

Thermally Stable 3,6-Disubstituted 1,2,4,5-Tetrazines

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Z. Naturforsch. **2013**, *68b*, 1310–1320 / DOI: 10.5560/ZNB.2013-3237

Received September 2, 2013

Several 3,6-disubstituted 1,2,4,5-tetrazines were synthesized by nucleophilic substitution using 3,6-bis-(3,5-dimethyl-pyrazol-1-yl)-1,2,4,5-tetrazine and 3,6-dichloro-1,2,4,5-tetrazine as electrophiles. All new compounds were characterized by ^1H NMR, ^{13}C NMR and vibrational spectroscopy, mass spectrometry and elemental analysis (C,H,N). For analysis of the thermostability, differential scanning calorimetry (DSC) was used. Especially, the symmetrically bis-3,5-diamino-1,2,4-triazolyl-substituted derivative shows a very high thermal stability up to 370 °C. Therefore its energetic properties were determined and compared with those of hexanitrostilbene (HNS). The crystal structures of 3,6-bishydrazino-1,2,4,5-tetrazine, 3,6-dichloro-1,2,4,5-tetrazine and 3-amino-6-(3,5-diamino-1,2,4-triazol-1-yl)-1,2,4,5-tetrazine dihydrate have been determined by low-temperature X-ray diffraction.

Key words: Tetrazines, Energetic Materials, Crystal Structures

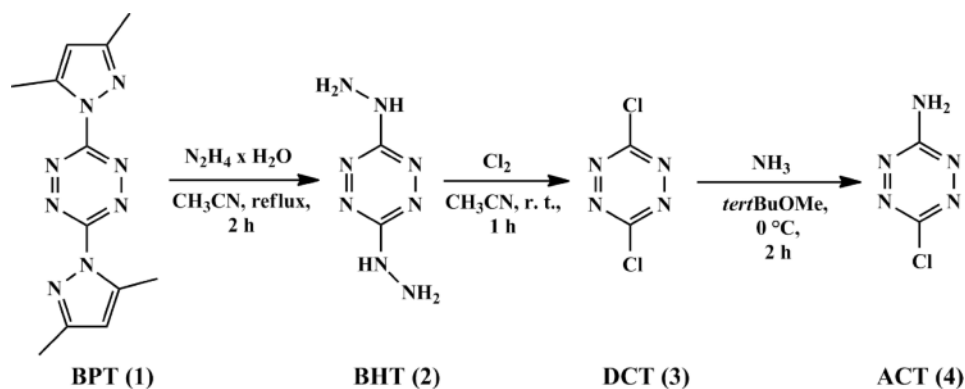
Introduction

1,2,4,5-Tetrazines, also known as *s*-tetrazines, have been first synthesized by Pinner in 1893 [1]. They have attracted attention of scientists in various fields of research: theoretical chemistry [2], coordination chemistry [3], pharmaceutical chemistry [4], and natural products chemistry [5] amongst others. Research for special applications of this compound class includes anti-corrosion agents [6] and sensors [7, 8]. A detailed review of the recent advantages and applications of *s*-tetrazine chemistry in general is given by Saracoglu *et al.* [9]. The properties of *s*-tetrazines are directly related to their electronic structure. Waluk *et al.* [10] have provided a simple model for the qualitative MO analysis of *s*-tetrazines.

A further interesting field of research are the energetic properties of 1,2,4,5-tetrazines, namely for secondary explosives, propellants and low smoke pyrotechnical fuels. Especially gun powder mixtures benefit from nitrogen-rich compounds. To get rid of the widely known problems of barrel corrosion in gun and rocket propellant systems, thermally stable compounds with low carbon and high nitrogen content are of great interest [11, 12]. The main contributors

to the chemistry of energetic *s*-tetrazines have been Chavez and Hiskey from the Los Alamos National Laboratory in New Mexico, USA [13–16]. Thermally stable secondary explosives are widely needed for special applications such as drilling deep oil-wells and space exploration. The research on heat-resistant explosives was reviewed *e. g.* by Urbanski and Vasudeva [17], Agrawal [18] and Sikder [19]. The state of the art reference in these applications is hexanitrostilbene (HNS), which is easily synthesized by oxidation of 2,4,6-trinitro-toluene (TNT) and is stable up to 318 °C.

In the work reported herein, further nitrogen-rich substituted 1,2,4,5-tetrazines were investigated. Especially the 3,6-bis-(3,5-diamino-triazol-1-yl)-1,2,4,5-tetrazine derivative (**8**) is of great interest because of its high thermostability and high weight percentage of nitrogen content. The detonation parameters of **8** were determined using the EXPLO5 V.5.05 and V6.01 computer code and compared with those calculated for HNS. Crystal structures of 3,6-bishydrazino-1,2,4,5-tetrazine (**2**), 3,6-dichloro-1,2,4,5-tetrazine (**3**) and 3-amino-6-(3,5-diamino-1,2,4-triazol-1-yl)-1,2,4,5-tetrazine (**9**) were determined by low-temperature X-ray diffraction.

Scheme 1. Known syntheses of 1,2,4,5-tetrazines **1–4**.

