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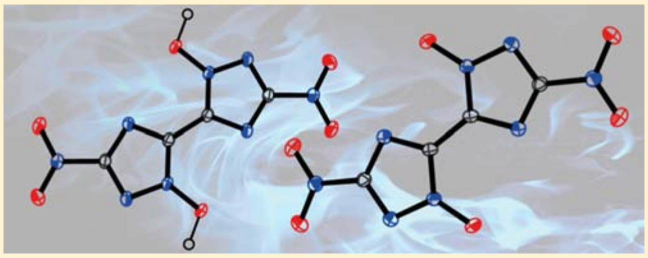
A Study of Dinitro-bis-1,2,4-triazole-1,1′-diol and Derivatives: Design of High-Performance Insensitive Energetic Materials by the Introduction of N-Oxides

Alexander A. Dippold and Thomas M. Klapötke*

Department of Chemistry, Ludwig-Maximilians Universität München, Butenandstr. 5-13, Haus D, 80539 Munich, Germany

Supporting Information



ABSTRACT: In this contribution we report on the synthesis and full structural as well as spectroscopic characterization of 3,3′-dinitro-5,5′-bis-1,2,4-triazole-1,1′-diol and nitrogen-rich salts thereof. The first synthesis and characterization of an energetic 1-hydroxy-bistriazole in excellent yields and high purity is presented. This simple and straightforward method of N-oxide introduction in triazole compounds using commercially available oxone improves the energetic properties and reveals a straightforward synthetic pathway toward novel energetic 1,2,4-triazole derivatives. X-ray crystallographic measurements were performed and deliver insight into structural characteristics and strong intermolecular interactions. The standard enthalpies of formation were calculated for all compounds at the CBS-4 M level of theory, revealing highly positive heats of formation for all compounds. The energetic properties of all compounds (detonation velocity, pressure, etc.) were calculated using the EXPLO5.05 program, and the ionic derivatives show superior performance in comparison to the corresponding compounds bearing no N-oxide. All substances were characterized in terms of sensitivities (impact, friction, electrostatic) and thermal stabilities, and the ionic derivatives were found to be high thermally stable, insensitive compounds that are exceedingly powerful but safe to handle and prepare.

INTRODUCTION

The chemistry of explosives, their development, and application are as old as 220 years BC, when blackpowder was discovered accidentally by the Chinese. Nowadays, not only the application for military purposes is studied but also the utilization of energetic materials for civilian use in mining, construction, demolition, and safety equipment, such as airbags, signal flares, and fire extinguishing systems is extensively studied.[1,2] The academic research mainly focuses on the work with novel energetic systems to determine factors affecting stability and performance and to bring new strategies into the design of energetic materials. The main challenge is the desired combination of a large energy content with a maximum possible chemical stability to ensure safe synthesis and handling. Several strategies for the design of energetic materials that combine the increasing demand for high-performing materials with high thermal and mechanical stabilities have been developed by numerous research groups over the last decades.[2−7]

Traditional energetic materials are based on the oldest strategy in energetic materials design: the presence of fuel and oxidizer in the same molecule. Modern heterocyclic energetic compounds derive their energy not only from the oxidation of their carbon backbone but also additionally from ring or cage strain, high-nitrogen content, and high heats of formation. Intense research is focused on the tailoring of new energetic molecules with performances and stability superior to that of 1,3,5-trinitro-1,3,5-triazinane (RDX). Unfortunately, the synthesis of modern explosives with high performance like 1,3,5,7-tetranitro-1,3,5,7-tetrazocane (HMX) or 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12hexazaiso-wurtzitane (CL-20) is often expensive and includes multiple steps which makes the industrial scale-up and practical use infeasible. Additionally, in many cases high performance and low sensitivity to mechanical stimuli appears to be mutually exclusive. Materials with sufficiently large energy content are often too sensitive to find practical use, and many energetic materials with adequate stability do not possess the performance requirements.

Nitrogen-rich heterocycles are promising compounds that fulfill many requirements in the challenging field of energetic materials research.[6,8−12] A prominent family of novel high-energy density materials (HEDMs) are azole-based compounds, since they are generally highly endothermic with high densities and low sensitivities toward outer stimuli. Owing to the high positive heats of formation resulting from the large number of N−N and C−N bonds[13] and the high level of environmental compatibility, triazole and tetrazole compounds have been studied over the last couple of years with growing interest. Numerous compounds with promising properties as energetic materials arose from the C−C connection of those heterocycles to 5,5′-bistetrazoles[14−18] and 5,5′-bistriazoles.[19−27]

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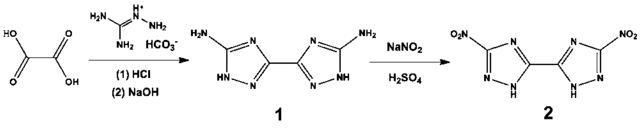
A further way of azole functionalization is the oxidation of the heterocycle to its corresponding N-hydroxy compound. The introduction of N-oxides is a recently reintroduced method using oxidizing agents like trifluoroperacetic acid,[28] potassium peroxomonosulfate (oxone),[29] or hypofluorous acid.[30] The additional oxygen atom generally leads to increased energetic properties due to a higher density and an even greater energy output.[29,31−34] The oxidation of tetrazole compounds has been successfully accomplished recently, resulting in high performance explosives with low sensitivities.[34,35]

Only few examples of the oxidation of 1,2,4-triazoles to 1-hydroxy-1,2,4-triazoles using H_2O_2/phtalic anhydride,[36] 3-chloro-benzenecarboperoxoic acid,[37] or hypofluorous acid[38] resulting in low yields and different isomers are known in literature. The focus of this contribution is on the synthesis of the previously unknown 3,3′-dinitro-5,5′-bis(1,2,4-triazole)-1,1′-diol as well as ionic derivatives thereof. We report on a simple and straightforward method of N-oxide introduction in triazole compounds to improve energetic performance. The compounds were characterized using infrared and Raman as well as multinuclear NMR spectroscopy. Additionally, X-ray crystallographic measurements were performed and deliver insight into structural characteristics as well as intermolecular interactions. The potential application of the synthesized compounds as energetic materials was studied and evaluated using the experimentally obtained values for the thermal decomposition and the sensitivity data as well as the calculated performance characteristics.

