Journal of Materials Chemistry A

RSC Publishing

PAPER

View Article Online
View Journal

N-Trinitroethylamino functionalization of nitroimidazoles: a new strategy for high performance energetic materials†

Cite this: DOI: 10.1039/c3ta11356f

Ping Yin,[a] Qinghua Zhang,[a] Jiaheng Zhang,[a] Damon A. Parrish[b] and Jean'ne M. Shreeve*[a]

An *N*-functionalized strategy, including *N*-amination and *N*-trinitroethylamination, was utilized for the synthesis of nitroimidazole-based energetic materials, giving rise to a new family of highly insensitive *N*-aminonitroimidazoles and oxygen-rich *N*-trinitroethylaminonitroimidazoles with good to excellent properties. These new energetic materials were fully characterized by IR, ^{1}H, and ^{13}C NMR, elemental analysis, and some high performance compounds were further confirmed by ^{15}N NMR (**4a**, **4d**, **6a**, **6b**, and **6d**), as well as single crystal X-ray diffraction (**6a** and **6b**). *N*-Functionalization of nitroimidazoles not only gives rise to the *N*-aminonitroimidazoles as impact insensitive and thermally stable materials (IS > 40 J; T_d: 144–308 °C), but also provides a series of *N*-trinitroethylaminoimidazoles, which have favorable densities (1.75–1.84 g cm^{-3}), good detonation properties (*P*: 27.6–35.9 GPa; v_D: 7815–8659 m s^{-1}), and moderate thermal stabilities (136–172 °C). These properties are better than some known energetic compounds, such as TNT (*P*: 19.5 GPa; v_D: 6881 m s^{-1}) and TATB (*P*: 31.2 GPa; v_D: 8114 m s^{-1}), and are comparable to RDX (*P*: 35.0 GPa; v_D: 8762 m s^{-1}).

Received 3rd April 2013
Accepted 10th May 2013

DOI: 10.1039/c3ta11356f

www.rsc.org/MaterialsA

Introduction

In the past decade, the design and synthesis of new high-energy density materials (HEDMs) with excellent performance characteristics have attracted significant interest in the field of energetic materials.[1] In general, the most widely used strategy for the design of HEDMs is to incorporate energy-containing groups such as nitro,[2] azido,[3] diazo,[4] amino,[5] and *N*-oxido[6] into the molecular backbone of some nitrogen-rich heterocycles. However, rational use of these functional groups in design of energetic materials requires not only pursuing the highest detonation velocity and pressure, but also addressing the problems of thermal stability and impact insensitivity in order to obtain final products with acceptable properties. Polynitro-functionalized compounds are among the most significant structural motifs in HEDMs, and, as such, they are ideal targets in the design of high performance energetic compounds. There are many polynitro-explosives used for military purposes and civilian applications, such as 2,4,6-trinitrotoluene (TNT),[7] triaminotrinitro benzene (TATB),[8] 1,3,5-trinitrotriazacyclohexane (RDX),[9] cyclo-1,3,5,7-tetramethylenene-2,4,6,8-tetranitramine (HMX),[10] 1,1-diamino-2,2-dinitroethene (FOX-7)[11] and 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclododecane (CL-20).[12]

The presence of several nitro groups in these energetic materials leads to high density and good oxygen balance. Of these nitro-based functional groups, the trinitroethyl functionality is one of the most energetic groups for the construction of HEDMs.[13] Since the trinitroethyl fragment has high nitrogen content, positive oxygen balance, and also high energy within the molecule, these functionalized compounds are expected to be excellent energetic materials with superior properties such as high density, good thermal stability, low sensitivity, and positive oxygen balance.

Recently the *N*-functionalized chemistry of five-membered azoles has made great progress and many functional groups, such as NO_2,[14] NH_2,[15] CH_3,[16] and CH_2ONO_2,[17] have been employed to develop new energetic materials with comprehensively good properties. While NO_2 and CH_2ONO_2 could improve performance with decreased stabilities, methyl-functionalized compounds are more stable but display poorer performances. Among the *N*-functionalized methodologies above, *N*-amination has become one of the most attractive strategies for preparing new energetic materials. The amino products with the additional N–N bond(s) have higher heats of formation, as well as improved detonation properties. Moreover, the amino group can undergo further functionalization, such as nitration,[18] diazotization,[4] or trinitroethylation[15a] to provide versatile energetic materials. In general, five-membered azoles or six-membered azines, with high heats of formation,

[a]Department of Chemistry, University of Idaho, Moscow, ID 83844-2343, USA. E-mail: jshreeve@uidhao.edu; Fax: +1-208-885-9146

[b]Naval Research Laboratory, Code 603, Washington, D.C. 20375-5001, USA

† Electronic Supplementary Information (ESI) available. CCDC 927838 and 927839. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3ta11356f

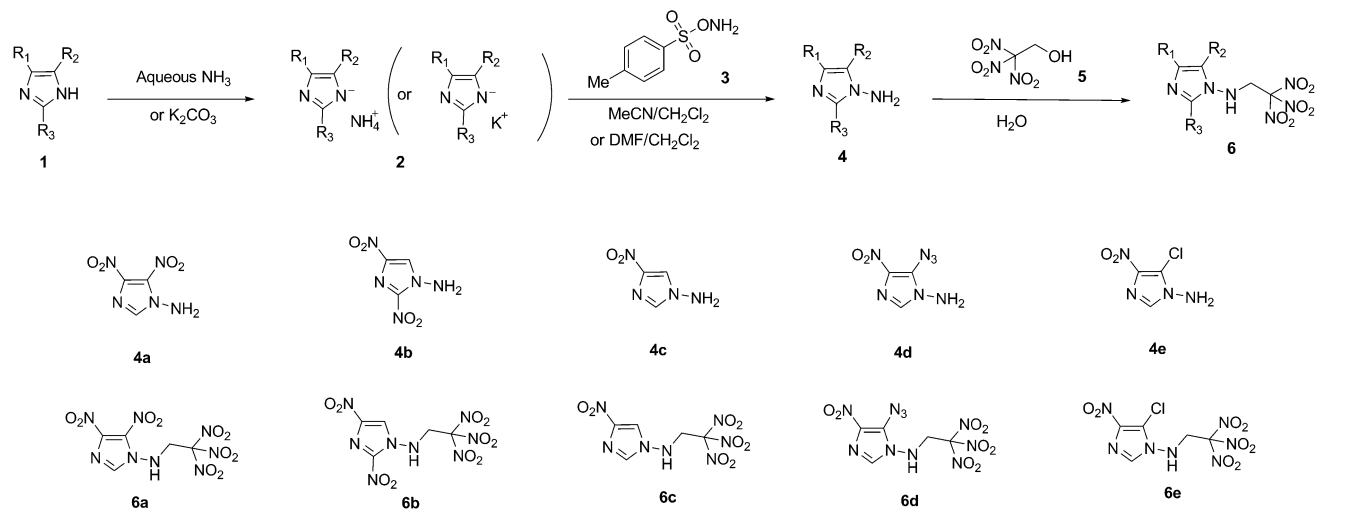
are considered to be favorable backbones for energetic materials. However, compared to linear trinitroethylamino compounds, studies on *N*-trinitroethylamino aromatic heterocycles are relatively rare and the contradictions between explosive performance and sensitivity still exist.[15a,19] To achieve a valuable balance of them, it make sense to choose more insensitive backbones but with favorable energetic properties for *N*-trinitroethylamino functionalization. On the other hand, it is likely that the *N*-trinitroethylamination strategy toward high performance compounds continues to face the challenge that nitro groups bonded to azoles improve their energy but make the *N*-amino groups inactive for further trinitroethylation. To the best of our knowledge, the *N*-trinitroethylamination of nitro-substituted azoles has remained undeveloped. In recent years, nitroimidazoles have attracted more attention as a new kind of energetic framework and various nitroimidazole derivatives have been explored, such as 2,4-dinitroimidazole, 4,5-dinitroimidazole, 2,4,5-trinitroimidazole, and 4,4′,5,5′-tetranitro-2,2′-biimidazole.[20] In the continuation of our efforts to search for new energetic materials, we are interested in developing new strategies for the synthesis of trinitroethyl-derived heterocylic materials. Herein we report the synthesis of *N*-aminonitroimidazoles and the corresponding *N*-trinitroethylaminonitroimidazoles.

Results and discussion

Syntheses

To study the detailed reaction activity and performance, a variety of substituted nitroimidazoles were chosen as starting materials. Previous studies provided many options to achieve the amination of the NH group embedded in nitrogen heterocycles.[15] The most common aminating reagents tested included hydroxylamine-*O*-sulfonic acid, *O*-tosylhydroxylamine, 2,4,6-trinitrophenyl-*O*-hydroxylamine, *etc.* After parallel tests, we found that *O*-tosylhydroxylamine was the optimal aminating reagent in comparison with other reagents for these systems. In this process, *O*-tosylhydroxylamine was more suitable with electron-poor nitroimidazoles, whereas hydroxylamine-*O*-sulfonic acid was preferred for some electron-rich nitrogen heterocycles.[21] On the other hand, bases which could neutralize the acidic nitroimidazoles to form more active salts also played an important role in the amination process. As a synthetic route shown in Scheme 1, reactions executed with aqueous ammonia gave rise to the corresponding ammonium nitroimidazolates in nearly quantitative yield, which subsequently could be readily converted to 1-aminonitroimidazoles (**4a**, 70% yield; **4b**, 55% yield). As a result of our work, it was found that the yield of **4b** was slightly improved using the ammonium salt rather than the potassium salt.[18] However, the other substituted ammonium nitroimidazolates gave only trace amounts of product with *O*-tosylhydroxylamine. Considering that aqueous ammonia is a weak base, other bases, such as K_2CO_3, KOH, NaOH, and NaH, were chosen to form potassium or sodium nitroimidazolates for amination. After optimization of reaction conditions, potassium carbonate was found to result in better isolated yields than the other bases. Although 1-amino-4-nitroimidazole (**4c**) was obtained only in low yield (21%), 1-amino-5-azido-4-nitroimidazole (**4d**) and 1-amino-5-chloro-4-nitro-imidazole (**4e**) were obtained in moderate to good yields, 73% and 75%, respectively. In addition, the attempt to aminate 2,4,5-trinitroimidazole was unsuccessful, which may be a result of steric hindrance.