Results and Discussion

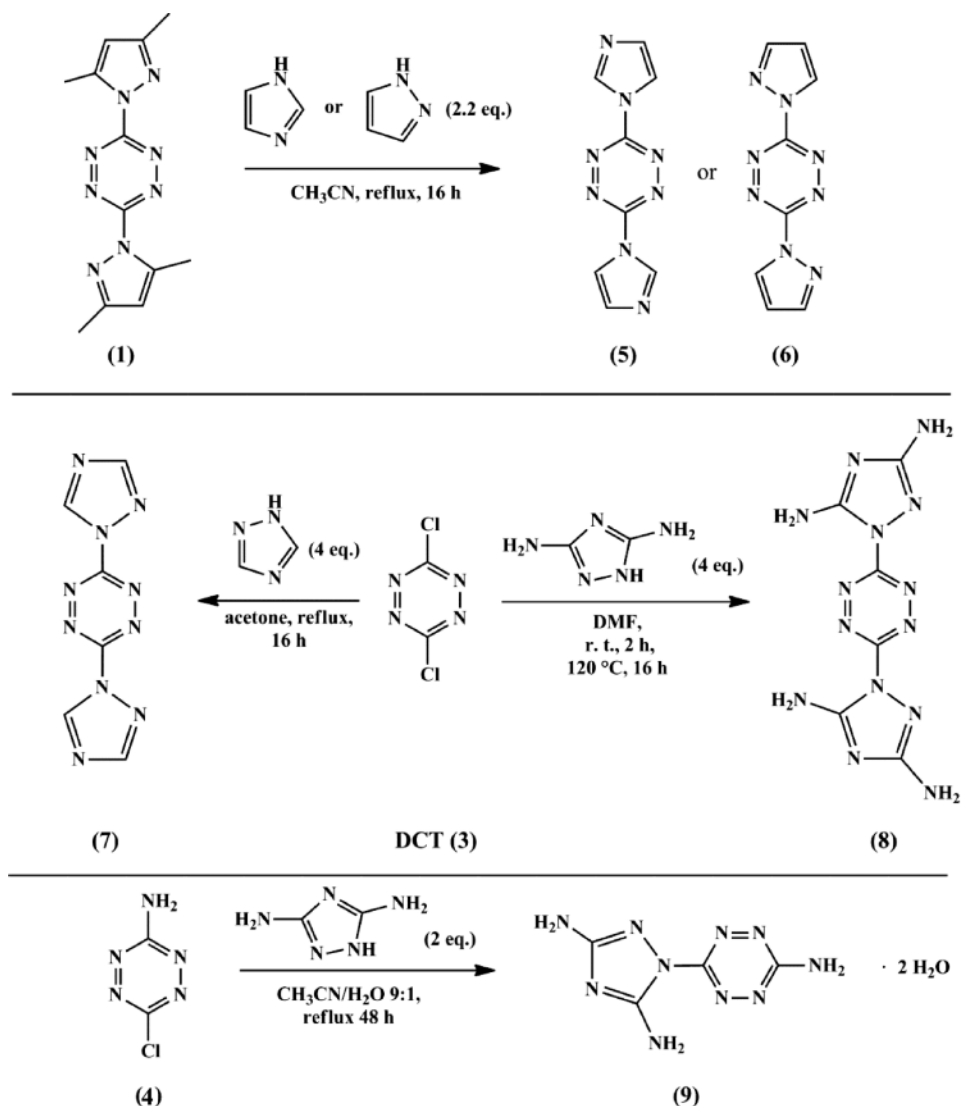
Syntheses

Scheme 1 illustrates already known syntheses of the commonly used 1,2,4,5-tetrazines, on which nucleophilic substitution reactions were carried out [13–16].

After preparing these four precursors (**1–4**), as described in the literature, we tested nucleophilic substitutions using imidazole, pyrazole, triazole, and 3,5-diamino-triazole. Compound **3** is not long-time stable on air. However, solutions in acetonitrile (0.6 M) proved to be stable at 4 °C for about one month. The purity of this solution was established by ¹³C NMR in CDCl₃, in which only one signal at 168.4 ppm of (**3**)

Table 1. Crystallographic data of compounds **2**, **3** and **9**.

	2	3	9 ·2 H ₂ O
Formula	C ₂ H ₆ N ₈	C ₂ Cl ₂ N ₄	C ₄ H ₁₀ N ₁₀ O ₂
<i>M_r</i> , g mol ^{−1}	142.15	150.95	230.19
Crystal system	monoclinic	orthorhombic	orthorhombic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>Pbca</i>	<i>Pbca</i>
Color, habitus	red block	orange block	red needle
Crystal size, mm ³	0.2 × 0.1 × 0.05	0.19 × 0.22 × 0.23	0.14 × 0.18 × 0.30
<i>a</i> , Å	4.0439(6)	6.4884(7)	16.175(3)
<i>b</i> , Å	5.6448(7)	5.6381(7)	6.6357(15)
<i>c</i> , Å	12.129(2)	14.0048(14)	17.625(3)
β, deg	99.124(15)	90.0	90.0
<i>V</i> , Å ³	272.91(7)	512.33(10)	1891.8(7)
<i>Z</i>	2	4	8
ρ _{calcd.} , g cm ^{−3}	1.73	1.96	1.62
μ (MoK _α), mm ^{−1}	0.1	1.1	0.1
<i>F</i> (000), e	148	296	960
λ (MoK _α), Å	0.71073	0.71073	0.71073
<i>T</i> , K	173	173	173
θ (min. / max.), deg	4.95 / 33.34	4.28 / 26.00	4.43 / 26.00
<i>hkl</i> range	−5 : 5; −7 : 6; −15 : 10	−8 : 7; −6 : 6; −9 : 17	−18 : 19; −8 : 8; −19 : 21
Absorption correction	multi-scan	multi-scan	multi-scan
Reflections collected	1459	2336	8937
Independent refl. / <i>R</i> _{int}	594 / 0.068	501 / 0.037	1851 / 0.066
Observed reflections	390	361	1327
Ref. parameters	59	37	185
<i>R</i> ₁ (obs.) / <i>wR</i> ₂ (all data)	0.0435 / 0.1038	0.0259 / 0.0627	0.0717 / 0.1013
<i>S</i>	0.887	0.881	1.033
Resd. dens. (min. / max.), e Å ^{−3}	−0.24 / 0.28	−0.12 / 0.24	−0.24 / 0.20



Scheme 2. Nucleophilic substitutions on 1,2,4,5-tetrazine precursors.

and those of acetonitrile (1.9 and 117.6 ppm) occurred. The investigated substitution reactions are illustrated in Scheme 2.

The reaction of **1** with imidazole yielded **5**, as carried out already by Russian researchers [20]. Pyrazole has not been used yet, so we successfully obtained **6** using the same reaction conditions. Remarkably, no reaction occurred when triazole was used as the nucleophile in this reaction. In contrast to this result, when **3** is used as electrophile, the yield of compound **7** is about 80%. For this reaction the choice of

the solvent is important. If only acetonitrile is used, no reaction occurs at all. Therefore an excess of acetone (10 : 1) was used in this reaction. All three compounds **5**, **6** and **7** precipitated during the reaction as fine orange powders. To enhance the thermostability of these symmetrically 3,6-disubstituted 1,2,4,5-tetrazine derivatives we also repeated the reaction with 3,5-diamino-1,2,4-triazole as nucleophile. Using **1** as electrophile only the mono-substituted product was obtained, which is not interesting for our applications, because of its high carbon content. The reactivity of

1,2,4,5-tetrazines in this type of processes was investigated comprehensively by Hungarian researchers in 2003 [21]. The reaction of **3** with 3,5-diamino-1,2,4-triazole results only in the disubstituted product **8**. We also tried the reaction of 3,5-diamino-triazole with 3-amino-6-chloro-tetrazine (**4**) as electrophile. This reaction gave compound **9** in 72% yield. We always used four equivalents of the nucleophile, if **3** was used as electrophile. Chavez *et al.* already have described that the reaction of **3** with four equivalents 3-azido-1,2,4-

triazolium hydrochloride as a side product. That means that two molecules HCl are intercepted by the nucleophile [22]. This hydrochloride species of the used nucleophile also precipitated in the reaction but could be removed by washing the crude compound with an excess of water. We also used more electron-deficient nucleophiles like 3-nitro-1,2,4-triazole, 3,5-dinitro-1,2,4-triazole and 5-nitro-tetrazole, but none of these reacted with 1,2,4,5-tetrazines as electrophiles. The crystal structures of compounds **2**, **3** and **9** were determined by low-temperature X-ray diffraction.