■ RESULTS AND DISCUSSION

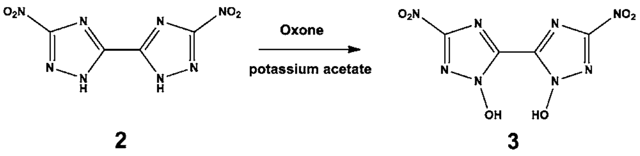
Synthesis. 3,3′-Diamino-5,5′-bis(1*H*-1,2,4-triazole) (**1**) and 3,3′-dinitro-5,5′-bis(1*H*-1,2,4-triazole) (**2**) were synthesized according to literature.[39] The synthesis is based on the reaction of oxalic acid and aminoguanidinium bicarbonate in concentrated hydrochloric acid and subsequent cyclization in basic media. Oxidation of DABT was accomplished by the well-known Sandmeyer reaction via diazotization in sulfuric acid and subsequent reaction with sodium nitrite (Scheme 1).

Scheme 1. Synthesis of 3,3′-Dinitro-5,5′-bis-1*H*-1,2,4-triazole



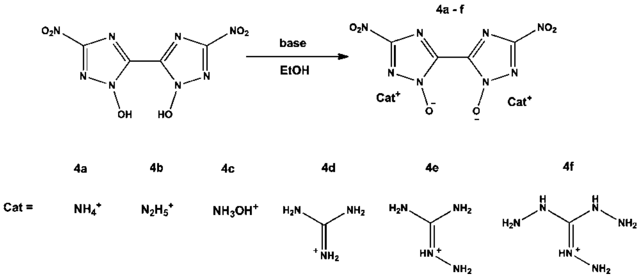
3,3′-Dinitro-5,5′-bis(1*H*-1,2,4-triazole) was successfully oxidized in an buffered aqueous solution of oxone at 40 °C similar to the recently published oxidation of 5-nitro- and 5-azidotetrazole[35,40] (Scheme 2). Best results were obtained with a portionwise addition of oxone and a carefully adjusted pH of 4−5, which leads to the selective oxidation to 3,3′-dinitro-5,5′-bis-1,2,4-triazole-1,1′-diol. The simple and straightforward method of N-oxide introduction in triazole compounds is based on the unique properties of oxone like suitable oxidation potential, moderate costs, simple handling, and sufficient long time stability. Other oxidation agents like organic peracids, perborates, hydrogen peroxide, or hyperfluoric acid are either more expensive or involve a larger effort regarding the whole process.

Scheme 2. Synthesis of 3,3′-Dinitro-5,5′-bis-1,2,4-triazole-1,1′-diol



The formation of the nitrogen-rich salts (**4a−f**) is straightforward. An ethanolic solution of the compound **3** was prepared, and 2 equiv of the corresponding nitrogen-rich base were added (Scheme 3). Due to the high solubility of DNBTO and the low solubility of compounds **4a−f** in ethanol, all ionic derivatives could be isolated in excellent yields and high purity.

Scheme 3. Synthesis of Ionic Derivatives Based on the 3,3′-Dinitro-5,5′-bis-1,2,4-triazole-1,1′-diolate Anion



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

NMR Spectroscopy. All compounds were investigated using ^{1}H, ^{13}C, and ^{14}N NMR spectroscopy. Additionally, ^{15}N NMR spectra were recorded for compounds **3** and **4c**. The two signals of the compounds **2** and **3** differ only slightly in the $^{13}C\{^{1}H\}$ NMR spectrum. One signal for the bridging carbon atom can be observed at 145.6 ppm for DNBT (**2**) and at 134.4 ppm for DNBTO (**3**). The oxidation of the triazole ring leads to a shift of the carbon atom (C-NO_2) signal toward higher field from 162.7 ppm (**2**) to 154.9 ppm for compound **3**. In the $^{14}N\{^{1}H\}$ NMR spectra, the nitro group of compound **3** can be identified by a broad singlet at −27 ppm.

The deprotonation of DNBTO with nitrogen-rich bases shifts the signals in the $^{13}C\{^{1}H\}$ NMR spectra to higher field. The carbon atom connecting both triazole rings can be found in the range of 132.7−133.2 ppm, the one connected to the nitro group is located in the range of 150.7−152.3 ppm. A trend for the shift of the nitro group signal in the $^{14}N\{^{1}H\}$ NMR spectra could not be observed, all signals appeared at chemical shifts of −20 to −33 ppm. The $^{14}N\{^{1}H\}$ NMR spectra of **4a** and **4b** additionally show the signal of the corresponding cation at −359 ppm. The signals of all nitrogen-rich cations in the ^{1}H NMR spectrum could be observed in the expected range.[27,41]

Four well-resolved resonances are detected in the ^{15}N NMR spectra for the four nitrogen atoms of both compounds **3** and **4c** (Figure 1). In addition, the signal of the hydroxylammonium cation could be observed for compound **4c** at −298.7 ppm. The assignments were based on comparison with theoretical

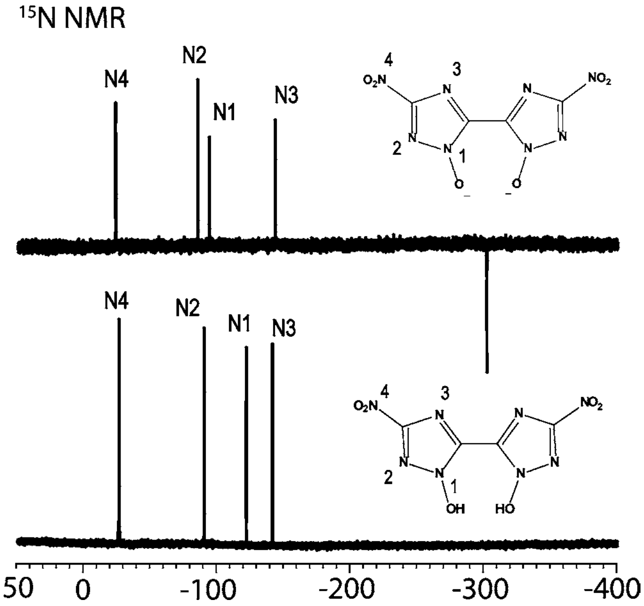


Figure 1. ^{15}N NMR spectra of compounds **3** and **4c** in DMSO-d_6; x-axis represents the chemical shift δ in ppm.

calculations using Gaussian 09 (MPW1PW91/aug-cc-pVDZ).[42] The signals mostly remain unchanged upon oxidation of the triazole ring in comparison to compound **2**.[39] Only the nitrogen atom N1, which is directly connected to the hydroxyl group is shifted toward higher field (−156.1 ppm (**2**), −121.5 ppm (**3**)). As expected, the nitrogen atoms N1 and N2 are shifted to lower field upon deprotonation in compound **4c**. The largest effect can be observed for the nitrogen atom N1, which can now be found at a chemical shift of −95.9 ppm (−121.5 ppm for **3**).