With 1-amino-nitroimidazoles in hand (**4a–4e**), we focused on further functionalization with trinitroethanol. In order to obtain *N*-trinitroethylaminoimidazoles, we chose 1-amino-2,4-dinitro-imidazole (**4b**) as the model substrate to determine optimal conditions. The starting material was dissolved in water at room temperature, then trinitroethanol was added to the dilute solution which resulted in trace amounts of 2,4-dinitro-*N*-(2,2,2-trinitroethyl)-1*H*-imidazol-1-amine (**6b**). Considering that **4b** was slightly soluble in water at room temperature, the amount of solvent required was reduced by preparing a saturated aqueous solution at 80 °C. Although the



Scheme 1 Synthesis of *N*-amino and *N*-trinitroethylaminoimidazoles.

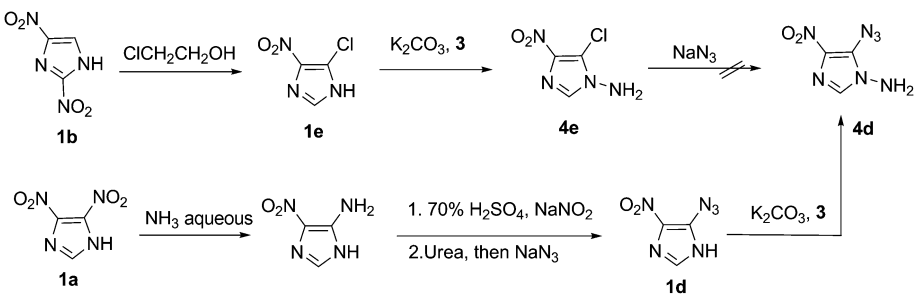
higher concentration of reactant accelerated conversion of the starting material, impurities generated at high temperature precipitated from the aqueous solution. Therefore, the reaction temperature was reduced slowly to room temperature after addition of trinitroethanol. After stirring overnight at ambient temperature, a white solid precipitated from the reaction to give **6b** in 61% yield. Likewise, treatment of other 1-amino-nitroimidazoles with trinitroethanol also gave the target products in moderate to good yields (**6a**, 72%; **6c**, 56%; **6d**, 53%; **6e**, 75%).

In the initial study, 5-azido-4-nitro-imidazole (**1d**) was synthesized from 4,5-dinitro-1*H*-imidazole (**1a**) by the known method, including aminolysis, diazotation, and nucleophilic substitution with sodium azide.[22] Because the separation of the sensitive diazonium salt was hard to handle and the overall yield of **1d** was very low, we combined the diazotation and following azido substitution as a one-pot procedure without separation of the diazonium salt, and the overall yield of **1d** was increased to 51% (Scheme 2). We had also attempted to prepare 5-azido-4-nitro-1*H*-imidazol-1-amine (**4d**) by the condensation of 5-chloro-4-nitro-1*H*-imidazol-1-amine (**4e**) and sodium azide but failed to obtain the desired product.

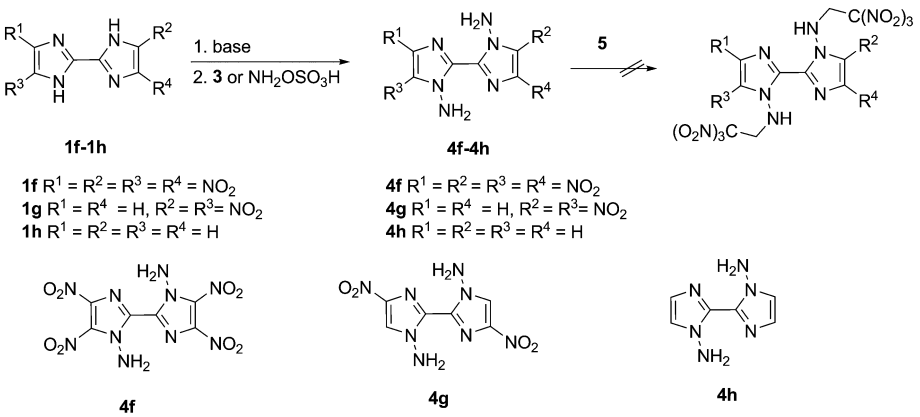
The syntheses of *N*-amino-biimidazoles and their trinitroethyl derivatives were undertaken (Scheme 3). When 4,4′,5,5′-tetranitro-1*H*,1′*H*-2,2′-biimidazole (**1f**) was treated with aqueous ammonia and *O*-tosylhydroxylamine (**3**) the desired diamino product was obtained as a yellow solid in a yield of 53%. Because of the basicity of the non-substituted biimidazole (**1g**) amination was performed using hydroxylamine-*O*-sulfonic acid. For dinitro-biimidazole (**1g**), amination could be processed from its potassium salt by using potassium carbonate with *O*-tosylhydroxylamine. Based on the basicity of non-substituted biimidazole (**1h**), amination of **1h** was performed with the use of hydroxylamine-*O*-sulfonic acid. However, the attempted trinitroethylation of these diamino-biimidazoles did not yield the desired products. Compounds **4f**, **4g**, and **4h** were verified by NMR spectroscopic data and elemental analysis.

Structure and physical properties

To assess the thermal stability of the new materials, differential scanning calorimetric (DSC) measurements was used for the new compounds. Most of the *N*-aminonitroimidazoles melted with sharp endothermic peaks at low temperature (**4a**, 64 °C; **4b**, 173 °C; **4c**, 93 °C; **4d**, 77 °C; **4e**, 123 °C) and decomposed at high temperature (**4a**, 264 °C; **4b**, 235 °C; **4c**, 211 °C; **4d**, 144 °C; **4e**, 274 °C). All *N*-trinitroethylaminonitroimidazoles decomposed without melting at moderate temperature (**6a**, 171 °C; **6b**, 172 °C; **6c**, 139 °C; **6d**, 136 °C; **6e**, 156 °C). For *N*-aminoimidazoles, all decomposed at high temperature (**4f**, 217 °C; **4g**, 308 °C; **4h**, 292 °C). In the IR spectra of the *N*-trinitroethylaminonitroimidazoles, characteristic absorption bands were observed at 1300–1600 cm^{-1}, which verified the multiple nitro groups from the imidazole ring and the trinitroethylamine. In the ^{13}C NMR spectra, the carbon atom bonded to three nitro groups was found at 125–128 ppm, while the carbon atoms of the imidazole ring appeared between 120 and 150 ppm.



Scheme 2 Reaction optimization of 5-azido-4-nitro-imidazole.



Scheme 3 Amination of biimidazoles.

In Fig. 1, the ^{15}N NMR spectra of 4,5-dinitro-1*H*-imidazol-1-amine (**4a**), 4,5-dinitro-*N*-(2,2,2-trinitroethyl)-1*H*-imidazol-1-amine (**6a**) 2,4-dinitro-*N*-(2,2,2-trinitroethyl)-1*H*-imidazol-1-amine (**6b**) and 5-azido-4-nitro-*N*-(2,2,2-trinitroethyl)-1*H*-imidazol-1-amine (**6d**) are displayed as measured in CD_3CN. The ^{15}N {H}NMR spectrum of **6a** shows six signals at $\delta = -24.14$ (N4), -30.78 (N6), -34.01 (N3), -135.32 (N2), -193.57 (N1), -309.71 (N5) ppm, while the nitrogen signals of **4a** are found in the similar position at $\delta = -24.02$ (N4), -34.08 (N3), -137.12 (N2), -198.52 (N1), -308.11 (N5). In the spectra of **6b** and **6d**, the nitrogen signals from NO_2 are observed between -32.83 and -23.38, as well as the typical nitrogen signals of NH, which are