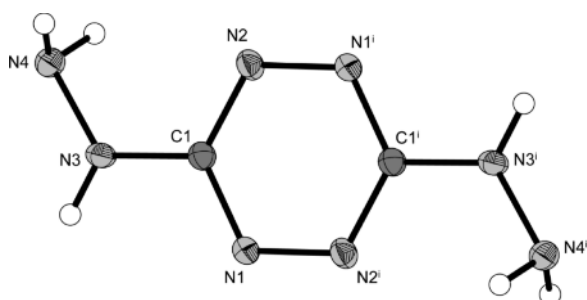


Fig. 1. Molecular unit of **2**. The non-hydrogen atoms are represented by displacement ellipsoids at the 50% probability level. Selected bond lengths (Å): N1–N2ⁱ 1.328(2), C1–N1 1.352(3), C1–N2 1.344(2), C1–N3 1.355(3), N3–N4 1.418(2); selected bond angles (deg): N2ⁱ–N1–C1 117.3(2), N1–C1–N3 116.2(2), N1–C1–N2 124.9(2), C1–N3–N4 121.9(2). Symmetry code: (i) 2 – x, 2 – y, –z.

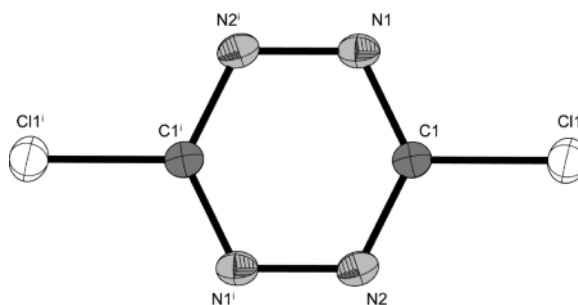
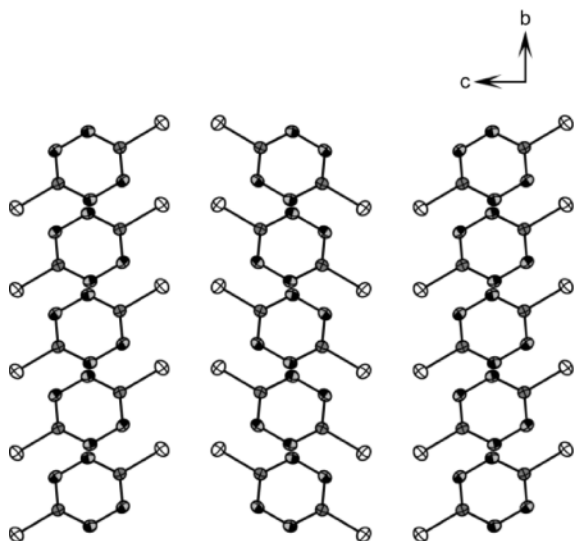


Fig. 2. Molecular unit of **3** showing the labeling scheme. Non-hydrogen atoms are represented by displacement ellipsoids at the 50% probability level. Selected bond lengths (Å): Cl1–C1 1.702(2), N1–N2ⁱ 1.324(2), N1–C1 1.327(3), N2–C1 1.332(2); selected bond angles (deg): N1ⁱ–N2–C1 116.4(2), N1–C1–N2 127.4(2), N1–C1–Cl1 116.3(2), N2–C1–Cl1 116.3(2). Symmetry code: (i) 1 – x, 1 – y, –z.

(a)



(b)

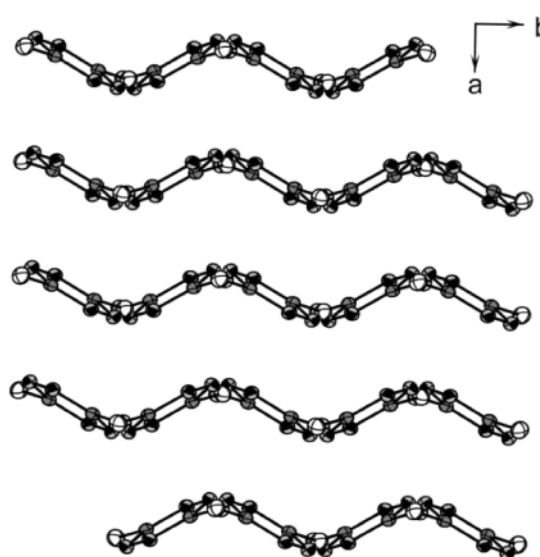


Fig. 3. View of the crystal structures of **3**, A) along the crystallographic *a* axis and B) along the *c* axis.

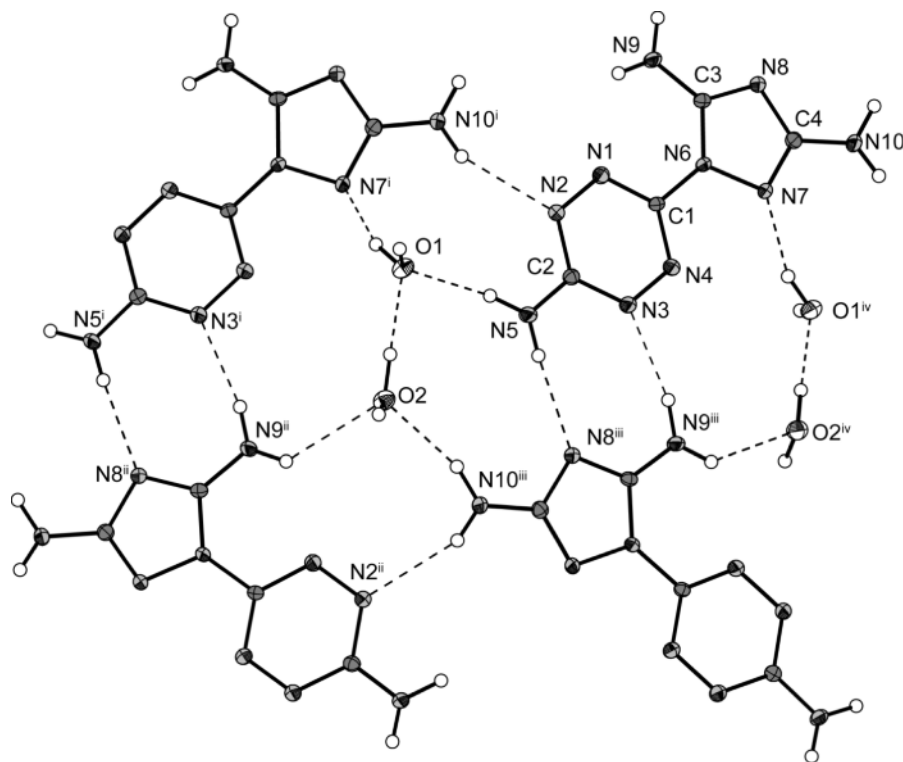


Fig. 4. Intermolecular hydrogen bond interactions in the solid state of **9**. Symmetry codes: (i) $x, 0.5 - y, 0.5 + z$; (ii) $-0.5 + x, y, 0.5 - z$; (iii) $-0.5 + x, 0.5 - y, 1 - z$; (iv) $x, 0.5 - y, 0.5 + z$.