Single Crystal X-ray Structure Analysis. Single crystal X-ray diffraction studies were accomplished for compounds **3** and **4a−f** at 173 K. All compounds were recrystallized from water and show high crystal densities (1.862 g cm^{-3} (**3** × 2 H_2O), 1.696 g cm^{-3} (**4a** × 2 H_2O), 1.841 g cm^{-3} (**4b**), 1.952 g cm^{-3} (**4c**), 1.788 g cm^{-3} (**4d**), 1.764 g cm^{-3} (**4e**), 1.730 g cm^{-3} (**4f** × 2 H_2O)). In the following, the structural properties of compounds **3** and **4c** will be discussed in detail to point out the structural characteristics of N-oxides in comparison to the parent compounds without hydroxy group. Selected crystallographic data of all compounds **4a−f** are compiled in Table S1. A comparison of selected bond length and bond angles of compounds **4a−f** with the values obtained for corresponding compounds bearing no N-oxide[27] is given in Table S3.

The bond lengths of both bistriazolate anions (with and without N-oxide) are comparable within the limits of error in contrast to their bond angles. The average $C_1-N_1-N_2$ angle of the N-oxide anions has an average value of 110.0° as compared to an average value of 106.1° for the N-oxide free 3,3′-dinitro-5,5′-bis-1,2,4-triazolate anion. Both neighboring angles $N_1-C_1-N_3$ (109.8°) and $N_1-N_2-C_2$ (100.8°) are smaller in comparison to the average value of the triazolate anions (113.7° and 103.6°).

This difference is not observed in the case of the corresponding free acids **2** and **3**. Both compounds show comparable values for bond length and bond angles. The $C_1-N_1-N_2$ angle is only slightly elongated from 110.2° (**2**) to 112.1° (**3**) due to the introduction of the N-hydroxy group.

The most striking difference between the N-oxide containing compounds and their parent relatives is observed in their extended structures. Each of the compounds **4a−f** has a higher crystal density (about 0.1 g cm^{-3}) compared to the corresponding N-oxide free compound as a consequence of the N-oxide being involved in multiple intermolecular bonding interactions as exemplified in the case of **4c**.

Hydroxylammonium 3,3′-dinitro-bis-(1,2,4-triazole)-1,1′-diolate **4c** crystallizes in the monoclinic spacegroup $P2_1/c$ with two molecular moieties in the unit cell. The calculated density at 173 K is 1.952 g cm^{-3}, which is notably higher than the corresponding hydroxylammonium salt of compound **2** (1.836 g cm^{-3}).[27] The remarkably high densities can be rationalized in terms of intermolecular interactions, as shown exemplarily for compound **4c** in the following. Each DNBTO^{2-} anion within the crystal structure of **4c** is surrounded by six hydroxylammonium cations via strong hydrogen bonds toward the nitrogen atoms of the triazole (N2, N3) ring and the oxygen O3 of the N-oxide (Figure 2). It is remarkable to note that all accessible hydrogen-bond acceptors in the triazole-N-oxide moiety are connected to the surrounding hydroxylammonium cations. All three contacts are well within the sum of van der Waals radii (r_w (O) + r_w (N) = 3.07 Å, r_w (N) + r_w (N) = 3.20 Å)[43] with a D···A length of 2.575(2), 3.144(2), and 2.874(2) Å (Table 1). The strong network is supported by several short contacts of the nitro group (O1, O2) with the nitrogen N5 of the cations (dashed lines in Figure 3). The O1···N5$^{\text{ii}}$ and O2···N5$^{\text{iv}}$ contact distance are in the range from 2.834(2) to 3.069(2) Å. Additionally, one of the oxygen atoms (O2) of the nitro group is involved in an interaction with the π-electrons of the

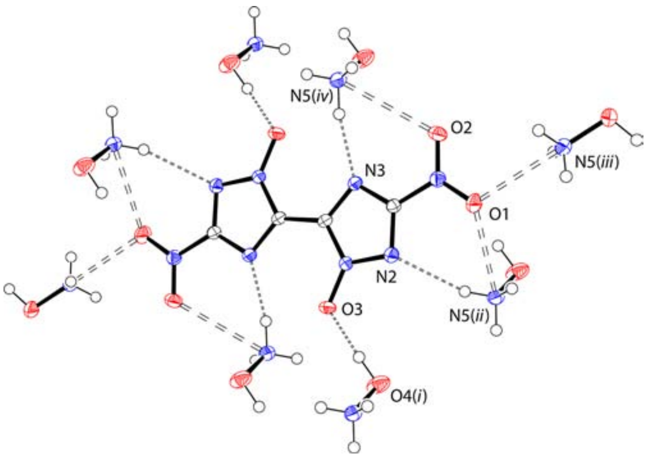


Figure 2. Surrounding of the DNBTO^{2-} anion in the crystal structure of **4c**, hydrogen bonds toward hydroxylammonium cations are marked as dotted lines, and short contacts as dashed lines. Thermal ellipsoids are set to 50% probability. Symmetry operators: (i) 1 + x, y, z; (ii) 1 + x, −1 + y, z; (iii) 1 − x, −1.5 + y, 1/2 − z; (iv) x, −1 + y, z.