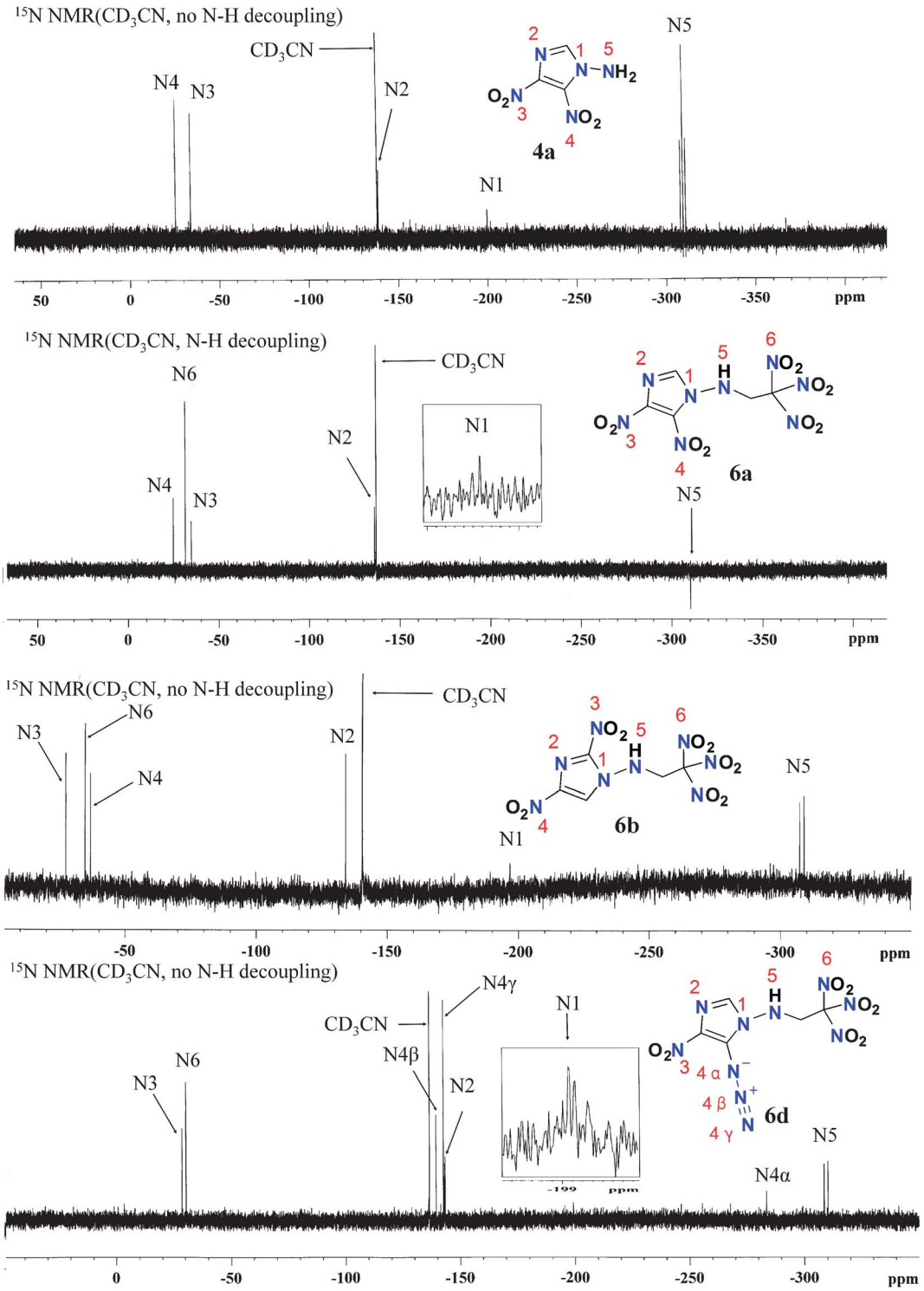


Fig. 1 Selective ^{15}N NMR spectra of *N*-aminoimidazoles and *N*-trinitroethylaminoimidazoles.

Table 1 Properties of the *N*-aminonitroimidazoles and *N*-trinitroethylaminonitroimidazoles

Comp.	T_m[a] [°C]	T_d[b] [°C]	d[c] [g cm^{-3}]	$\Delta H_f(g)$[d] [kJ mol^{-1}]	ΔH_{sub}[e] [kJ mol^{-1}]	ΔH_f[f] [kJ mol^{-1}]/[kJ g^{-1}]	P[g] [GPa]	v_D[h] [m s^{-1}]	IS[i] [J]	OB[j]/OP[k] [%]
4a	64	235	1.72	261.4	63.4	146.5/0.85	28.7	8137	>40	−4.62/36.97
4b	173	264	1.75	200.8	83.9	116.9/0.68	29.3	8174	>40	−4.62/36.97
4c	96	237	1.56	195.3	69.4	125.9/0.98	20.1	7363	>40	−37.50/24.98
4d	77	144	1.65	536.1	65.8	470.3/2.78	25.9	8048	3.5	−23.66/18.92
4g	285	308	1.75	400.3	104.9	295.4/1.16	25.6	7939	>40	−28.57/25.28
6a[l]	163	171	1.83 (1.867[m])	190.4	82.0	108.4/0.32	35.9	8659	2.5	14.29/47.60
6b[l]	—	172	1.84 (1.869[m])	175.0	83.7	91.3/0.27	35.8	8649	7	14.29/47.60
6c	—	139	1.75	164.3	77.5	86.8/0.30	30.4	8218	10	2.75/43.96
6d	—	136	1.79	494.6	75.8	418.8/1.26	33.0	8513	2	4.82/38.54
6e	—	156	1.76	144.5	75.8	68.7/0.21	27.6	7815	7	4.91/39.31
TNT	80.4	295	1.65	—	—	−67.0/−0.30	19.5	6881	15	−24.66/42.27
TATB	324	324	1.93	—	—	−140/−0.54	31.2	8114	50	−18.60/37.19
RDX	205	230	1.80	192	112	80/0.36	35.0	8762	7.5	0.00/43.22

[a] Melting temperature. [b] Decomposition temperature. [c] Density measured by gas pycnometer (25 °C). [d] Gas phase enthalpy of formation. [e] Enthalpy of sublimation (calculated with Trouton's rule). [f] Heat of formation. [g] Detonation pressure (calculated with Explo 5.05). [h] Detonation velocity (calculated with Explo 5.05). [i] Impact sensitivity. [j] Oxygen balance (based on CO) for $C_aH_bO_cN_d$ $1600(c - a - b/2)/M_w$, M_w = molecular weight. [k] Oxygen content. [l] The calculation of detonation properties is based on crystal densities. [m] Calculated density from single crystal X-ray diffraction (20 °C).

found at the highest field (−309.37 and −304.19). The identification for each nitrogen atom is further confirmed by ^{1}H, and ^{15}N-HMBC experiments (see ESI†).

Densities of energetic materials, which represent one of the most important physical properties, were measured with a gas pycnometer. The densities of *N*-amino-imidazoles are in

Table 2 Crystallographic data for **6a** and **6b**

	6a	**6b**
Empirical formula	$C_5H_4N_8O_{10}$	$C_5H_4N_8O_{10}$
Formula weight	336.16	336.16
CCDC number	927838	927839
Crystal size [mm^{-3}]	0.48 × 0.46 × 0.01 mm^3	0.48 × 0.34 × 0.24 mm^3
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/n$	$Pna2_1$
a [Å]	8.3893(5)	11.1074(7)
b [Å]	10.0156(6)	9.5233(6)
c [Å]	14.3147(8)	10.9770(7)
α [°]	90	90
β [°]	103.532(2)	90
γ [°]	90	90
V [Å^3]	1169.39(12)	1161.14(13)
Z	4	4
T [K]	150(2) K	150(2) K
ρ_{calcd} [mg cm^{-3}]	1.909 (−123 °C) 1.867(20 °C)	1.923 (−123 °C) 1.869 (20 °C)
μ [mm^{-1}]	0.185	0.187
F(000)	680	680
θ [°]	2.51 to 26.39	2.82 to 26.40
Index ranges	$-10 \le h \le 10$, $-12 \le k \le 12$, $-17 \le l \le 16$	$-13 \le h \le 13$, $-10 \le k \le 11$, $-13 \le l \le 13$
Reflections collected	10 968	7852
Independent reflections (R_{int})	2396 [R_{int} = 0.0235]	2270 [R_{int} = 0.0309]
Data/restraints/parameters	2396/0/211	2270/1/208
Goodness-of-fit on F^2	1.044	1.061
R_1 ($I > 2\delta(I)$)[a]	0.0292	0.0387
wR_2 ($I > 2\delta(I)$)[b]	0.0750	0.1071
R_1 (all data)	0.0337	0.0412
wR_2 (all data)	0.0779	0.1096
Largest diff. peak and hole ([e Å^{-3}])	0.286 and −0.268	0.424 and −0.418

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

the range of 1.56–1.75 g cm^{-3}, while *N*-trinitroethylaminonitroimidazoles show higher densities lying between 1.75 and 1.84 g cm^{-3}. The densities of **6a** and **6b** calculated based on the single-crystal X-ray diffraction are slightly higher (**6a**, 1.867 g cm^{-3} at 20 °C; **6b**, 1.869 g cm^{-3} at 20 °C) than the measured densities (**6a**, 1.83 g cm^{-3} at 20 °C; **6b**, 1.84 g cm^{-3} at 20 °C).

Sensitivity and computational analyses

In order to obtain the detonation properties, the Gaussian 03 (Revision D.01) suite of programs was used to calculate the gas phase enthalpies of formation of the resulting compounds.[23] Employing Trouton's rule, the enthalpy of sublimation for each compound was calculated. The heats of formation of these energetic compounds fall between 68.7 kJ mol^{-1} and 470.1 kJ mol^{-1}. As shown in Table 1, **4d** and **6d** which contain an azido group, not surprisingly, have higher heats of formation and good detonation velocities (**4d**, 2.78 kJ g^{-1}, 8048 m s^{-1}; **6d**, 1.26 kJ g^{-1}, 8513 m s^{-1}) than the other compounds in Table 1.