Crystal and molecular structures

Single crystals suitable for XRD were obtained of **2**, **3** and **9**. Selected data and parameters from the low-temperature (173 K) X-ray data collection and refinements are given in Table 1. Further information regarding the crystal structure determinations have been deposited with the Cambridge Crystallographic Data Centre [23].

Single crystals of **2** in the form of small red blocks were grown from an acetonitrile/water mixture. The compound crystallizes in the monoclinic space group $P2_1/c$ with 2 formula units per unit cell and a density of 1.73 g cm^{-3} . Figure 1 shows the molecular unit with its center of inversion in the middle of the tetrazine moiety. The packing of the molecules is directed by three N–H hydrogen bonds involving all of the hydrogen atoms of the hydrazine groups, the strongest being observed between N3 and N4ⁱⁱ (N3–H3...N4ⁱⁱ, 0.88(3), 2.12(3), 2.980(2) Å, 165.3(19)°; (ii) $1 - x, 0.5 + y, 0.5 - z$.)

Single crystals of **3** were obtained by slow evaporation of a 0.6 M solution in acetonitrile. **3** crystallizes

in the orthorhombic space group $Pbca$ with 4 formula units per unit cell and a high density of 1.96 g cm^{-3} at a temperature of 173 K. Again the molecular unit, which is shown in Fig. 2, features a center of inversion.

Molecules of **3** are stacked in alternating AB layers (Fig. 3A). In these layers A and B the molecules have different orientations. Figure 3B shows a larger section of the wave-like layer structure along the c axis. The distance between two molecules lying above each other along the a axis is 6.488(3) Å.

Single crystals of the dihydrate of **9** suitable for XRD were obtained from water. After a concentrated solution was cooled to 4 °C, red needles slowly started to crystallize. Compound **9** crystallizes in the orthorhombic space group $Pbca$ with 8 formula units in the unit cell and a density of 1.62 g cm^{-3} (at 173 K). Figure 4 shows an excerpt of four molecules of **9** with respect to the intermolecular hydrogen bond interactions. The corresponding data are presented in Table 2. Combinations of all common (N–H...N, N–H...O, O–H...N and O–H...O) hydrogen donor-acceptor interactions can be observed. Either the amino groups of the triazole and the

Table 2. Hydrogen bond interactions in compound **9**^a.

D–H...A	<i>d</i> (D–H) (Å)	<i>d</i> (H...A) (Å)	<i>d</i> (D...A) (Å)	∠(D–H...A) (deg)
N10 ⁱ –H10B ⁱ ...N2	0.87(3)	2.28(3)	3.085(3)	154.(2)
N5–H5B...N8 ⁱⁱⁱ	0.87(3)	2.17(3)	3.039(3)	175.(2)
O1–H1A...N7 ⁱ	0.90(4)	1.97(4)	2.832(2)	162.(3)
N10 ⁱⁱⁱ –H10A ⁱⁱⁱ ...O2	0.92(2)	2.02(2)	2.909(3)	162.(2)
N9 ⁱⁱⁱ –H9A ⁱⁱⁱ ...N3	0.92(3)	2.13(3)	3.036(3)	167.(2)
N5–H5A...O1	0.94(3)	2.03(3)	2.969(3)	172.(2)
N9–H9A...N1	0.84(3)	2.25(3)	2.828(3)	126.(2)
N9 ⁱⁱ –H9B ⁱⁱ ...O2	0.84(3)	2.51(3)	3.136(3)	132.(2)
O2–H2A...O1	0.95(4)	1.80(4)	2.741(3)	171.(3)

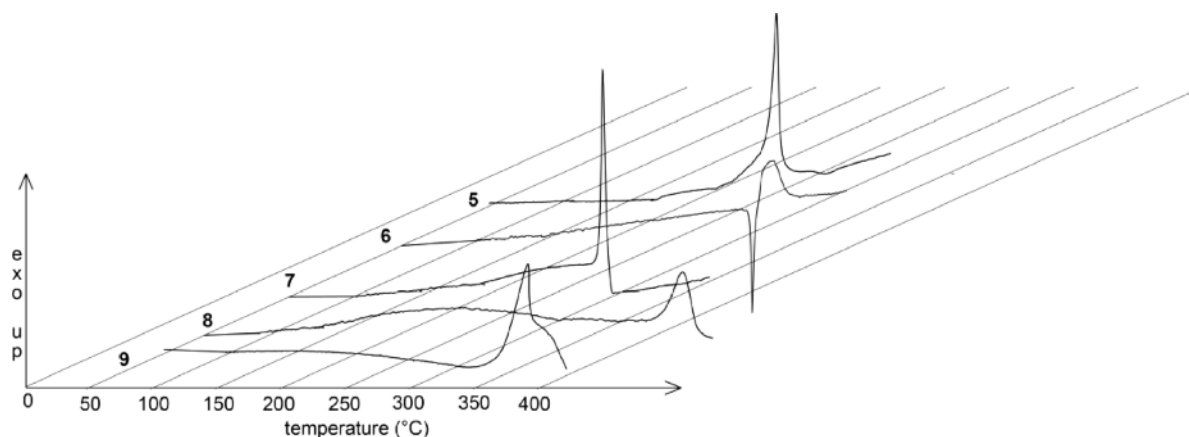
^a Symmetry codes: (i) $x, 0.5 - y, 0.5 + z$; (ii) $-0.5 + x, y, 0.5 - z$; (iii) $-0.5 + x, 0.5 - y, 1 - z$.

tetrazine, or the nitrogen atoms of the rings participate in the hydrogen bonding network. In total a wave-like layer structure of the tetrazine molecules is formed. Between the layers of molecules, the water molecules form strong hydrogen bonds, between themselves and the triazole moieties, stabilizing the structure.

Energetic properties and thermostability

Fig. 5 shows the curves of the differential scanning calorimetry (DSC) measurements of compounds **5–9** with a heating rate of 5 K min^{−1}. In Table 3

the decomposition temperatures are listed in °C. The 1*H*-triazole substituted 1,2,4,5-tetrazine (**7**) is about 45 °C more stable than the imidazole derivative **5**. Compound **6** is the only one which decomposes after melting. A significant increase in thermostability can be accomplished by using 3,5-diamino-1,2,4-triazole as substituent. Both compounds **8** and **9** show a significant increase in thermo-stability in comparison to all other investigated compounds. Compound **9** is the thermally most stable 1,2,4,5-tetrazine derivative known in the literature. In comparison to the 3,6-bis-(3-amino-5-nitro)-1,2,4,5-tetrazine, synthesized by

Fig. 5. DSC curves of compounds **5–9**.

Compound	<i>T</i> _{dec.} °C) ^a
3,6-Bis-(1,3-imidazol-1-yl)-1,2,4,5-tetrazine (5)	200
3,6-Bis-(1,2-pyrazol-1-yl)-1,2,4,5-tetrazine (6)	260
3,6-Bis-(1,2,4-triazol-1-yl)-1,2,4,5-tetrazine (7)	245
3,6-Bis-(3,5-diamino-1,2,4-triazol-1-yl)-1,2,4,5-tetrazine (8)	370
3-Amino-6-(3,5-diamino-1,2,4-triazol-1-yl)-1,2,4,5-tetrazine (9)	314

^a Onset decomposition temperature at a heating rate of $\beta = 5$ K min^{−1}.