Table 1. Hydrogen Bonds Present in 4c[a]

D−H···A	d (D−H) [Å]	d (H···A) [Å]	d (D−H···A) [Å]	∠(D−H···A) [°]
O4$^{\text{i}}$−H4···O3	0.92(2)	1.65(2)	2.575(2)	176(2)
N5$^{\text{ii}}$−H5c···N2	0.86(2)	2.33(2)	3.144(2)	159(2)
N5$^{\text{iv}}$−H5b···N3	0.93(2)	1.96(2)	2.874(2)	169(2)

[a] Symmetry Operators: (i) 1 + x, y, z; (ii) 1 + x, −1 + y, z; (iii) 1 − x, −1.5 + y, 1/2 − z; (iv) x, −1 + y, z.

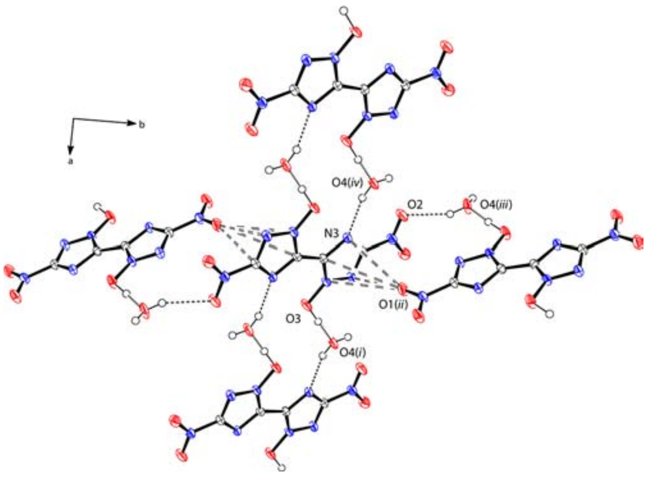


Figure 3. Intermolecular interactions in the crystal structure of **3** (view along *c*-axis), hydrogen bonds are marked as dotted lines, dashed lines indicate the interaction between the oxygen atom O1 of the nitro group and the π-electrons of the triazole (contact distance: 3.041(1) Å [$O1^{ii}\cdots Cg(\pi_{ring})$]). Thermal ellipsoids are set to 50% probability. Symmetry operators: (*i*) $-x$, $1 - y$, $1 - z$; (*ii*) x, $0.5 - y$, $0.5 + z$; (*iii*) x, $0.5 - y$, $0.5 + z$; (*iv*) $-1 - x$, $-y$, $1 - z$.

overlying triazole ring, which leads to a stacking along the *b*-axis.

The structure of the free acid **3** (dihydrate) at 100 K has monoclinic symmetry ($P2_1/c$) with two molecular moieties in the unit cell. The calculated density is 1.883 g cm^{-3}, which is again notably above the density of the dihydrate of compound **2** (1.764 g cm^{-3}).[44] As expected the N1−O3 bond is elongated from 1.30 Å (average value for compounds **4a−f**) to 1.349(2) Å by protonation. The structure is also dominated by several intermolecular interactions such as strong hydrogen bonds (Table 2) and an interaction of the oxygen atom O1 of the nitro group with the π-electrons of the triazole ring (Figure 3).

Table 2. Hydrogen Bonds Present in 3[a]

D−H···A	*d* (D−H) [Å]	*d* (H···A) [Å]	*d* (D−H···A) [Å]	∠(D−H···A) [°]
$O3-H3\cdots O4^{i}$	1.10(2)	1.34(2)	2.439(9)	174(2)
$O4^{iii}-H42\cdots O2$	0.83(3)	2.26(3)	2.949(7)	141(2)
$O4^{iv}-H41\cdots N3$	0.91(3)	2.00(3)	2.890(11)	164(2)

[a] Symmetry Operators: (i) $-x$, $1 - y$, $1 - z$; (ii) x, $0.5 - y$, $0.5 + z$; (iii) x, $0.5 - y$, $0.5 + z$; (iv) $-1 - x$, $-y$, $1 - z$.

Physicochemical Properties: Heat of Formation, Detonation Parameters, And Thermal Stability. The heats of formation of **3** and **4a−f** and RDX have been calculated using the atomization energy method and utilizing experimental data (for further details and results refer to the Supporting Information). All compounds show highly endothermic enthalpies of formation in the range from 98 kJ mol^{-1} (**4d**) to 812 kJ mol^{-1} (**4f**). The enthalpy of formation for compound **3** (290 kJ mol^{-1}) is similar in comparison to the starting material **2** (285 kJ mol^{-1}).[27] To estimate the detonation performances of the prepared compounds, selected key parameters were calculated with EXPLO5 (version 5.05)[45] and compared to RDX. The calculated detonation parameters using experimentally determined densities (gas pycnometry at 25 °C, all compounds were dried before the measurements at 110 °C to remove moisture and crystal water) and above-mentioned heats of formation are summarized in Table 3.

The N-hydroxy compound **3** shows the same sensitivities toward impact and friction and a lower decomposition temperature of 191 °C compared to the starting compound **2** (251 °C),[27] as it is expected for N-hydroxy azoles.[34,35] Since salts of energetic compounds tend to be more stable in comparison to the nonionic parent compound, the nitrogen-rich salts of DNBTO are expected to show an improved stability.

The decomposition temperatures of all ionic compounds are higher than that of compound **3** in the range from 207 °C (**4f**) to 329 °C (**4d**) and similar to the ones of the ionic derivatives of compound **2**.[27] The thermal stability decreases in the row of compounds **4a−c** with the ammonium salt (**4a**) showing the highest value of 257 °C and the hydroxylammonium salt (**4c**) having a decomposition onset at 217 °C. The same trend can be observed for the series of guaninidium derivatives (**4d−f**). The guanidinium salt (**4d**) shows the highest decomposition temperature with 329 °C, followed by the amminoguanidinium salt (**4e**) (246 °C) and the triaminoguanidinium salt (**4f**) with a decomposition onset at 207 °C. In addition, compounds **4a−f** are mostly insensitive toward friction and impact, merely the hydrazinium compound **4b** is sensitive toward outer stimuli (15 J, 324 N).

The detonation velocities were calculated to lie within the range from 8102 m s^{-1} (**4d**) to 9087 m s^{-1} (**4c**). In comparison to the ionic derivatives of compound **2**,[27] a marked performance increase is seen. The detonation velocities increase in the range from 400 to 600 ms^{-1}.The introduction of the N-oxide also positively influences other detonation parameters like the detonation pressure or the energy of explosion, which are also a remarkably increased.