With the exception of **4d**, all *N*-aminonitroimidazoles are thermally stable (T_d > 210 °C) and insensitive to impact (IS > 40 J). Among them, detonation properties of **4a** (*P*, 28.7 GPa; v_D, 8137 m s^{-1}) and **4b** (*P*, 29.3 GPa; v_D, 8174 m s^{-1}) are higher than TNT (*P*, 19.5 GPa; v_D, 6881 m s^{-1}), and comparable to TATB (*P*, 31.2 GPa; v_D, 8114 m s^{-1}). Compared with *N*-aminonitroimidazoles, *N*-trinitroethylaminonitroimidazoles exhibit better detonation performances due to their higher densities. Their calculated detonation velocities lie in the range of 7815 to 8659 m s^{-1}, while detonation pressures range from 27.6 to 35.9 GPa. Although the heats of formation of *N*-trinitroethylaminonitroimidazoles (0.21–1.26 kJ g^{-1}) are lower than the corresponding *N*-aminonitroimidazoles (0.68–2.78 kJ g^{-1}), most of them possess unique positive oxygen balances (OB, 2.75–14.92) and good oxygen content (OC, 37.19–47.60). The measurements of impact sensitivities, obtained by using a BAM drop hammer apparatus, indicated that *N*-trinitroethylaminonitroimidazoles are more sensitive than the corresponding *N*-aminonitroimidazoles. However, their densities and detonation performances are superior with 2,4-dinitro-*N*-(2,2,2-trinitroethyl)-1*H*-imidazol-1-amine (**6b**) showing excellent overall properties (*d*, 1.869 g cm^{-3}; *P*, 35.8 GPa; v_D, 8649 m s^{-1}; IS, 7 J; OB, 14.29; OC, 47.60), which is comparable to RDX (*d*, 1.80 g cm^{-3}; *P*, 35.0 GPa; v_D, 8762 m s^{-1}; IS, 7.4 J; OB, 0.00; OC, 43.22).

X-ray crystallography

Crystals of **6a** and **6b** suitable for crystal-structure analysis were obtained by recrystallization from chloroform and acetonitrile. Their crystallographic data are summarized in Table 2, and structures are shown in Fig. 2 and 3, respectively. As can be seen in Table 2, **6a** crystallizes in the monoclinic $P2_1/n$ space group with a calculated density of 1.867 g cm^{-3} (20 °C). For C–NO_2 groups, the length of the C–N bonds in the trinitroethyl groups (1.5152(16) Å–1.5220(16) Å: C(8)–N(15), 1.5152(16); C(8)–N(12), 1.5218(16); C(8)–N(9), 1.5220(16)) are longer than the other two C–N (C–NO_2) bond distances in the substituted imidazole (1.4396(16) Å-1.4517(16) Å: C(4)–N(18), 1.4517(16); C(5)–N(21), 1.4396(16)). The atoms in the imidazole core with three substituted nitrogen atoms are nearly planar with torsion angles (such as N(1)–C(2)–N(3)–C(4)–0.27(14), N(6)–N(1)–C(2)–N(3)–179.27(11), and C(2)–N(3)–C(4)–N(18)–177.03(11)). However, the nitro groups bonded to imidazole are considerably twisted relative to each other with a torsion angle of (C(4)–C(5)–N(21)–O(22)–149.29(14), N(1)–C(5)–N(21)–O(23)–142.85(12), N(3)–C(4)–N(18)–O(20)–158.46(11), C(5)–C(4)–N(18)–O(19)–162.58(12)). Intermolecular hydrogen bonds are found between the NH group and imidazole in **6a** (N(6)–H(6)···N(3)#1).

Compared with **6a**, **6b** crystallizes in an orthorhombic $Pna2_1$ space group with a calculated density of 1.869 g cm^{-3}(20 °C). The length of the C–N bonds joining the trinitroethyl groups are also different from substituted nitro groups joining the imidazole moieties [such as C(8)–N(9) 1.536(3), C(8)–N(15) 1.503(4), and C(4)–N(21) 1.443(3)]. Interestingly, the two nitro groups are planar with the imidazole ring with torsion angles of N(3)–C(2)–N(18)–O(19) 6.7(4), N(1)–C(2)–N(18)–O(20) 7.0(4), C(5)–C(4)–N(21)–O(23)–0.1(4), N(3)–C(4)–N(21)–O(22) 1.6(4), while the two nitro groups of **6a** are twisted with imidazole. As a result, **6b** could be more stable, which may be reflected by the values of their different impact sensitivities (**6a**, 2.5 J; **6b**, 7 J). In addition, the planar structure tends to have a higher density, which can be seen in Table 2:

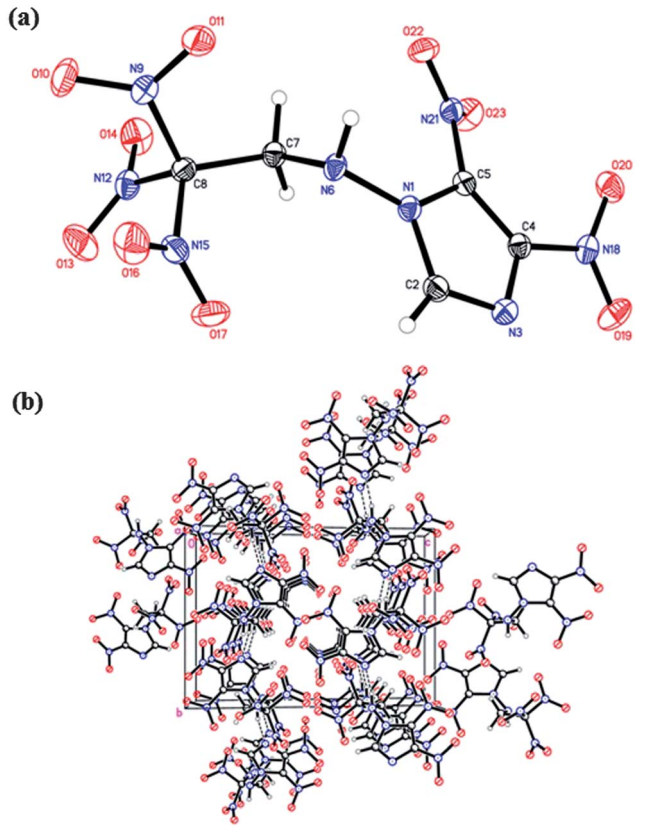


Fig. 2 (a) Thermal ellipsoid plot (50%) and labeling scheme for **6a**. Hydrogen atoms are included but are unlabeled for clarity. (b) Ball and stick packing diagram of **6a** viewed down the *a* axis. The dashed lines indicate strong hydrogen bonding.

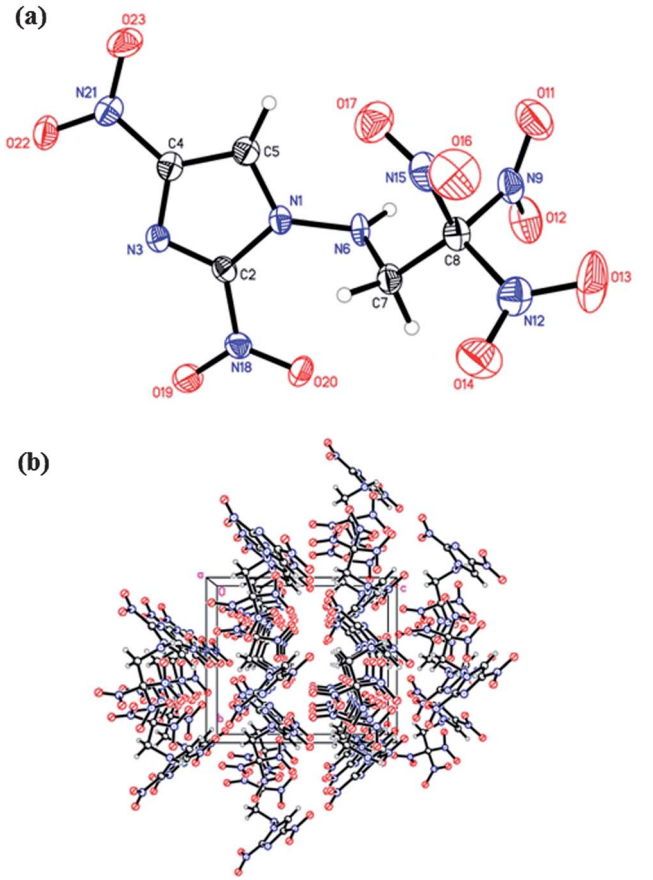


Fig. 3 (a) Thermal ellipsoid plot (50%) and labeling scheme for **6b**. Hydrogen atoms are included but are unlabeled for clarity. (b) Ball and stick packing diagram of **6b** viewed down the *a* axis.

6a, 1.867 g cm^{-3} (20 °C), 1.909 g cm^{-3} (−123 °C); **6b**, 1.869 g cm^{-3} (20 °C), 1.923 g cm^{-3} (−123 °C).

Conclusion

N-Trinitroethylaminoimidazoles were obtained from ammonium or potassium nitroimidazolates by a facile linear synthesis, including *N*-amination followed by *N*-trinitroethylation. These new compounds were characterized by IR, and NMR spectroscopic data and elemental analysis. Compounds **6a** and **6b** were structured using single-crystal X-ray diffraction which allowed correlation of configuration relationships with densities and impact sensitivities. *N*-Aminonitroimidazoles with excellent thermal stabilities and impact sensitivities are better than TNT and comparable to TATB. Moreover, all of the *N*-trinitroethylaminonitroimidazole compounds have positive oxygen balances and good oxygen content, best exemplified by **6b** which exhibits high density, good oxygen content, moderate thermal stability, and high detonation performance and may serve as a promising alternative to some known explosives such as RDX. Detailed properties of these imidazole-based compounds show good compatibilities with *N*-trinitroethylamination, thereby providing a promising *N*-functionalized strategy toward high performance energetic materials.

Experimental section

Safety precautions

Although we have encountered no difficulties in preparing all of the compounds in this work, manipulations must be carried out by using appropriate standard safety precautions. Eye protection and leather gloves must be worn. Mechanical actions of these energetic materials involving scratching or scraping must be avoided.