Table 3. Thermostability data of compounds **5–9**.

	8	HNS
Formula	C ₄ H ₈ N ₁₄	C ₁₄ H ₆ N ₆ O ₁₂
M_r	276.24	450.24
IS, J^a	> 40	5
FS, N^b	> 360	> 360
ESD, J^c	> 1	0.3
$N, \%^d$	70.99	18.67
$\Omega, \%^e$	−92.70	−67.52
$T_{Dec.}, ^\circ C^f$	370	318
$\rho, g\ cm^{-3}$	1.75 ^g	1.74
$\Delta_f H_m^\circ, kJ\ mol^{-1h}$	707.5	78.3
$\Delta_f U^\circ, kJ\ kg^{-1i}$	2659.4	240.6
EXPLO5 5.05 and 6.01 values		
$-\Delta_{Ex} U^\circ, kJ\ kg^{-1j}$	3039(3052)	5474(5143)
$T_{Det.}, K^k$	2382(2237)	3982(3681)
$P_{CJ}, kbar^l$	227(225)	242(244)
$V_{Det.}, m\ s^{-1m}$	7733(8035)	7446(7612)
$V_o, L\ kg^{-1n}$	680(740)	530(602)

Table 4. Energetic properties of compound **8** in comparison to HNS.

^a Impact sensitivity (BAM drophammer, 1 of 6); ^b friction sensitivity (BAM friction tester 1 of 6); ^c electrostatic discharge device; ^d nitrogen content; ^e oxygen balance; ^f decomposition temperature from DSC ($\beta = 5^\circ C\ min^{-1}$); ^g from pycnometric measurements at 25 °C and 1 bar; ^h calculated heat of formation; ⁱ energy of formation; ^j energy of explosion; ^k explosion temperature; ^l detonation pressure; ^m detonation velocity; ⁿ assuming only gaseous products.

Coburn *et al.* in 1991, **8** is more stable by about 109 °C [24].

Because of the high decomposition temperature of **8** we calculated the enthalpy ($\Delta_f H^\circ$) and energy of formation ($\Delta_f U^\circ$) using the CBS-4M method. Gas phase heats of formation [$\Delta_f H^\circ(g, M)$] were calculated with the atomization method using CBS-4M enthalpies (computed by GAUSSIAN09W.A.02) [25–30]. The gas phase enthalpies of formation $\Delta H_m(g)$ were converted into the solid-state enthalpies of formation [$\Delta H_m(s)$] by using the Trouton rule [31, 32].

From these values it is possible to calculate the detonation parameters of compound **8** in comparison to HNS, using EXPLO5 V.5.05 and the most recent version V.6.01 [33–35]. For this calculation the density of compound **8** ($\rho = 1.75\ g\ cm^{-3}$) was obtained by pycnometric density measurements. An overview of the energetic properties of compound **8** in comparison to HNS is given in Table 4.

As can be seen from Table 4 compound **8** has a much higher heat of formation than HNS. This is related to the high content of endothermic N–N and C–N single and double bonds. HNS, however, consists of six exothermic nitro groups and two aromatic benzene moieties. The densities of **8** and HNS are in the same range. Whereas the two compounds are insensitive towards friction, HNS decomposes in the BAM drophammer test when impact energies larger than

5 Joules are used. Tetrazine **8** is insensitive towards impact stimulus. Regarding the detonation parameters one can assume that HNS is superior relating to the explosion energy ($-\Delta_{Ex} U^\circ$). The most significant values for secondary explosives are the detonation pressure (P_{CJ}), the detonation velocity ($V_{Det.}$), the thermostability ($T_{Dec.}$) and the sensitivities towards external stimuli, as described above. Regarding $V_{Det.}$, P_{CJ} and $T_{Dec.}$, one can assume that compound **8** is superior to HNS.

Low combustion temperatures ($T_{comb.}$) and a high N₂/CO ratio in the combustion gases are desirable in order to reduce gun barrel erosion problems caused by the formation of iron carbide [36]. State of the art gun propellants are nitrocellulose, mixtures of nitrocellulose and nitroguanidine, and nitroglycerine. Nitrocellulose (12 % nitrogen content) has a combustion temperature of 2310 K but a high content of carbon, what accelerates the wear of gun barrels. Compound **8** has a nitrogen content of 71 % but does not burn completely without residue in the flame. Compound **8** can be used as additive in mixtures with nitroguanidine or nitroglycerine to enhance the nitrogen content of the whole composition.

Small-scale reactivity test (SSRT)

The SSRT of compound **8** was carried out in comparison to HNS. A defined volume (HNS: 470 mg,

density: 1.74 g cm^{-3} , **8**: 473 mg, density: 1.75 g cm^{-3}) was pressed into a perforated steel block [37]. This was topped with a commercially available detonator (Orica, DYNADET-C2-0ms). Initiation of the tested explosive resulted in denting a separate aluminum block, which was placed right underneath the steel block. The volume of the dent was then filled with sand to compare the performance of HNS and **8**. The test showed that HNS is superior and the dent could be filled with 672 mg sand in comparison to **8** where only a very small dent was detected, which is caused by the used detonator. The non-initiation of compound **8** could be explained by the assumption that the critical diameter, which could not be determined at the time, is too high.

Conclusion

- The crystal structures of 3,6-bis-hydrazino-1,2,4,5-tetrazine, 3,6-dichloro-1,2,4,5-tetrazine and 3-amino-6-(3,5-diamino-1,2,4-triazol-1-yl)-1,2,4,5-tetrazine could be determined by low-temperature X-ray diffraction.
- The disubstituted products, using imidazole, pyrazole and 1,2,4-triazole as nucleophiles, could be synthesized in high yields.
- Synthesizing 3,6-bis-(1,2,4-triazol-1-yl)-1,2,4,5-tetrazine (**7**) requires different solvent combinations and 3,6-dichloro-1,2,4,5-tetrazine as a strong electrophile in comparison to compounds **5** and **6**, which are accessible using 3,6-bis(3,5-dimethyl-pyrazol-1-yl)-1,2,4,5-tetrazine as electrophile.
- When 3,5-diamino-1,2,4-triazole is used as nucleophile the resulting products **8** and **9** show very high thermal stability.
- Compound **8** appears to be the thermally most stable 1,2,4,5-tetrazine compound known in the literature so far.
- Compound **8** could not be initiated in a SSRT setup. A potential explanation could be the fixed diameter of the test setup (predefined volume), which was possibly below the critical diameter of **8**.

Experimental Section

General procedures

The single-crystal X-ray diffraction data were collected using an Oxford Xcalibur3 diffractometer with a Spellman generator (voltage 50 kV, current 40 mA) and a KappaCCD

detector. The data collections were undertaken using the CRYSLIS CCD software [38], and the data reductions were performed with the CRYSLIS RED software [39]. The structures were solved with SIR-92 [40], refined with SHELXL-97 [41] and finally checked using PLATON [42]. In all structures the hydrogen atoms were located and refined. The absorption was corrected using the SCALE3 ABSPACK multi-scan method [43].