As potential replacements for commonly used secondary explosive, two compounds show the most suitable values regarding the detonation parameters, sensitivities and thermal stability. The best compounds competing with RDX are the triaminoguanidinium (**4f**) as well as the hydroxylammonium salt (**4c**), taking into account the performance values and sensitivities. Compound **4c** displays the best performance with a calculated detonation velocity of 9087 ms^{-1}, a detonation pressure of 390 kbar and a decomposition temperature of 217 °C. The triaminoguanidinium compound exhibits energetic properties in the same range with 8919 m s^{-1}, a detonation pressure of 328 kbar and a decomposition temperature of 207 °C. Both compounds outperform RDX by calculations and show lower sensitivities along with a higher nitrogen content. Especially the hydroxylammonium salt **4c** exhibits sufficient performance requirements and adequate stability in order to find application.

Although lower performance values (ν_{det} = 8102 m s^{-1}, p_{C-J} = 263 kbar) were calculated for the guanidinium salt **4d** in comparison to **4c** and **4f**, this compound displays an excellent decomposition temperature of 329 °C together with an insensitivity toward friction and impact and could therefore be a potential replacement for hexanitrostilbene (HNS).

■ CONCLUSION

In this contribution we reported on the synthesis and full structural as well as spectroscopic characterization of 3,3′-dinitro-5,5′-bis-1,2,4-triazole-1,1′-diol and nitrogen-rich salts thereof. It is possible to oxidize 3,3′-dinitro-5,5′-bis-1*H*-1,2,4-triazole to the corresponding 1,1′-dihydroxy compound under

Table 3. Physicochemical Properties of Compounds 3 and 4a−f in Comparison to Hexogen (RDX)

	(**3**)	NH4(**4a**)	Hy(**4b**)	Hx(**4c**)	G(**4d**)	AG(**4e**)	TAG(**4f**)	RDX[n]
formula	$C_4H_2N_8O_6$	$C_4H_8N_{10}O_6$	$C_4H_{10}N_{12}O_6$	$C_4H_8N_{10}O_8$	$C_6H_{12}N_{14}O_6$	$C_4H_{14}N_{16}O_6$	$C_6H_{18}N_{20}O_6$	$C_3H_6N_6O_6$
molecular mass [g mol^{-1}]	258.1	292.2	322.2	324.2	376.2	406.3	466.3	222.1
impact sensitivity [J][a]	10	>40	15	>40	>40	35	>40	7
friction sensitivity [N][b]	360	360	324	>360	>360	>360	>360	120
ESD test [J]	0.40	0.80	0.15	0.50	0.80	0.24	0.20	–
N [%][c]	43.4	47.9	52.2	43.2	52.1	55.2	60.0	37.8
Ω [%][d]	−18.6	−32.9	−34.8	−19.7	−51.0	−51.2	−51.5	−21.6
$T_{\text{dec.}}$ [°C][e]	191	257	228	217	329	246	207	210
ρ [g cm^{-3}][f]	1.92	1.76	1.80	1.90	1.75	1.72	1.78	1.80
$\Delta_f H_m°$ [kJ mol^{-1}][g]	290	104	413	213	98	339	812	70
$\Delta_f U°$ [kJ kg^{-1}][h]	1201	457	1391	756	366	944	1858	417
EXPLO5 values, V5.05								
$-\Delta_E U°$ [kJ kg^{-1}][i]	5786	4999	5654	5985	4161	4540	5106	6125
T_E [K][j]	4529	3628	3842	4153	3060	3212	3372	4236
p_{C-J} [kbar][k]	362	297	342	390	263	272	328	349
$V_{\text{det.}}$ [m s^{-1}][l]	8729	8388	8915	9087	8102	8268	8919	8748
gas vol. [L kg^{-1}][m]	647	763	795	734	770	790	818	739

[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] Density values are based on gas pycnometer measurements at 25 °C of anhydrous compounds, except **4c**: density derived from X-ray structure measurement at 25 °C. [g] Molar enthalpy of formation (for further details refer to the Supporting Information). [h] Energy of formation. [i] Energy of explosion. [j] Explosion temperature. [k] Detonation pressure. [l] Detonation velocity. [m] Assuming only gaseous products. [n] values based on ref 46 and the EXPLO5.05 database.

mild, aqueous conditions in high yield. The ionic compounds **4a−f** were synthesized by reaction of the neutral compound **3** with the corresponding nitrogen-rich bases. The simple and straightforward method of N-oxide introduction in triazole compounds using commercially available oxone improves the energetic properties and reveals a new synthetic pathway toward novel energetic 1,2,4-triazole derivatives. All compounds were characterized using infrared and Raman as well as multinuclear NMR spectroscopy, and X-ray crystallographic measurements were performed for the first time and deliver insight into structural characteristics and strong intermolecular interactions. The most striking difference between the N-oxide containing compounds **4a−f** and their parent relatives is a higher crystal density (about 0.1 g cm^{-3}) compared to the corresponding N-oxide free compounds as a consequence of the N-oxide being involved in multiple intermolecular bonding interactions as exemplified in the case of **4c**.

The standard enthalpies of formation were calculated for all compounds at the CBS-4 M level of theory, revealing highly positive heats of formation in all cases. The energetic properties (detonation velocity, pressure, etc.) were calculated using the EXPLO5.05 program, all compounds show superior performance in comparison to the corresponding ones bearing no N-oxide. All compounds were characterized in terms of sensitivities (impact, friction, electrostatic) and thermal stabilities. In general, the deprotonation of 3,3′-dinitro-5,5′-bis-1*H*-1,2,4-triazole-1,1′-diol influences the thermal stability as well the sensitivity values positively. Decomposition temperatures range from 207 to 329 °C, indicating the 3,3′-dinitro-5,5′-bis-1*H*-1,2,4-triazole-1,1′-dioxide anion has the ability to form thermally stable energetic materials with appropriate cation pairing. In addition, compounds **4a−f** are mostly insensitive toward friction and impact; merely the hydrazinium compound **4b** is sensitive toward outer stimuli (15 J, 324 N). In summary, the ionic derivatives were found to be high thermally stable, insensitive compounds that are highly powerful but safe to handle and prepare. The most promising compound for industrial scale-up and practical use is the hydroxylammonium salt **4c**, which shows a straightforward synthesis including only four cheap and facile steps. Especially the combination of a exceedingly high performance superior to RDX and insensitivity to mechanical stimuli highlights this compound as potential high explosive, which could find practical use as RDX replacement.