General methods

All chemicals were pure analytical grade materials obtained from Aldrich or Acros Organics and used as received. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz nuclear magnetic resonance spectrometer operating at 300 MHz and 75 MHz, respectively. ^{15}N NMR spectra were recorded on a Bruker 500 MHz nuclear magnetic resonance spectrometer operating at 50.7 MHz. Chemical shifts in ^{1}H, and ^{13}C NMR spectra are reported relative to Me_4Si and in ^{15}N NMR to $MeNO_2$. To obtain the ^{15}N spectrum for **6b** required ~48 h, while the others were recorded in ~12 h. CD_3CN was used as a locking solvent unless otherwise stated. Elemental analyses (C, H, N) were performed on a CE-440 Elemental Analyzer. Impact sensitivity tests were carried out using the BAM fallhammer method. Melting and decomposition points were recorded on a differential scanning calorimeter (DSC, TA Instruments Q10) at a scan rate of 5 °C min^{-1}. IR spectra were recorded using KBr pellets with a Biorad Model 3000 FTS spectrometer. Densities were determined at room temperature by employing a Micromeritics AccuPyc 1330 gas pycnometer.

X-ray crystallography

A yellow plate of dimensions 0.48 × 0.46 × 0.01 mm^3 for **6a** and a colorless plate of dimensions 0.48 × 0.34 × 0.24 mm^3 for **6b** were mounted on a MiteGen MicroMesh using a small amount of Cargille Immersion Oil. Data were collected on a Bruker three-circle platform diffractometer equipped with a SMART APEX II CCD detector. The crystals were irradiated using graphite monochromated MoK_α radiation (λ = 0.71073). An Oxford Cobra low temperature device was used to keep the crystals at a constant 150(2) K during data collection. Data collection was performed and the unit cell was initially refined using *APEX2* [v2010.3-0].[24] Data reduction was performed using *SAINT* [v7.68A][25] and *XPREP* [v2008/2].[26] Corrections were applied for Lorentz, polarization, and absorption effects using *SADABS* [v2008/1].[27] The structure was solved and refined with the aid of the programs in the *SHELXTL-plus* [v2008/4] system of programs.[28] The full-matrix least-squares refinement on F^2 included atomic coordinates and anisotropic thermal parameters for all non-H atoms. The H atoms were included using a riding model.

Theoretical study

Computations were performed by using the Gaussian 03 (Revision D.01) suite of programs. The geometric optimization of the structures and frequency analyses were carried out by

using the B3-LYP functional with the 6-31+G** basis set 19, and single-point energies were calculated at the MP2/6-311++G** level. All of the optimized structures were characterized to be true local energy minima on the potential-energy surface without imaginary frequencies.

According to the method of isodesmic reactions, the gas phase enthalpies of formation were computed and the enthalpy of reaction is obtained by combining the MP2/6-311++G** energy difference for the reactions, the scaled zero point energies, and other thermal factors. Thus, the gas phase enthalpy of the species being investigated can be readily extracted. The enthalpy of sublimation was calculated by using Trouton's rule.[29] Solid-state heats of formation of the resulting compounds were calculated with eqn (1) in which T_m is the melting temperature.

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

With densities and heats of formation in hand, the detonation pressure (P) and velocity (v_D), were calculated using the program package EXPLO 5.05.

General procedure

***O*-Tosylhydroxylamine.** *O*-Tosylhydroxylamine was prepared by the literature method.[15a] Freshly prepared ethyl *O*-*p*-tolylsulphonylacetohydroximate (15 mmol, 3.86 g) was added to 25 mL of 60% $HClO_4$. The mixture was stirred at room temperature for 2 h. Hydrolysis of ethyl *O*-*p*-tolylsulphonylacetohydroximate was monitored by thin layer chromatography (TLC). When the reaction was completed, the white slurry was poured into ice and extracted with CH_2Cl_2 (4 × 25 mL). The organic portions were combined, dried over Na_2SO_4, and used for *N*-amination reactions.

4,5-Dinitro-1*H*-imidazol-1-amine (4a). 4,5-Dinitroimidazole was prepared based on the literature.[30] To a 200 mL round bottomed flask, 4,5-dinitroimidazole (1.58 g, 10 mmol) was dissolved in excess aqueous ammonia. The solvent was removed by blowing air over the liquid surface and the residue was dried *in vacuo*. Acetonitrile (100 mL) was added to the ammonium salt and followed by the freshly prepared *O*-tosylhydroxylamine in CH_2Cl_2 (100 mL, prepared as above). The mixture was stirred at room temperature for 12 h. The solvent was removed by rotary evaporation and ethyl acetate (50 mL) was added. The white precipitate was filtered and ethyl acetate was removed. The residue was purified by chromatography with hexane–ethyl acetate (100 : 50), to give **4a**. Yellow solid (1.21 g, 70%); M.p. 64 °C, 235 °C (dec.); ^{1}H NMR: δ 7.66 (s, 1H), 5.80 (s, 2H); ^{13}C NMR: δ 138.8, 136.8, 133.1; ^{15}N NMR: δ −24.02, −34.08, −137.12 (d, J = 12.68 Hz), −198.52 (dt, J = 6.59 Hz, 1.52 Hz), −308.11 (t, J = 73.01 Hz); IR (KBr pellet): 3358, 3250, 3203, 3140, 1558, 1526, 1489, 1363, 1314, 1209, 1154, 954, 812, 643 cm^{-1}; elemental analysis (%) calcd for $C_3H_3N_5O_4$ (173.09): C, 20.82; H, 1.75; N, 40.46; found: C, 20.99; H, 1.78; N, 39.77. Density: 1.72 g cm^{-3}. Impact sensitivity: >40 J.

2,4-Dinitro-1*H*-imidazol-1-amine (4b).[18] After using the same procedure as for **4a**, 2,4-dinitro-1*H*-imidazol-1-amine (**4b**) was obtained by chromatography with hexane–ethyl acetate (100 : 35). Yellow solid (947 mg, 55%); M.p. 173 °C, 265 °C (dec.); ^{1}H NMR: δ 8.12 (s, 1H), 6.22 (s, 2H); ^{13}C NMR: δ 141.6, 141.2, 126.1; IR (KBr pellet): 3343, 3267, 3205, 3148, 1548, 1494, 1342, 1315,1145, 1025, 857, 821 cm^{-1}; elemental analysis (%) calcd for $C_3H_3N_5O_4$ (173.09): C, 20.82; H, 1.75; N, 40.46; found: C, 21.19; H, 1.76; N, 39.67. Density: 1.75 g cm^{-3}. Impact sensitivity: >40 J.

4-Nitro-1*H*-imidazol-1-amine (4c). 4-Nitro-1*H*-imidazol-1-amine was prepared by using the potassium salt. To a 200 mL round bottomed flask, 4-nitro-1*H*-imidazole (1.13 g, 10 mmol) and potassium hydroxide (728 mg, 13 mmol) were added to 20 mL MeOH. The mixture was stirred at 50 °C for 0.5 h. The solvent was removed by evaporation and DMF (20 mL) was added to the residue. Freshly prepared *O*-tosylhydroxylamine in CH_2Cl_2 (100 mL, prepared by the procedure described above) was added to the DMF solution at 0 °C. After addition the temperature was allowed to rise to room temperature and stirred for 12 h. The organic solvent was removed by rotary evaporation. Ethyl acetate (50 mL) was added to dissolve the aminoimidazole remaining and the mixture was filtered; the filtrate was washed with brine, and dried over Na_2SO_4. The ethyl acetate solution was evaporated and the crude product was purified by chromatography with hexane–ethyl acetate (100 : 50) to give **4c**. White solid (268 mg, 21%). M.p. 96 °C, 237 °C (dec.); ^{1}H NMR: δ 7.87 (s, 1H), 7.69 (s, 1H), 5.63 (s, 2H); ^{13}C NMR: δ 142.9, 139.2, 132.0; IR (KBr pellet): 3304, 3206, 3133, 1655, 1532, 1468, 1382, 1271, 1111, 1002, 853, 824, 649 cm^{-1}; elemental analysis (%) calcd for $C_3H_4N_4O_2$ (128.09): C, 28.13; H, 3.15; N, 43.74; found: C, 28.13; H, 3.11; N, 42.91. Density: 1.56 g cm^{-3}. Impact sensitivity: >40 J.

5-Azido-4-nitro-1*H*-imidazol-1-amine (4d). 5-Azido-4-nitro-1*H*-imidazole was prepared from 4,5-dinitroimidazole in two steps. 4,5-Dinitroimidazole (15.8 g, 0.1 mol) was dissolved in aqueous ammonia (200 mL) and stirred at 100 °C for 15 h. The yellow solution was concentrated to appropriate 20 mL by passing air over the liquid surface. The precipitate was then removed by filtration and 5-amino-4-nitroimidazole was obtained, which was used for the next step without purification. ^{1}H NMR: δ 7.32 (s, 2H), 7.23 (s, 1H).

5-Amino-4-nitroimidazole was dissolved in H_2SO_4 (70%, 200 mL) and the solution was cooled to 0 °C. A solution of sodium nitrite (6.90 g, 0.1 mol) in water (30 mL) was added to the stirred solution. After addition, the reaction mixture was stirred at room temperature for 1 h, cooled to 0 °C and diluted with 500 mL H_2O. Urea (3.03 g, 0.05 mol) was added, and then NaN_3 (6.50 g, 0.1 mol) was added in small portions and the reaction was stirred for additional 3 h. The final yellow aqueous solution was extracted with ethyl ether (5 × 100 mL), and the ether solution was evaporated under reduced pressure to give 5-azido-4-nitro-1*H*-imidazole. Yellow solid (7.81 g, 51% overall yield). ^{1}H NMR: δ 7.32 (s, 2H), 7.23 (s, 1H).