Raman spectra were recorded with a Bruker Multi-RAM FT-Raman instrument fitted with a liquid nitrogen cooled germanium detector and a Nd:YAG laser ($\lambda = 1064 \text{ nm}$). Infrared spectra were measured with a Perkin-Elmer Spectrum BX-FTIR spectrometer equipped with a Smiths DuraSamplIR II ATR device. All spectra were recorded at ambient temperature, the samples were solids. NMR spectra were recorded at 25°C with a Jeol Eclipse 400 ECX instrument, and chemical shifts were determined with respect to external Me_4Si (^1H , 400.2 MHz; ^{13}C , 100.6 MHz). Mass spectrometric data were obtained with a Jeol MStation JMS 700 spectrometer (DCI+). Elemental analyses (C/H/N) were performed with a Elementar Vario EL analyzer. Melting points were determined in capillaries with a Büchi Melting Point B-540 instrument and are uncorrected. Decomposition points were determined by differential scanning calorimetry (DSC) measurements with a Linseis DSC-PT10, using a heating rate of 5°C min^{-1} . Pycnometric measurements were carried out with a Quantachrome helium gas pycnometer. Sensitivity data (impact and friction) were performed using a drophammer and friction tester according to BAM (recommendations from Bundesanstalt für Materialforschung und -prüfung) [44–49]. Electrostatic sensitivities were measured with a OZM small scale electrostatic discharge tester [50].

3,6-Bis-(1,3-imidazol-1-yl)-1,2,4,5-tetrazine (**5**)

3,6-Bis-(3,5-dimethyl-pyrazol-1-yl)-1,2,4,5-tetrazine (**1**) (4.05 g 15.0 mmol) and 1*H*-imidazole (2.35 g 35.0 mmol) were suspended in 25 mL acetonitrile and the mixture refluxed for 3 h. After cooling the resulting precipitate was filtered and washed with large amounts of water (1 L), followed by acetonitrile and dichloromethane. 2.69 g (12.6 mmol 84%) of **5** was isolated as an orange powder. – Elemental analysis ($\text{C}_8\text{H}_6\text{N}_8$, 214.19) exp. (calcd.) in %: C 44.90 (44.86), N 52.03 (52.32), H 2.90 (2.82). – DSC (5°C min^{-1}): $T_{\text{dec.}}$: 200°C (onset). – ^1H NMR ($[\text{D}_6]\text{DMSO}$, 25°C , ppm): $\delta = 7.35$ (m, 1H, C-H), 8.16 (m, 1H, C-H), 8.81 (m, 1H, C-H). – ^{13}C NMR ($[\text{D}_6]\text{DMSO}$, 25°C , ppm): $\delta = 117.1$ (1C), 121.5 (1C), 132.4 (1C), 153.1 (1C). – Raman: $\tilde{\nu}$ (cm^{-1}) = 3158 (10), 3126 (5), 3113 (10), 1912 (5), 1537 (7), 1500 (8), 1490 (100), 1407 (13), 1372 (2), 1318 (13), 1282 (7), 1254 (2), 1129 (5), 1091 (16), 1048 (4), 962 (54), 895 (5), 858 (3), 801 (33), 747 (2), 665 (3), 613

(2). – IR (25 °C, ATR): $\tilde{\nu}$ (cm⁻¹) = 3155 (w), 3122 (w), 3110 (w), 1775 (vw), 1702 (vw), 1648 (vw), 1614 (vw), 1531 (w), 1522 (w), 1475 (s), 1366 (w), 1321 (s), 1301 (m), 1260 (m), 1233 (w), 1214 (m), 1153 (w), 1104 (m), 1068 (m), 1038 (vs), 971 (s), 946 (s), 926 (m), 898 (s), 854 (vs), 762 (vs), 693 (w).

3,6-Bis-(1,2-pyrazol-1-yl)-1,2,4,5-tetrazine (**6**)

3,6-Bis-(3,5-dimethyl-pyrazol-1-yl)-1,2,4,5-tetrazine (5.4 g 20 mmol) (**1**) and 1H-pyrazole (3.4 g 50 mmol) were suspended in 30 mL acetonitrile and the mixture refluxed for 2 h. After cooling the resulting precipitate was filtered and washed with large amounts (1 L) of water, followed by acetonitrile and diethyl ether. 2.2 g (10 mmol, 50%) of **6** was isolated as an orange powder. – Elemental analysis (C₈H₆N₈, 214.19) exp. (calcd.) in %: C 44.87 (44.86), N 51.53 (52.32), H 2.71 (2.82). – DSC (5 °C min⁻¹): $T_{\text{dec.}} = T_{\text{melt.}}$: 260 °C (onset). – ¹H NMR ([D₆]DMSO, 25 °C, ppm): δ = 6.80 (dd, 1H, C-H, ³J_{H-H} = 2.6 Hz, ³J_{H-H} = 1.5 Hz), 8.10 (d, 1H, C-H, ³J_{H-H} = 1.5 Hz), 8.87 (d, 1H, C-H, ³J_{H-H} = 2.6 Hz). – ¹³C NMR ([D₆]DMSO, 25 °C, ppm): δ = 111.1 (1C), 130.8 (1C), 145.8 (1C), 158.9 (1C). – Raman: $\tilde{\nu}$ (cm⁻¹) = 3149 (21), 3131 (14), 3104 (13), 1926 (4), 1541 (4), 1503 (65), 1483 (100), 1407 (4), 1400 (22), 1379 (3), 1352 (18), 1206 (2), 1115 (15), 1036 (8), 926 (41), 908 (6), 883 (2), 801 (22), 741 (3), 661 (2). – IR (25 °C, ATR): $\tilde{\nu}$ (cm⁻¹) = 3145 (w), 3127 (w), 3102 (w), 1834 (vw), 1797 (vw), 1759 (vw), 1661 (vw), 1522 (m), 1479 (s), 1398 (s), 1376 (m), 1254 (m), 1213 (w); 1184 (m), 1164 (m), 1075 (m), 1042 (w), 1026 (s), 953 (m), 918 (vs), 888 (m), 775 (vs).