■ EXPERIMENTAL SECTION

Caution: Due to the fact that energetic triazole compounds are to some extend unstable against outer stimuli, proper safety precautions should be taken when handling the materials. Especially dry samples are able to explode under the influence of impact or friction. Lab personnel and the equipment should be properly grounded and protective equipment like grounded shoes, leather coat, Kevlar gloves, ear protection and face shield is recommended for the handling of any energetic material.

All chemical reagents and solvents were obtained from Sigma-Aldrich Inc. or Acros Organics (analytical grade) and were used as supplied without further purification. ^1H, $^{13}C\{^1H\}$, $^{14}N\{^1H\}$, and ^{15}N NMR spectra were recorded on a JEOL Eclipse 400 instrument in DMSO-d_6 at 25 °C. The chemical shifts are given relative to tetramethylsilane (^1H, ^{13}C) or nitro methane (^{14}N, ^{15}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), "weak" (w), and "very weak" (vw). Raman spectra were recorded on 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. Melting and decomposition points were determined by differential scanning calorimetry (Linseis PT 10 DSC, calibrated with standard pure indium and zinc). Measurements were performed at a heating rate of 5 °C min^{-1} in closed aluminum sample pans with a 1 μm hole in the lid for gas release to avoid an unsafe increase in pressure under a nitrogen flow of 20 mL min^{-1} with an empty identical aluminum sample pan as a reference.

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,[47] modified according to WIWeB instruction 4-5.1.02[48] using a BAM[49] drop hammer. The friction sensitivity tests were carried out according to STANAG 4487[50] and modified according to WIWeB instruction 4-5.1.03[51] using the BAM friction tester. The electrostatic sensitivity tests were accomplished according to STANAG 4490[52] using an electric spark testing device ESD 2010 EN (OZM Research).

The single-crystal X-ray diffraction data of **3**, **4a**−**c** were collected using an Oxford Xcalibur3 diffractometer equipped with a Spellman generator (voltage 50 kV, current 40 mA), Enhance molybdenum Kα radiation source (λ = 71.073 pm), Oxford Cryosystems Cryostream cooling unit, four circle kappa platform, and a sapphire CCD detector. Data collection and reduction were performed with CrysAlisPro.[53] The structures were solved with SIR97,[54] refined with SHELXL-97,[55] and checked with PLATON,[56] and all integrated into the WinGX software suite.[57] The finalized CIF files were checked with checkCIF.[58] Intra- and intermolecular contacts were analyzed with Mercury.[59] CCDC 934360 (**3**), 934361 (**4a**), 934362 (**4b**), 934363 (**4c**), 934364 (**4d**), 934365 (**4e**), and 934366 (**4f**) contain 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.

3,3′-Diamino-5,5′-bis(1H-1,2,4-triazole) (**1**) and 3,3′-Dinitro-5,5′-bis(1H-1,2,4-triazole) (**2**) were synthesized according to literature.[39]

3,3′-Dinitro-5,5′-bis-1H-1,2,4-triazole-1,1′-diol (3). 3,3′-Dinitro-5,5′-bis(1*H*-1,2,4-triazole) (5.0 g, 19 mmol) was dissolved in a solution of water (125 mL) and potassium acetate (25.0 g, 0.25 mol) and heated to 40 °C. Oxone (83.0 g, 0.27 mol) was added portion wise within 2 h, and the pH was meanwhile carefully adjusted to 4−5 by dropwise addition of potassium acetate (38.0 g, 0.38 mol) in water (50 mL). The mixture was subsequently stirred at 40 °C for 48 h. The solution was acidified with sulfuric acid (50 wt %, 150 mL) and extracted with ethyl acetate (4 × 100 mL). The combined organic phases were dried over magnesium sulfate, and the solvent was evaporated in vacuum to yield **3** (4.0 g, 16 mmol, 81%) as a colorless solid.

^{1}H NMR (DMSO-d_6): δ (ppm) = 9.01 (s, 2H, *O*H) ppm; ^{13}C NMR (DMSO-d_6): δ (ppm) = 154.9 (*C*-NO$_2$), 134.4 (*C*-C); ^{14}N NMR (DMSO-d_6): δ (ppm) = −27 (*N*O$_2$); ^{15}N NMR (DMSO-d_6): δ (ppm) = −28.4 (N4), −90.7 (N2), −121.5 (N1), −140.6 (N3); IR: ν (cm^{-1}) = 3502(m), 3462(s), 3346(s), 1628(m), 1550(vs), 1461(s), 1407(m), 1346(w), 1314(m), 1232(m), 1177(m), 1041(w), 1006(w), 872(w), 831(m), 803(m), 760(w), 753(w), 732(w), 669(w). Raman (200 mW): ν (cm^{-1}) = 1670(15), 1664(15), 1653(14), 1619(23), 1591(74), 1557(18), 1486(46), 1467(62), 1435(39), 1409(98), 1328(37), 1255(46), 1182(100), 1036(65), 779(10), 767(9), 717(5), 473(3), 458(9), 415(12), 290(4), 271(6), 214(3), 214(3); EA ($C_4H_2N_8O_6$): calcd: C 18.61, H 0.78, N 43.41; found: C 18.77, H 0.94, N 42.13 *m*/*z* (FAB$^-$): 257.0 [$C_4N_8O_6H^-$]. Sensitivities (grain size: <100 μm): BAM friction: 360 N, BAM impact: 10 J, ESD: 0.4 J; DSC (onset, 5 °C min^{-1}): T$_{\text{Dec}}$: 191 °C.

Diammonium 3,3′-dinitro-5,5′-bis-1,2,4-triazole-1,1-diolate (4a). Ammonia (gaseous) was led through a solution of **3** (0.30 g, 1.2 mmol) in ethanol (50 mL) for one minute. The precipitate was collected by filtration to give **4a** (0.29 mg, 1.0 mmol, 83%) as orange powder.