5-Azido-4-nitro-1*H*-imidazole (1.54 g, 10 mmol) was dissolved in 30 mL DMF. Potassium carbonate (2.07 g, 15 mmol) was added and stirred at 50 °C for 2 h. To the reaction mixture in an ice bath was added freshly prepared *O*-tosylhydroxylamine in CH_2Cl_2 (100 mL, prepared as above) cooled below 10 °C. The reaction mixture was allowed to warm, and stirred at room

temperature for 24 h. The organic solvent was removed by rotary evaporation. Ethyl acetate (50 mL) was added to dissolve the aminoimidazole and the mixture was filtered, washed with brine, and dried over Na_2SO_4. The ethyl acetate solution was evaporated and the crude product was purified by chromatography with hexane–ethyl acetate (100 : 40) to give **4d**. Yellow solid (1.23 g, 73%). M.p. 77 °C, 144 °C (dec.); ^{1}H NMR: δ 7.61 (s, 1H), 5.64 (s, 2H); ^{13}C NMR: δ 141.4, 140.4, 126.6; ^{15}N NMR: δ −27.26, −140.50, −141.65, −144.93 (d, J = 11.66 Hz), −205.04, −285.43, −307.38 (t, J = 70.98 Hz); elemental analysis (%) calcd for: $C_3H_3N_7O_2$ (169.10): C, 21.31; H, 1.79; N, 57.98; found: C, 21.37; H, 1.82; N, 57.61; IR (KBr pellet): 3375, 3307, 3120, 2143, 1541, 1501, 1461, 1417, 1360, 1329, 1177, 1146, 948, 839 cm^{-1}. Density: 1.65 g cm^{-3}. Impact sensitivity: 3.5 J.

5-Chloro-4-nitro-1*H*-imidazol-1-amine (4e). 5-Chloro-4-nitro-1*H*-imidazole was prepared based on the literature.[31] After using the same procedure as for **4d**, 5-chloro-4-nitro-1*H*-imidazol-1-amine (**4e**) was obtained by chromatography with hexane–ethyl acetate (100 : 50 to 100:100). White solid (1.22 g, 75%). M.p. 123 °C, 274 °C (dec.); ^{1}H NMR: δ 8.01 (s, 1H), 5.20 (s, 2H); ^{13}C NMR: δ 144.0, 134.7, 125.1; elemental analysis (%) calcd for $C_3H_3ClN_4O_2$ (162.53): C, 22.17; H, 1.86; N, 34.47; found: C, 22.15; H, 1.82; N, 33.52.

4,4′,5,5′-Tetranitro-1*H*,1′*H*-2,2′-biimidazole-1,1′-diamine (4f).[32] Compound **4f** was obtained by using the same procedure as for **4a**. 4,4′,5,5′-Tetranitro-1*H*,1′*H*-2,2′-biimidazole-1,1′-diamine (**4f**) was isolated by chromatography with hexane/ethyl acetate (100 : 50). White solid (1.82 g, 53%). M.p. 206 °C, 217 °C (dec.); ^{1}H NMR (d_6-DMSO): δ 8.55 (s, 2H), 6.87 (s, 4H); ^{13}C NMR (d_6-DMSO): δ 137.0, 134.8, 131.6; IR (KBr pellet): 3360, 3259, 1532, 1504, 1389, 1366, 1312, 1147, 849, 816 cm^{-1}; elemental analysis (%) calcd for $C_6H_4N_{10}O_8$ (344.16): C, 20.94; H, 1.17; N, 40.70; found: C, 21.09; H, 1.17; N, 40.09.

4,4′-Dinitro-1*H*,1′*H*-2,2′-biimidazole-1,1′-diamine (4g). The starting material (4,4′-dinitro-1*H*,1′*H*-2,2′-biimidazole) was prepared according to literature.[33] Compound **4g** was obtained by using the same procedure as for **4d** and isolated by chromatography with hexane–ethyl acetate (100 : 100 to 10 : 100). Yellow solid (1.07 g, 42%). M.p. 285 °C, 308 °C (dec.); ^{1}H NMR (d_6-DMSO): δ 8.57 (s, 2H), 6.87 (s, 4H); ^{13}C NMR (d_6-DMSO): δ 143.3, 133.4, 123.6; IR (KBr pellet): 3330, 3266, 3127, 1541, 1498, 1399, 1344, 1298, 1001, 820 cm^{-1}; elemental analysis (%) calcd for $C_6H_6N_8O_4$ (254.16): C, 28.35; H, 2.38; N, 44.09; found: C, 28.55; H, 2.44; N, 43.89. Density: 1.75 g cm^{-3}. Impact sensitivity: >40 J.

1*H*,1′*H*-2,2′-Biimidazole-1,1′-diamine (4h). A suspension of 1*H*,1′*H*-2,2′-biimidazole (**1h**, 134 mg, 1 mmol) in aqueous KOH (560 mg of KOH in 20 mL of distilled water) was stirred at 90 °C for 0.5 h. The reaction temperature was allowed to cool to 40 °C and hydroxylamine-*O*-sulfonic acid (684 mg, 6 mmol) was added over 20 min with the temperature maintained below 50 °C. After stirring at 50 °C overnight, the mixture was extracted by ethyl ether (5 × 10 mL). The organic portions were combined, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by chromatography with hexane/ethyl acetate (20 : 100). White solid (39 mg, 24%). M.p. 154 °C, 292 °C (dec.); ^{1}H NMR: δ 7.24 (s, 2H), 6.96 (s, 2H), 6.87 (s, 4H); ^{13}C NMR: δ 134.5, 125.0, 120.9; IR (KBr pellet): 3267, 3180, 3119, 1637, 1504, 1437, 1411, 1327, 1294, 1106, 1023, 751 cm^{-1}; elemental analysis (%) calcd for $C_6H_8N_6$ (164.17): C, 43.90; H, 4.91; N, 51.19; found: C, 44.04; H, 4.86; N, 50.88.

4,5-Dinitro-*N*-(2,2,2-trinitroethyl)-1*H*-imidazol-1-amine (6a). A suspension of 4,5-dinitro-1*H*-imidazol-1-amine (**4a**, 173 mg, 1 mmol) in distilled water (30 mL) was stirred at 80 °C for 1 h. The resulting clear yellow solution was allowed to cool to 50 °C and 2,2,2-trinitroethanol (362 mg, 2 mmol) was added. Then the reaction was stirred overnight at ambient temperature. The precipitate was filtered, washed with water, and dried under vacuo. Pale yellow solid (243 mg, 72%). M.p. 163 °C, 171 °C (dec.); ^{1}H NMR: δ 8.13 (s, 1H), 7.21 (s, 1H), 5.04 (d, J = 5.4 Hz, 2H); ^{13}C NMR: δ 140.7, 138.2, 131.2, 127.5, 54.4; ^{15}N NMR: δ −24.14, −30.78 (t, J = 2.03 Hz), −34.01, −135.32 (d, J = 6.08 Hz), −193.57, −309.71 (d, J = 85.68 Hz); IR (KBr pellet): 3210, 3119, 3019, 1616, 1590, 1542, 1463, 1344, 1305, 1207, 1111, 849, 807 cm^{-1}; elemental analysis (%) calcd for $C_5H_4N_8O_{10}$ (336.13): C, 17.87; H, 1.20; N, 33.34; found: C, 18.25; H, 1.27; N, 32.51. Density: 1.83 g cm^{-3}. Impact sensitivity: 2.5 J.

2,4-Dinitro-*N*-(2,2,2-trinitroethyl)-1*H*-imidazol-1-amine (6b). A suspension of 2,4-dinitro-1*H*-imidazol-1-amine (**4b**, 173 mg, 1 mmol) in distilled water (40 mL) was stirred at 80 °C for 1 h. The resulting clear yellow solution was allowed to cool to 50 °C and 2,2,2-trinitroethanol (362 mg, 2 mmol) was added. The reaction was stirred overnight at ambient temperature. The precipitate was filtered, washed with water and dried under vacuum. White solid (204 mg, 61%), 172 °C (dec.); ^{1}H NMR: δ 8.13 (s, 1H), 7.21 (s, 1H); 5.04 (d, J = 5.4 Hz, 2H); ^{13}C NMR: δ 141.4, 140.9, 127.3, 125.8, 54.5; ^{15}N NMR: δ −23.38, −30.75, −32.83, −130.14, −192.82, −304.19 (d, J = 84.67 Hz); IR (KBr pellet): 3275, 3140, 3008, 1597, 1552, 1512, 1340, 1308, 853, 802 cm^{-1}; elemental analysis (%) calcd for $C_5H_4N_8O_{10}$ (336.13): C, 17.87; H, 1.20; N, 33.34; found: C, 17.88; H, 1.21; N, 32.60. Density: 1.84 g cm^{-3}. Impact sensitivity: 7 J.