3,6-Bis-(1,2,4-triazol-1-yl)-1,2,4,5-tetrazine (**7**)

1,2,4-Triazole (3.5 g 50 mmol) was dissolved in 200 mL acetone, and 20 mL (12 mmol) of a 0.6 M solution of 3,6-dichloro-tetrazine in acetonitrile was added. The solution was refluxed for 20 h. After cooling the resulting precipitate was washed with water and acetone. 2.1 g (9.9 mmol, 83%) of (**7**) was isolated as an orange powder. – Elemental analysis (C₆H₄N₁₀, 212.21) exp. (calcd.) in %: C 33.43 (33.34), N 64.33 (64.80), H 1.87 (1.87). – DSC (5 °C min⁻¹): $T_{\text{dec.}}$: 245 °C (onset). – ¹H NMR ([D₆]DMSO, 25 °C, ppm): δ = 8.34 (s, 1H, C-H), 9.46 (s, 1H, C-H). – ¹³C NMR ([D₆]DMSO, 25 °C, ppm): δ = 144.9 (1C), 147.2 (1C), 154.2 (1C). – MS ((+)-DEI): m/z = 216 [M]⁺ (50), 94 (100), 67 (92). – Raman: $\tilde{\nu}$ (cm⁻¹) = 3139 (8), 3124 (12), 1912 (2), 1557 (2), 1511 (63), 1483 (100), 1426 (4), 1379 (21), 1336 (2), 1293 (2), 1264 (12), 1135 (19), 980 (43), 947 (5), 813 (20), 662 (2). – IR (25 °C, ATR): $\tilde{\nu}$ (cm⁻¹) = 3135 (w), 3120 (w), 1813 (vw), 1755 (vw), 1551 (vw), 1514 (s), 1480 (vs), 1384 (m), 1365 (m), 1337 (w), 1293 (vs), 1266

(m), 1196 (s), 1170 (vw), 1155 (s), 1116 (s), 1112 (s), 1054 (s), 976 (vs), 953 (m), 939 (m), 910 (m), 880 (m), 672 (vs).

3,6-Bis-(3,5-diamino-1,2,4-triazol-1-yl)-1,2,4,5-tetrazine (**8**)

3,5-Diamino-1,2,4-triazole (2.40 g 24.2 mmol) was dissolved in 50 mL DMF at ambient temperature, and 10 mL (6 mmol) of a 0.6 M solution of dichlorotetrazine in acetonitrile was added *via* a dropping funnel. The solution was stirred for 2 h at ambient temperature. The product started to precipitate rather quickly. The suspension was heated to 120 °C for 16 h. After filtration the product was successively washed with large amounts of DMF, water and acetonitrile to gain 1.40 g (5.07 mmol, 85%) of **8** as a brownish-red powder. – Elemental analysis (C₆H₈N₁₄, 276.22) exp. (calcd.) in %: C 26.25 (26.09), N 69.99 (70.99), H 2.90 (2.92). – DSC (5 °C min⁻¹): $T_{\text{dec.}}$: 370 °C (onset). – ¹H NMR ([D₆]DMSO, 80 °C, ppm): δ = 7.34 (2H, NH₂), 5.66 (2H, NH₂). – ¹³C NMR ([D₆]DMSO, 80 °C, ppm): δ = 162.5 (1C), 155.5 (1C), 152.6 (1C). – MS ((+)-DEI): m/z = 276 [M]⁺ (23), 99 [C₂H₅N₅]⁺ (100), 124 [C₂N₅H₄-CN]⁺ (21). – Raman: $\tilde{\nu}$ (cm⁻¹) = 1931 (6), 1643 (4), 1622 (9), 1560 (2), 1546 (12), 1498 (100), 1420 (15), 1368 (12), 1166 (17), 1058 (4), 844 (45), 797 (2), 780 (29), 746 (3), 658 (2), 591 (2), 478 (3), 415 (8), 372 (2). – IR (25 °C, ATR): $\tilde{\nu}$ (cm⁻¹) = 3416 (w), 3383 (w), 3272 (w), 3214 (w), 3131 (w, br), 1620 (s), 1554 (m), 1474 (s), 1448 (vs), 1388 (m), 1331 (w), 1151 (m), 1134 (m), 1083 (w), 1054 (m), 1028 (m), 956 (m), 828 (m), 758 (m), 704 (m), 669 (m), 655 (vw). – Density: ρ (g cm⁻³): 1.75. – Sensitivity data: *IS*: > 40 J; *FS*: > 360 N; *ESD*: > 1 J.

3-Amino-6-(3,5-diamino-1,2,4-triazol-1-yl)-1,2,4,5-tetrazine dihydrate (**9**)

3-Amino-6-chloro-1,2,4,5-tetrazine (**4**) (1.00 g, 7.60 mmol) was dissolved in a mixture of 16.0 mL acetonitrile and 2.0 mL water. To the stirred solution 3,5-diamino-1,2,4-triazole (1.51 g, 15.2 mmol) was added. The mixture was heated to 90 °C and refluxed for 16 h. The precipitate was filtered and washed with water and acetonitrile. The product (**9**) was recrystallized from water. After standing overnight at ambient temperature, the crystals were filtered and dried. 1.33 g (5.78 mmol; 76%) of red needles of **9** were yielded. – Elemental analysis (C₄H₁₀N₁₀O₂, 230.19) exp. (calcd.) in %: C 20.62 (20.87); H 4.18 (4.38); N 60.37 (60.85). – DSC (5 °C min⁻¹, °C): $T_{\text{dec.}}$: c314 °C. – ¹H NMR ([D₆]DMSO, 25 °C, ppm): δ = 5.38 (s, 2H, NH₂ triazole), 6.94 (s, 2H, NH₂ triazole), 7.83 (s, 2H, NH₂ tetrazine). – ¹³C NMR ([D₆]DMSO, 25 °C, ppm): δ = 155.5 (1C, C-NH₂ triazole), 156.3 (1C, C-NH₂ triazole), 162.7 (1C, C-tetrazine), 162.9 (1C, C-tetrazine). – MS ((+)-DEI): m/z = 194.1 (100) [C₄H₆N₁₀]⁺, 124.1 (43) [C₃H₄N₆]⁺, 99.1 (5) [C₂H₅N₂]⁺, 82.1 (19) [C₂H₂N₅]⁺. – Raman: $\tilde{\nu}$ (cm⁻¹) = 3250 (2), 3184 (5), 1648 (7), 1570 (5), 1555 (12),

1526 (5), 1477 (90), 1399 (4), 1371 (8), 1335 (6), 1158 (10), 1027 (18), 866 (100), 828 (4), 669 (7), 580 (9), 456 (5), 356 (4), 345 (7), 321 (6). – Sensitivity data: *IS*: > 40 J; *FS*: > 360 N; *ESD*: > 1 J.

Acknowledgement

Financial support of this work by the Ludwig-Maximilian University of Munich (LMU), the U. S. Army Research Laboratory (ARL) under grant no. W911NF-09-2-0018, the Armament Research, Development and Engineering Center (ARDEC) under grant no. R&D 1558-TA-01, and the Office

of Naval Research (ONR) under grant nos. ONR.N00014-10-1-0535 and ONR.N00014-12-1-0538 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 Sucasca (Brodarski Institute, Croatia) in the development of new computational codes to predict the detonation and propulsion parameters of novel explosives. We are indebted to and thank Drs. Betsy M. Rice and Brad Forch (ARL, Aberdeen, Proving Ground, MD). Last but not least the authors thank Mr. St. Huber for sensitivity measurements.