^{1}H NMR (DMSO-d_6): δ (ppm) = 6.93 (s, 8H, N*H*$_4^+$) ppm; ^{13}C NMR (DMSO-d_6): δ (ppm) = 151.1 (*C*-NO$_2$), 132.8 (*C*-C); ^{14}N NMR (DMSO-d_6): δ (ppm) = −26 (*N*O$_2$), −359 (*N*H$_4^+$); IR: ν (cm^{-1}) = 3401(s), 3192(s), 2993(vs), 2877(s), 2132(w), 1680(w), 1640(w), 1530(m), 1445(vs), 1412(vs), 1394(vs), 1387(vs), 1354(s), 1299(s), 1186(s), 1103(vs), 1028(vs), 885(w), 835(m), 764(w), 754(w), 740(m), 680(w), 680(w). Raman (200 mW): ν (cm^{-1}) = 1589(56), 1546(4), 1463(25), 1432(3), 1363(100), 1306(36), 1243(15), 1191(3), 1141(50), 1106(10), 1089(6), 1027(42), 862(2), 782(5), 559(3), 461(2), 442(2). EA ($C_4H_8N_{10}O_4$): calcd: C 16.44, H 2.76, N 47.94; found: C 16.04, H 2.99, N 45.61; *m*/*z* (FAB +): 18 [NH$_4^+$]; *m*/*z* (FAB$^-$): 257.0 [$C_4N_8O_6H^-$]; Sensitivities (grain size: <100 μm): friction: 360 N, impact: 40 J, ESD: 0.8 J; DSC (onset, 5 °C min^{-1}): T_{Dec}: 297 °C.

Dihydrazinium 3,3′-dinitro-5,5′-bis-1,2,4-triazole-1,1-diolate (4b). Compound **3** (0.30 g, 1.2 mmol) was dissolved in ethanol (50 mL), and hydrazine (50 wt % in water, 0.12 mL, 2.4 mmol) was added. The precipitate was collected by filtration to give **4b** (0.33 mg, 1.0 mmol, 86%) as orange powder.

^{1}H NMR (DMSO-d_6): δ (ppm) = 4.64 (s, 6H, N$_2$*H*$_5^+$) ppm; ^{13}C NMR (DMSO-d_6): δ (ppm) = 152.3 (*C*-NO$_2$), 133.2 (*C*-C); ^{14}N NMR (DMSO-d_6): δ (ppm) = −22 (*N*O$_2$), −356 (*N*$_2$H$_5^+$); IR: ν (cm^{-1}) (rel. int.) = 3350(w), 3293(w), 3065(w), 2932(m), 2799(m), 2718(m), 2644(m), 2529(w), 1640(w), 1617(w), 1585(w), 1551(m), 1514(m), 1463(m), 1386(s), 1356(s), 1297(s), 1173(s), 1115(s), 1093(vs), 1037(s), 1023(s), 965(vs), 965(vs), 838(s), 750(s), 680(s). Raman: 1591(15), 1466(9), 1447(4), 1408(3), 1376(100), 1315(15), 1249(14), 1130(10), 1113(22), 1031(15), 868(4), 560(2), 469(1), 453(2), 369(1), 309(4), 293(2), 207(1). EA (C4H10N12O6): calcd: C 14.91, H 3.13, N 52.17; found: C 15.25, H 2.97, N 51.94; *m*/*z* (ESI−) 257.0 [C4N8O6H−]. Sensitivities: (grain size: <100 μm): friction: 324 N, impact: >15 J, ESD: 0.15 J; DSC (onset, 5 °C min−^{1}): T_{Dec}: 228 °C.

Dihydroxylammonium 3,3′-dinitro-5,5′-bis-1,2,4-triazole-1,1-diolate (4c). Compound **3** (0.30 g, 1.2 mmol) was dissolved in ethanol (50 mL) and hydroxylamine (50 wt % in water, 0.12 mL, 2.4 mmol) was added. The precipitate was collected by filtration to give **4c** (0.36 g, 1.1 mmol, 93%) as orange powder.

^{1}H NMR (DMSO-d_6): δ (ppm) = 10.24 (s, 6H, N*H*$_3$OH$^+$) ppm; ^{13}C NMR (DMSO-d_6): δ (ppm) = 152.3 (*C*-NO$_2$), 133.3 (*C*-C); ^{14}N NMR (DMSO-d_6): δ (ppm) = −29 (*N*O$_2$), −359 (*N*H$_3$OH$^+$); ^{15}N NMR (DMSO-d_6): δ (ppm) = −27.4 (N4), −87.4 (N2), −95.9 (N1), −144.0 (N3), −298.7 (*N*H$_3$OH$^+$); IR: ν (cm^{-1}) = 3261(w), 2361(w), 2332(w), 1534(m), 1519(m), 1466(s), 1408(s), 1394(s), 1358(s), 1302(vs), 1171(s), 1035(vs), 1016(s), 837(s), 740(s), 679(m). Raman: ν (cm^{-1}) = 1601(52), 1465(16), 1437(4), 1363(100), 1317(64), 1247(10), 1143(72), 1035(49), 872(9), 790(3), 756(2), 721(2), 565(8), 463(7), 451(3), 343(3), 298(2). EA ($C_4H_8N_{10}O_8$): calcd: C 14.82, H 2.49, N 43.21; found: C 15.11, H 2.37, N 43.27; *m*/*z* (FAB$^+$): 34.0 [NH$_4$O$^+$]; *m*/*z* (FAB$^-$): 256.9 [$C_4N_8O_6H^-$]. Sensitivities: (grain size: <100 μm): friction: 360 N, impact: >40 J, ESD: 0.5 J; DSC (onset, 5 °C min^{-1}): T_{Dec}: 217 °C.

Diguanidinium 3,3′-dinitro-5,5′-bis-1,2,4-triazole-1,1-diolate (4d). Guanidinium carbonate (0.20 g, 1.2 mmol) was added to a solution of compound **3** (0.30 g, 1.2 mmol) in ethanol (50 mL). The mixture was refluxed at 60 °C for 30 min, and the precipitate was collected by filtration to give **4d** (0.31 g, 0.84 mmol, 71%) as orange powder.

