO2005035466A2, 2005; b) C. G. Miller, G. K. Williams, Automotive Systems Laboratory, Inc., patent WO2006050442A2, 2006.
- [13] R. N. Shreve, R. K. Charlesworth, Purdue Research Foundation, US 2744116, 1956.
- [14] J. P. Agrawal, Organic Chemistry of Explosives, Wiley-VCH, Weinheim, Germany, 2007.
- [15] a) T. P. Kofman, *Russ. J. Org. Chem.* 2002, 38, 1231–1243; b)
 E. V. Nikitina, G. L. Starova, O. V. Frank-Kamenetskaya, M. S. Pevzner, *Kristallografiya* 1982, 27, 485–488.
- [16] a) A. F. Hollemann, E. Wiberg, N. Wiberg, *Lehrbuch der anor-ganischen Chemie*, de Gruyter, New York, **2007**; b) F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc. Perkin Trans.* 2 **1987**, S1–S19.
- [17] a) M. Hesse, Spektroskopische Methoden in der organischen Chemie, 7th ed., Thieme, Stuttgart, Germany, 2005; b) F. Billes, H. Endredi, G. Keresztury, THEOCHEM 2000, 530, 183–200.
- [18] A. A. Dippold, M. Feller, T. M. Klapötke, Cent. Eur. J. Energ. Mater. 2011, 8, 261–278.
- [19] H. H. Licht, H. Ritter, H. R. Bircher, P. Bigler, Magn. Reson. Chem. 1998, 36, 343–350.
- [20] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Mar-

tin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian G09W*, version 7.0, Gaussian Ltd., Wallingford, CT, **2009**.

- [21] a) J. A. Montgomery Jr., M. J. Frisch, J. W. Ochterski, G. A. Petersson, J. Chem. Phys. 2000, 112, 6532–6542; b) J. W. Ochterski, G. A. Petersson, J. A. Montgomery Jr., J. Chem. Phys. 1996, 104, 2598–2619.
- [22] P. J. Lindstrom, W. G. Mallard, NIST Chemistry Webbook, NIST Standard Reference 69, June 2005, National Institute of Standards and Technology, Gaithersburg, MD (http://webbook.nist.gov).
- [23] a) E. F. C. Byrd, B. M. Rice, J. Phys. Chem. A 2006, 110, 1005–1013;
 b) B. M. Rice, J. J. Hare, J. Phys. Chem. A 2002, 106, 1770–1783;
 c) B. M. Rice, S. V. Pai, J. Hare, Combust. Flame 1999, 118, 445–458.
- [24] a) F. Trouton, *Philos. Mag.* 1884, 18, 54–57; b) M. S. Westwell,
 M. S. Searle, D. J. Wales, D. H. Williams, *J. Am. Chem. Soc.* 1995, 117, 5013–5015.
- [25] a) H. D. B. Jenkins, D. Tudela, L. Glasser, *Inorg. Chem.* 2002, 41, 2364–2367; b) H. D. B. Jenkins, H. K. Roobottom, J. Passmore, L. Glasser, *Inorg. Chem.* 1999, 38, 3609–3620.
- [26] M. Sućeska, EXPLO5.5, Brodarski Inst., Zagreb, Croatia, 2010.
- [27] a) M. Sućeska, *Mater. Sci. Forum* 2004, 465–466; M. Sućeska, *Mater. Sci. Forum* 2004, 325–330; b) M. Suceska, *Prop. Explos. Pyrot.* 1999, 24, 280–285; c) M. Suceska, *Prop. Explos. Pyrot.* 1991, 16, 197–202.
- [28] R. Meyer, J. Köhler, A. Homburg, *Explosives*, 6th ed., Wiley-VCH, Weinheim, 2007.
- [29] R. Wang, H. Xu, Y. Guo, R. Sa, J. M. Shreeve, J. Am. Chem. Soc. 2010, 132, 11904–11905.
- [30] NATO standardization agreement (STANAG) on explosives and impact tests, no. 4489, 1st ed., Sept. 17, 1999.
- [31] WIWEB-Standardarbeitsanweisung 4–5.1.02, Ermittlung der Explosionsgefährlichkeit, hier: der Schlagempfindlichkeit mit dem Fallhammer, Nov. 08, 2002.
- [32] http://www.bam.de.
- [33] NATO standardization agreement (STANAG) on explosives, friction tests, no. 4487, 1st ed., Aug. 22, 2002.
- [34] WIWEB-Standardarbeitsanweisung 4–5.1.03, Ermittlung der Explosionsgefährlichkeit, hier: der Reibempfindlichkeit mit dem Reibeapparat, Nov. 08, 2002.
- [35] NATO standardization agreement (STANAG) on explosives, electrostatic discharge sensitivity tests, no. 4490, 1st ed., Feb. 19, 2001.
- [36] CrysAlis CCD, Oxford Diffraction Ltd., version 1.171.27p5 beta (release 01–04–2005, CrysAlis171.NET).
- [37] CrysAlis RED, Oxford Diffraction Ltd., version 1.171.27p5 beta (release 01–04–2005, CrysAlis171.NET).
- [38] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, J. Appl. Crystallogr. 1993, 26, 343–350.
- [39] G. M. Sheldrick, SHELXS-97, Crystal structure solution, version 97–1, University of Göttingen, Germany, 1990.
- [40] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, Germany, 1997.
- [41] L. Farrugia, J. Appl. Crystallogr. 1999, 32, 837-838.
- [42] A. L. Spek, Platon, A Multipurpose Crystallographic Tool, Utrecht University, The Netherlands, 1999.

Published Online: June 19, 2012

Received: March 5, 2012