- [1] A. Pinner, *Ber. Dtsch. Chem. Ges.* **1893**, 26, 2126–2135.
- [2] S. Ryu, R. M. Stratt, K. K. Baeck, P. M. Weber, *J. Phys. Chem. A* **2004**, 108, 1189–1199.
- [3] W. Kaim, *Coord. Chem. Rev.* **2002**, 230, 127–139.
- [4] W.-X. Hu, G.-W. Rao, Y.-Q. Sun, *Bioorg. Med. Chem. Lett.* **2004**, 14, 1177–1181.
- [5] D. L. Boger, C. W. Boyce, M. A. Labroli, C. A. Sehon, Q. Jin, *J. Am. Chem. Soc.* **1998**, 121, 54–62.
- [6] F. Zucchi, G. TrabANELLI, G. Brunoro, *Corros. Sci.* **1992**, 33, 1135–1139.
- [7] Y.-H. Gong, F. Miomandre, R. Méallet-Renault, S. Badré, L. Galmiche, J. Tang, P. Audebert, G. Clavier, *Eur. J. Org. Chem.* **2009**, 35, 6121–6128.
- [8] Y.-H. Gong, École Normale Supérieure de Cachan, Cachan (France) **2007**.
- [9] N. Saracoglu, *Tetrahedron* **2007**, 63, 4199–4236.
- [10] J. Waluk, J. Spanget-Larsen, E. W. Thulstrup, *Chem. Phys.* **1995**, 200, 201–213.
- [11] D. E. Chavez, M. A. Hiskey, D. L. Naud, *J. Pyrotech.* **1999**, 10, 17–36.
- [12] T. M. Klapötke, *Chemistry of High-Energy Materials*, Walter de Gruyter, Berlin, New York, **2011**, pp. 90–91.
- [13] D. E. Chavez, M. A. Hiskey, R. D. Gilardi, *Org. Lett.* **2004**, 6, 2889–2891.
- [14] D. E. Chavez, M. A. Hiskey, *J. Energ. Mater.* **1999**, 17, 357–377.
- [15] M. D. Coburn, G. A. Buntain, B. W. Harris, M. A. Hiskey, K. Y. Lee, D. G. Ott, *J. Heterocyclic Chem.* **1991**, 28, 2049–2050.
- [16] D. E. Chavez, M. A. Hiskey, *J. Heterocyclic Chem.* **1998**, 35, 1329–1332.
- [17] T. Urbanski, S. K. Vasudeva, *J. Sci. Ind. Res.* **1978**, 37, 250–255.
- [18] J. P. Agrawal, *Propellants. Explos. Pyrotech.* **2005**, 30, 316–328.
- [19] A. K. Sikder, N. Sikder, *J. Hazard. Mater.* **2004**, A112, 1–15.
- [20] G. L. Rusinov, N. I. Latosh, I. I. Ganebnykh, R. I. Ishmetova, N. K. Ignatenko, O. N. Chupakhin, *Russ. J. Org. Chem.* **2006**, 42, 757–765.
- [21] Z. Novák, B. Bostai, M. Csékei, *Heterocycles* **2003**, 60, 2653–2668.
- [22] D. E. Chavez, R. D. Gilardi, *J. Energ. Mater.* **2009**, 27, 110–117.
- [23] CCDC 948331 (2), 948330 (3), and 948329 (9) 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.
- [24] K.-Y. Lee, C. B. Storm, M. A. Hiskey, M. D. Coburn, *J. Energ. Mater.* **1991**, 9, 415–428.
- [25] 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. Martin, 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 09, (revision A.2), Gaussian, Inc., Wallingford CT (USA) **2009**.

- [26] J. W. Ochterski, G. A. Petersson, and J. A. Montgomery, Jr., *J. Chem. Phys.* **1996**, *104*, 2598–2619.
- [27] J. A. Montgomery, Jr., M. J. Frisch, J. W. Ochterski, G. A. Petersson, *J. Chem. Phys.* **2000**, *112*, 6532–6542.
- [28] L. A. Curtiss, K. Raghavachari, P. C. Redfern, J. A. Pople, *J. Chem. Phys.* **1997**, *106*, 1063–1079.
- [29] B. M. Rice, S. V. Pai, J. Hare, *Comb. Flame* **1999**, *118*, 445–458.
- [30] E. F. C. Byrd, B. M. Rice, *J. Phys. Chem. A* **2006**, *110*, 1005–1013.
- [31] M. S. Westwell, M. S. Searle, D. J. Wales, D. H. Williams, *J. Am. Chem. Soc.* **1995**, *117*, 5013–5015.
- [32] F. Trouton, *Philos. Mag.* **1884**, *18*, 54–57.
- [33] M. Sueska, EXPLO5 V5.04, Zagreb, Croatia, **2010**; M. Sueska, *Propellants, Explos., Pyrotech.* **1991**, *16*, 197–202.
- [34] M. Sueska, *Propellants, Explos., Pyrotech.* **1999**, *24*, 280–285.
- [35] M. L. Hobbs, M. R. Baer, *Proc. of the 10th Symp. (International) on Detonation*, ONR 33395–12, Boston, MA, July 12–16, **1993**, p. 409.
- [36] Ref. [12] p. 20.
- [37] H. W. Sandusky, R. H. Granholm, D. G. Bohl, U. S. Patent 7669460, **2010**.
- [38] CRYVALIS CCD (version 1.171.27p5 beta, release 01-04-2005 CrysAlis171.NET), Oxford Diffraction Ltd., Abingdon, Oxford (U. K.) **2005**.
- [39] CRYVALIS RED, (version 1.171.27p5 beta, release 01-04-2005 CrysAlis171.NET), Oxford Diffraction Ltd., Abingdon, Oxford (U. K.) **2005**.
- [40] A. Altomare, G. Casciaro, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* **1993**, *26*, 343–350.
- [41] G. M. Sheldrick, SHELXL-97. Program for the Refinement of Crystal Structures, University of Göttingen, (Germany) **1994**.
- [42] A. L. Spek, *Acta Crystallogr.* **2009**, *D65*, 148–155.
- [43] SCALE 3 ABSPACK – An Oxford Diffraction program (1.0.4; gui: 1.0.3), Oxford Diffraction Ltd., Abingdon, Oxford (U. K.) **2005**.
- [44] M. Sueska, *Test Methods for Explosives*, Springer, New York, **1995**; p. 21 (impact), p. 27 (friction).
- [45] <http://www.bam.de> (accessed October 2013).
- [46] NATO standardization agreement (STANAG) on explosives, *impact sensitivity tests*, no. 4489, Ed. 1, Sept. 17, **1999**.
- [47] WIWEB-Standardarbeitsanweisung 4–5.1.02, *Ermittlung der Explosionsgefährlichkeit, hier der Schlagempfindlichkeit mit dem Fallhammer*, Nov. 8, **2002**.
- [48] <http://www.reichel-partner.de> (accessed October 2013).
- [49] NATO standardization agreement (STANAG) on explosives, *friction sensitivity tests*, no. 4487, Ed. 1, Aug. 22, **2002**.
- [50] <http://www.ozm.cz/en/sensitivity-tests/esd-2008a-small-scale-electrostatic-spark-sensitivity-test/>