^{1}H NMR (DMSO-d_6): δ (ppm) = 7.06 (s, 6H, N*H*$_2$) ppm; ^{13}C NMR (DMSO-d_6): δ (ppm) = 158.1 (*C*-NH$_2$), 151.1 (*C*-NO$_2$), 132.9 (*C*-C); ^{14}N NMR (DMSO-d_6): δ (ppm) = −33 (*N*O$_2$); IR: ν (cm^{-1}) = 3464(m), 3423(m), 3335(m), 3262(m), 3204(m), 3135(m), 2790(m), 2703(m), 2491(w), 2363(m), 2339(m), 1653(vs), 1571(m), 1499(m), 1454(s), 1387(s), 1367(vs), 1299(s), 1151(s), 1043(s), 1028(s), 837(m), 756(s), 756(s), 733(m). Raman: ν (cm^{-1}) = 1588(41), 1502(3), 1455(6), 1431(4), 1369(100), 1314(35), 1245(21), 1136(42), 1029(40), 863(16), 562(2), 542(2), 517(2), 465(4), 449(6), 303(7), 284(5), 236(3). EA ($C_6H_{12}N_{14}O_6$): calcd: C 19.25, H 3.21, N 52.12; found: C 19.30, H 3.09, N 50.85; *m*/*z* (FAB$^+$): 60.1 [CH$_6$N$_3^+$]. *m*/*z* (FAB$^-$): 257.0 [$C_4N_8O_6H^-$]. Sensitivities: (grain size: <100 μm): friction: 360 N, impact: >40 J, ESD: 0.8 J; DSC (onset, 5 °C min^{-1}): T_{Dec}: 329 °C.

Di(aminoguanidinium) 3,3′-dinitro-5,5′-bis-1,2,4-triazole-1,1-diolate (4e). Guanidinium carbonate (0.32 g, 2.3 mmol)) was added to a solution of compound **3** (0.30 g, 1.2 mmol) in ethanol (50 mL). The mixture was refluxed at 60 °C for 30 min, and the precipitate was collected by filtration to give **4e** (0.39 g, 0.96 mmol, 83%) as orange powder.

^{1}H NMR (DMSO-d_6): δ (ppm) = 7.36 (s, 4H, N*H*$_2$), 5.56 (s, 1H, N*H*), 4.61 (s, 2H, N*H*$_2$) ppm; ^{13}C NMR (DMSO-d_6): δ (ppm) = 158.9 (*C*-NH$_2$), 150.9 (*C*-NO$_2$), 132.7 (*C*-C); ^{14}N NMR (DMSO-d_6): δ (ppm) = −22 (*N*O$_2$); IR: ν (cm^{-1}) = 3744(vw), 3449(m), 3413(m), 3372(m), 3345(m), 3183(m), 2700(w), 2496(w), 2370(w), 1675(m), 1647(s), 1627(m), 1520(s), 1464(s), 1380(s), 1355(s), 1298(vs), 1199(w), 1156(s), 1040(m), 1028(s), 920(s), 836(s), 836(s), 748(s), 690(w), 673(w). Raman: ν (cm^{-1}) = 1578(30), 1502(1), 1463(11), 1401(6), 1361(100), 1314(25), 1239(18), 1165(3), 1132(43), 1103(5), 1028(36), 922(6), 859(9), 847(2), 788(2), 559(2), 513(3), 463(5), 340(2), 289(2), 273(4), 236(1), 208(1), 208(1). EA ($C_6H_{14}N_{16}O_6$): calcd: C 17.74, H 3.47, N 55.16; found: C 18.14, H 3.89, N 51.73; m/z (FAB$^+$): 75.0 [$CH_7N_3^+$]; m/z (FAB$^-$): 256.9 [$C_4N_8O_6H^-$]. Sensitivities: (grain size: <100 μm): friction: 360 N, impact: 35 J, ESD: 0.24 J; DSC (onset, 5 °C min^{-1}): T_{Dec}: 246 °C.

Di(triaminoguanidinium) 3,3′-dinitro-5,5′-bis-1,2,4-triazole-1,1-diolate (4f). Triaminoguanidine (0.24 g, 2.3 mmol)) was added to a solution of compound **3** (0.30 g, 1.2 mmol) in ethanol (50 mL). The mixture was stirred for 30 min, and the precipitate was collected by filtration to give **4f** (0.42 g, 0.95 mmol, 79%) as orange powder.

^{1}H NMR (DMSO-d_6): δ (ppm) = 8.58 (s, 3H, N*H*), 4.46 (s, 6H, N*H*$_2$) ppm; ^{13}C NMR (DMSO-d_6): δ (ppm) = 159.1 (*C*-NH$_2$), 150.7 (*C*-NO$_2$), 132.9 (*C*-*C*); ^{14}N NMR (DMSO-d_6): δ (ppm) = −20 (*N*O$_2$); IR: ν (cm^{-1}) = 3743(vw), 3627(w), 3341(m), 3180(m), 2918(w), 2849(w), 2362(w), 1675(s), 1652(s), 1539(w), 1510(m), 1456(s), 1379(s), 1340(s), 1293(vs), 1190(w), 1129(vs), 1034(m), 1020(s), 989(m), 953(m), 921(s), 834(m), 834(m), 752(s), 693(w), 678(w). Raman: ν (cm^{-1}) = 3372(2), 1683(3), 1589(100), 1521(2), 1499(3), 1455(26), 1426(15), 1399(14), 1376(75), 1348(61), 1308(71), 1247(48), 1203(5), 1112(71), 1013(94), 860(28), 847(3), 791(3), 750(2), 555(8), 463(11), 305(3), 287(3), 287(3), 257(1), 226(2). EA ($C_6H_{18}N_{20}O_6$): calcd: C 15.45, H 3.89, N 60.07; found: C 15.32, H 3.96, N 57.12; m/z (FAB$^+$): 105.1 [$CH_9N_6^+$]; m/z (FAB$^-$): 257.0 [$C_4N_8O_6H^-$]. Sensitivities: (grain size: <100 μm): friction: 360 N, impact: 40 J, ESD: 0.2 J; DSC (onset, 5 °C min^{-1}): T_{Dec}: 207 °C.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic files for all compounds, selected bond length and angles as well as the methodology and details for the heats of formation calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

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

Notes

The authors declare no competing financial interest.

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