4-Nitro-*N*-(2,2,2-trinitroethyl)-1*H*-imidazol-1-amine (6c). 2,2,2-Trinitroethanol (543 mg, 2 mmol) was added to a solution of 4-nitro-1*H*-imidazol-1-amine (**4c**, 128 mg, 1 mmol) in water (30 mL) at 50 °C. The resulting solution was stirred at 50 °C until a white precipitate formed. The reaction mixture was cooled and stirred overnight at room temperature. The precipitate was filtered, washed with water and dried under vacuum. White solid (163 mg, 56%), 139 °C (dec.); ^{1}H NMR: δ 7.95 (s, 1H), 7.65 (s, 1H), 6.94 (s, 1H), 4.93 (d, J = 5.1 Hz, 2H); ^{13}C NMR: δ 143.8, 138.5, 133.1, 128.1, 55.0; IR (KBr pellet): 3142, 1590, 1535, 1510, 1381, 1119, 808 cm^{-1}; elemental analysis (%) calcd for $C_5H_5N_7O_8$ (291.14): C, 20.63; H, 1.73; N, 33.68; found: C, 20.81; H, 1.74; N, 33.27. Density: 1.75 g cm^{-3}. Impact sensitivity: 10 J.

5-Azido-4-nitro-*N*-(2,2,2-trinitroethyl)-1*H*-imidazol-1-amine (6d). 2,2,2-Trinitroethanol (543 mg, 3 mmol) was added to the solution of 5-azido-4-nitro-1*H*-imidazol-1-amine (**4d**, 169 mg, 1 mmol) in water (50 mL) at 50 °C. The resulting solution was stirred at 50 °C until a white precipitate was formed. The reaction mixture was cooled and stirred overnight at room temperature. The precipitate was filtered, washed with water and dried under vacuum. White solid (177 mg, 53%), 136 °C (dec.). ^{1}H NMR: δ 7.59 (s, 1H), 6.90 (s, 1H), 4.88 (d, J = 4.5 Hz,

2H); ^{13}C NMR: δ 142.5, 141.1, 128.0,125.2, 55.0; IR (KBr pellet): 3303, 2136, 1605, 1555, 1525, 1408, 1362, 1323, 1175, 803, 775 cm^{-1}; ^{15}N NMR: δ −28.57, −30.25 (t, J = 2.03 Hz), −34.01, −139.31, −142.55, −143.14 (d, J = 6.08 Hz), −199.06, −283.43, −309.37 (d, J = 84.67 Hz); elemental analysis (%) calcd for $C_5H_4N_{10}O_8$ (332.15): C, 18.08; H, 1.21; N, 42.17; found: C, 18.09; H, 1.22; N, 41.11. Density: 1.79 g cm^{-3}. Impact sensitivity: 2 J.

5-Chloro-4-nitro-*N*-(2,2,2-trinitroethyl)-1*H*-imidazol-1-amine (6e). A suspension of 5-chloro-4-nitro-1*H*-imidazol-1-amine (**4e**, 163 mg, 1 mmol) in distilled water (30 mL) was stirred at 80 °C for 1 h. The resulting clear yellow solution was allowed to cool to 50 °C and 2,2,2-trinitroethanol (362 mg, 2 mmol) was added. The reaction was stirred overnight at ambient temperature. The precipitate was filtered, washed with water, and dried under vacuum. White solid (140 mg, 43%), 156 °C (dec.); ^{1}H NMR: δ 8.12 (s, 1H), 6.69 (s, 1H), 4.95 (s, 2H); ^{13}C NMR: δ 144.3, 134.5, 127.6, 123.9, 54.2; IR (KBr pellet): 3215, 3171, 2994, 1604, 1557, 1471, 1381, 1302, 1279, 1124, 997, 801 cm^{-1}; elemental analysis (%) calcd for $C_5H_4ClN_7O_{10}$ (325.58): C, 18.45; H, 1.24; N, 30.11; found: C, 18.52; H, 1.16; N, 29.43. Density: 1.76 g cm^{-3}. Impact sensitivity: 7 J.

Acknowledgements

The authors gratefully acknowledge the support of ONR (N00014-12-1-0536); and (N00014-11-AF-0-0002).

References

1 (*a*) T. M. Klapötke, C. Petermayer, D. G. Piercey and J. Stierstorfer, *J. Am. Chem. Soc.*, 2012, **134**, 20827–20836; (*b*) N. Fischer, D. Fischer, T. M. Klapötke, D. G. Piercey and J. Stierstorfer, *J. Mater. Chem.*, 2012, **22**, 20418–20422; (*c*) H. X. Gao and J. M. Shreeve, *Chem. Rev.*, 2011, **111**, 7377–7436; (*d*) Y. H. Joo and J. M. Shreeve, *Angew. Chem., Int. Ed.*, 2010, **49**, 7320–7323; (*e*) Y. H. Joo and J. M. Shreeve, *J. Am. Chem. Soc.*, 2010, **132**, 15081–15090; (*f*) M. Gobel, K. Karaghiosoff, T. M. Klapötke, D. G. Piercey and J. Stierstorfer, *J. Am. Chem. Soc.*, 2010, **132**, 17216–17226; (*g*) Y. H. Joo and J. M. Shreeve, *Angew. Chem., Int. Ed.*, 2009, **48**, 564–567.

2 (*a*) V. Thottempudi and J. M. Shreeve, *J. Am. Chem. Soc.*, 2011, **133**, 19982–19992; (*b*) V. Thottempudi, H. X. Gao and J. M. Shreeve, *J. Am. Chem. Soc.*, 2011, **133**, 6464–6471; (*c*) G. Herve, C. Roussel and H. Graindorge, *Angew. Chem., Int. Ed.*, 2010, **49**, 3177–3181; (*d*) J. R. Cho, K. J. Kim, S. G. Cho and J. K. Kim, *J. Heterocycl. Chem.*, 2001, **38**, 141–147.

3 (*a*) T. M. Klapötke, F. A. Martin and J. Stierstorfer, *Angew. Chem., Int. Ed.*, 2011, **50**, 4227–4229; (*b*) T. M. Klapötke and J. Stierstorfer, *J. Am. Chem. Soc.*, 2009, **131**, 1122–1134; (*c*) K. Banert, Y. H. Joo, T. Ruffer, B. Walfort and H. Lang, *Angew. Chem., Int. Ed.*, 2007, **46**, 1168–1171; (*d*) M. H. V. Huynh, M. A. Hiskey, D. E. Chavez, D. L. Naud and R. D. Gilardi, *J. Am. Chem. Soc.*, 2005, **127**, 12537–12543; (*e*) M. H. V. Huynh, M. A. Hiskey, J. G. Archuleta, E. L. Roemer and R. Gilardi, *Angew. Chem., Int. Ed.*, 2004, **43**, 5658–5661.

4 (*a*) C. Qi, S. H. Li, Y. C. Li, Y. Wang, X. X. Zhao and S. P. Pang, *Chem.–Eur. J.*, 2012, **18**, 16562–16570; (*b*) C. Qi, S. H. Li, Y. C. Li, Y. A. Wang, X. K. Chen and S. P. Pang, *J. Mater. Chem.*, 2011, **21**, 3221–3225; (*c*) Y. C. Li, C. Qi, S. H. Li, H. J. Zhang, C. H. Sun, Y. Z. Yu and S. P. Pang, *J. Am. Chem. Soc.*, 2010, **139**, 12172–12173.

5 (*a*) V. M. Boddu, D. S. Viswanath, T. K. Ghosh and R. Damavarapu, *J. Hazard. Mater.*, 2010, **181**, 1–8; (*b*) R. D. Schmidt, G. S. Lee, P. R. Pagoria, A. R. Mitchell and R. Gilardi, *J. Heterocycl. Chem.*, 2001, **38**, 1227–1230.

6 (*a*) G. Clavier and P. Audebert, *Chem. Rev.*, 2010, **110**, 3299–3314; (*b*) A. Y. Tyurin, O. Y. Smirnov, A. M. Churakov, Y. A. Strelenko and V. A. Tartakovsky, *Russ. Chem. Bull.*, 2009, **58**, 361–365; (*c*) H. B. Li, B. B. Cheng, H. Z. Li, F. D. Nie, J. S. Li, Z. Huang and S. J. Liu, *Chin. J. Org. Chem.*, 2007, **27**, 112–115; (*d*) A. M. Churakov and V. A. Tartakovsky, *Chem. Rev.*, 2004, **104**, 2601–2616.

7 (*a*) C. E. Gregory, *Explosives for North American Engineers*, Trans Tech Publications, Clausthal-Zellerfeld, Germany, vol. 5, 1984; (*b*) T. L. Davis, *The Chemistry of Powder and Explosives*, Wiley, New York, vol. 2, 1943.

8 (*a*) V. M. Boddu, D. S. Viswanath, T. K. Ghosh and R. Damavarapu, *J. Hazard. Mater.*, 2010, **181**, 1–8; (*b*) J. Sun, B. Kang, C. Xue, Y. Liu, Y. X. Xia, X. F. Liu and W. Zhang, *J. Energ. Mater.*, 2010, **28**, 189–201; (*c*) C. M. Tarver, *J. Phys. Chem. A*, 2010, **114**, 2727–2736.

9 (*a*) A. S. Kumar, V. B. Rao, R. K. Sinha and A. S. Rao, *Propellants, Explos., Pyrotech.*, 2010, **35**, 359–364; (*b*) H. W. Qiu, V. Stepanov, A. R. Di Stasio, T. M. Chou and W. Y. Lee, *J. Hazard. Mater.*, 2011, **185**, 489–493; (*c*) J. D. Zhang, X. L. Cheng and F. Zhao, *Propellants, Explos., Pyrotech.*, 2010, **35**, 315–320.

10 (*a*) C. W. An, J. Y. Wang, W. Z. Xu and F. S. Li, *Propellants, Explos., Pyrotech.*, 2010, **35**, 365–372; (*b*) Y. Bayat, M. Eghdamtalab and V. Zeynali, *J. Energ. Mater.*, 2010, **28**, 273–284; (*c*) Y. Q. Wu and F. L. Huang, *J. Hazard. Mater.*, 2010, **183**, 324–333; (*d*) G. X. Zhang and B. L. Weeks, *Propellants, Explos., Pyrotech.*, 2010, **35**, 440–445.

11 (*a*) G. Herve, G. Jacob and N. Latypov, *Tetrahedron*, 2005, **61**, 6743–6748; (*b*) N. V. Latypov, J. Bergman, A. Langlet, U. Wellmar and U. Bemm, *Tetrahedron*, 1998, **54**, 11525–11536.

12 (*a*) F. H. Crocker, K. J. Indest and H. L. Fredrickson, *Appl. Microbiol. Biotechnol.*, 2006, **73**, 274–290; (*b*) U. R. Nair, R. Sivabalan, G. M. Gore, M. Geetha, S. N. Asthana and H. Singh, *Combust., Explos. Shock Waves*, 2005, **41**, 121–132; (*c*) H. Singh, *Explosion*, 2005, **15**, 120–132; (*d*) S. V. Sysolyatin, A. A. Lobanova, Y. T. Chernikova and G. V. Sakovich, *Russ. Chem. Rev.*, 2005, **74**, 757–764.

13 (*a*) T. N. Hall, *Tetrahedron*, 1963, **19**, 115–120; (*b*) K. F. Mueller, R. H. Renner, W. H. Gilligan, H. G. Adolph and M. J. Kamlet, *Combust. Flame*, 1983, **50**, 341–349; (*c*) F. R. Schenck and G. A. Wetterholm, *U.S. Pat.*, 2 731 460, 1956; (*d*) R. Schenck and G. A. Wetterholm, *Chem. Abstr.*, 1956, **50**, 7125; (*e*) L. O. Atovmyan, R. G. Gafurov, N. I. Golovina, L. T. Eremenko and B. S. Fedorov, *Zh. Strukt. Khim.*, 1980, **21**, 135–141; (*f*) L. O. Atovmyan,

N. I. Golovina, L. T. Eremenko, N. G. Zhitomirskaya, G. V. Oreshko and M. A. Fadeev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1984, 549–555; (*g*) M. D. Lind, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1970, **26**, 590–596; (*h*) T. M. Klapötke, B. Krumm, M. Scherr, G. Spier and F. X. Steemann, *Z. Anorg. Allg. Chem.*, 2008, **634**, 1244–1246; (*i*) N. I. Golovina, L. O. Atovmyan, N. V. Chukanov, G. V. Oreshko, R. F. Trofimova, M. A. Fadeev and L. T. Eremenko, *Zh. Strukt. Khim.*, 1990, **31**, 126–131.

14 (*a*) V. Thottempudi, F. Forohor, D. A. Parrish and J. M. Shreeve, *Angew. Chem., Int. Ed.*, 2012, **51**, 9881–9885; (*b*) E. V. Tatarnikova, V. V. Sizov and I. V. Tselinskii, *Russ. J. Org. Chem.*, 2009, **45**, 872–878; (*c*) E. V. Tatarnikova, V. V. Sizov, A. V. Aleksandrov and I. V. Tselinskii, *Russ. J. Org. Chem.*, 2009, **45**, 1523–1527.

15 (*a*) T. M. Klapötke, D. G. Piercey and J. Stierstorfer, *Dalton Trans.*, 2012, **41**, 9451–9459; (*b*) Y. Q. Zhang, D. A. Parrish and J. M. Shreeve, *J. Mater. Chem. A*, 2013, **1**, 585–593; (*c*) G. Herve, C. Roussel and H. Graindorge, *Angew. Chem., Int. Ed.*, 2010, **49**, 3177–3181.

16 (*a*) N. Latypov, G. Jacob, P. Goede, G. Herve and S. Ek, *New Trends in Research of Energetic Materials, Proceedings of the 12th Seminar*, Pardubice, Czech Republic, 2009, vol. 2, pp. 494–500; (*b*) T. M. Klapötke, C. M. Sabate and J. Stierstorfer, *New J. Chem.*, 2009, **33**, 136–147; (*c*) A. C. Tome, *Sci. Synth.*, 2004, **13**, 415–601; (*d*) T. I. Godovikova, S. A. Vozchikova, E. L. Ignat'eva, L. I. Khmel'nitskii and B. L. Korsunskii, *Chem. Heterocycl. Compd.*, 2000, **35**, 1176–1182.

17 (*a*) Y. Li, W. Liu and S. Pang, *Molecules*, 2012, **17**, 5040–5049; (*b*) I. V. Tselinskii, V. V. Tolstyakov, S. M. Putis and S. F. Mel'nikova, *Russ. Chem. Bull.*, 2009, **58**, 2356–2361; (*c*) O. P. Shitov, V. L. Korolev and V. A. Tartakovsky, *Russ. Chem. Bull.*, 2009, **58**, 2347–2355; (*d*) I. B. Starchenkov, V. G. Andrianov and A. F. Mishnev, *Chem. Heterocycl. Compd.*, 1999, **34**, 1081–1085; (*e*) G. I. Koldobskii, D. S. Soldatenko, E. S. Gerasimova, N. R. Khokhryakova, M. B. Shcherbinin, V. P. Lebedev and V. A. Ostrovskii, *Russ. J. Org. Chem.*, 1997, **33**, 1771–1783; (*f*) A. R. Katritzky, J. Wu, L. Wrobel, S. Rachwal and P. J. Steel, *Acta Chem. Scand.*, 1993, **47**, 167–175.

18 R. Duddu, P. R. Dave, R. Damavarapu, N. Gelber and D. Parrish, *Tetrahedron Lett.*, 2010, **51**, 399–401.

19 (*a*) M. Gobel and T. M. Klapotke, *Adv. Funct. Mater.*, 2009, **19**, 347–365; (*b*) I. V. Ovchinnikov, A. S. Kulikov, M. A. Epishina, N. N. Makhova and V. A. Tartakovsky, *Russ. Chem. Bull.*, 2005, **54**, 1346–1349.

20 (*a*) S. Bulusu, R. Damavarapu, J. R. Autera, R. Behrens, Jr, L. M. Minier, J. Villanueva, K. Jayasuriya and T. Axenrod, *J. Phys. Chem.*, 1995, **99**, 5009–5015, and references therein; (*b*) S. G. Cho, Y. G. Cheun and B. S. Park, *THEOCHEM*, 1998, **432**, 41–53; (*c*) M. D. Coburn, *U.S. Pat.* 4028154, 1977; (*d*) S. G. Cho, B. S. Park and J. R. Cho, *Propellants, Explos., Pyrotech.*, 1999, **24**, 343–348; (*e*) H. X. Gao, C. F. Ye, O. D. Gupta, J. C. Xiao, M. A. Hiskey, B. Twamley and J. M. Shreeve, *Chem.–Eur. J.*, 2007, **13**, 3853–3860; (*f*) T. M. Klapötke, A. Preimesser and J. Stierstorfer, *Z. Anorg. Allg. Chem.*, 2012, **638**, 1278–1286.

21 (*a*) V. M. Vinogradov, I. L. Dalinger and S. A. Shevelev, *Khim.-Farm. Zh.*, 1994, **28**, 37–46; (*b*) A. Ohsawa, H. Arai, H. Ohnishi, T. Itoh, T. Kaihoh, M. Okada and H. Igeta, *J. Org. Chem.*, 1985, **50**, 5520–5523.

22 V. S. Mokrushin, I. S. Selezneva, T. A. Pospelova, V. K. Usova, S. M. Malinskaya, G. M. Anoshina, T. E. Zubova and Z. V. Pushkareva, *Khim.-Farm. Zh.*, 1982, **16**, 303–307.

23 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, 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, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, A. L. G. Liu, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03, Revision D. 01*, Gaussian, Inc., Wallingford, CT, 2004.

24 Bruker, APEX2v2010.3-0, Bruker AXS Inc., Madison, Wisconsin, USA, 2010.

25 Bruker, SAINT v7.68A, Bruker AXS Inc., Madison, Wisconsin, USA, 2009.

26 Bruker, XPREP v2008/2, Bruker AXS Inc., Madison, Wisconsin, USA, 2008.

27 Bruker, SADABS v2008/1, Bruker AXS Inc., Madison, Wisconsin, USA, 2008.

28 Bruker, SHELXTL v2008/4, Bruker AXS Inc., Madison, Wisconsin, USA, 2008.

29 (*a*) M. S. Westwell, M. S. Searle, D. J. Wales and D. H. Williams, *J. Am. Chem. Soc.*, 1995, **117**, 5013–5015; (*b*) A. A. Dippold, T. M. Klapötke and N. Winter, *Eur. J. Inorg. Chem.*, 2012, 3474–3484.

30 (*a*) M. Smiglak, C. C. Hines, T. B. Wilson, S. Singh, A. S. Vincek, K. Kirichenko, A. R. Katritzky and R. D. Rogers, *Chem.–Eur. J.*, 2010, **16**, 1572–1584; (*b*) M. R. Grimmett, S.-T. Hua, K. C. Chang, S. A. Foley and J. Simpson, *Aust. J. Chem.*, 1989, **42**, 1281–1289.

31 K. C. Agrawal, K. B. Bears, R. K. Sehgal, J. N. Brown, P. E. Rist and W. D. Rupp, *J. Med. Chem.*, 1979, **22**, 583–586.

32 M. M. Breiner, D. E. Chavez and D. A. Parrish, *Synlett*, 2013, 519–521.

33 P. Melloni, W. Logemann and C. I. De Erba, Ger. Offen. DE 2149825A, 1972.