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Synthesis, single crystal structure and performance of N-substituted derivatives of dinitroimidazole†

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Kehui Hou,‡ Congming Ma‡ and Zuliang Liu*

The N-substituted derivatives of dinitroimidazoles have been synthesized for application as energetic materials. The synthesized compounds were fully characterized by ^{1}H ^{13}C NMR spectroscopy and elemental analysis. Most of them were determined by single crystal X-ray diffraction. The calculated densities of the compounds range between 1.89 and 1.91 g cm^{-3} and the experimental densities between 1.75 and 1.84 g cm^{-3}, as obtained by X-ray crystallographic analysis. Notably, densities of the N-substituted derivatives of dinitroimidazoles are increased when two amino groups are introduced but decreased when one amino group is introduced.

Introduction

The synthesis and development of new, insensitive energetic materials that contain aromatic nitrogen-containing heterocyclic core units have attracted attention due to their more favorable elemental composition with relatively higher energetic performance with regard to oxygen balance, density, and other thermodynamic properties when compared to their carbon-only analogous aromatic compounds.[1–4]

It has been reported in the literature that imidazole derivatives with two or more than two nitro groups have been predicted to be highly powerful, but insensitive explosives.[5–9] 4,5-Dinitroimidazole crystallizes with two crystallographically unique molecules in the monoclinic space group $P2_1/n$ with unit cell parameters a = 11.5360(8) Å, b = 9.071(1) Å, c = 11.822(1) Å, Z = 8, and has a density of 1.781 g cm^{-3}.[10] 2,4-Dinitroimidazole crystallizes in the orthorhombic space group *Pbca* with unit cell parameters a = 110.127(2) Å, b = 18.497(2) Å, c = 6.333(2) Å, Z = 8, and has a density of 1.770 g cm^{-3}.[11] Cho *et al.*'s study[5] showed that 1-methyl-2,4,5-trinitroimidazole is a promising candidate as a highly insensitive explosive, with explosive performance comparable to that of Hexogen (RDX). H. S. Jadhav and co-workers[2] reported the synthesis and characterization of *N*-methyl, *N*-ester and *N*-picryl derivatives of 2,4,5-trinitroimidazole using triiodoimidazole as substrate. R. Duddu and co-workers[6] developed a new, molten-state nitration method for the synthesis of 1-methyl-2,4,5-trinitroimidazole. 1-(2,4,6-Tri-nitrophenyl)-2,4-dinitroimidazole was obtained by the reaction of picryl fluoride with 2,4-dinitroimidazole in the literature, the same as for 1-(2,4,6-trinitrophenyl)-4,5-dinitroimidazole.[12]

The substituted combination of amino and nitro groups provides the inter and intra molecular hydrogen bonding that stabilizes the molecule and increases the crystal density. It is with this background and in continuation of our effort aimed at synthesis of new dinitroimidazole-based energetic materials that we have focused on the 2,4- and 4,5-dinitroimidazoles with one 2,4,5-trinitrophenyl substituent including either 0, 1 or 2 amino groups inside, evaluated their performance by using DFT and the nitrogen equivalent equation, analyzed the single crystal structure and laid special stress on studying the effect of substituent groups on the spatial arrangement.

Results and discussion

Theoretical study

The heat of formation (HOF) and density are important parameters in evaluating the performance of energetic materials. We have calculated energetic properties of the compounds **1–6** by using DFT. The gas-phase HOF values (ΔH_f^o gas) have been predicted by designing appropriate isodesmic reactions.[13,14]

Calculations were carried out using the Gaussian 09 program suite.[15] The geometry optimization of the structures and frequency analyses were carried out using the B3LYP functional with the 6-31G* basis set.[16] All of the optimized structures were characterized by true local energy minima on the potential-energy surface without imaginary frequencies. The designed

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School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing 210094, PR China. E-mail: liuzl@mail.njust.edu.cn; Fax: +86-25-8431-5030; Tel: +86-25-8431-8865

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‡ These authors contributed equally to this work and should be considered co-first authors.

isodesmic reactions for the prediction of (ΔH_f^o gas) are discussed in the ESI.†

Detonation velocity (D) and detonation pressure (P) are the most important targets for scaling the detonation characteristics of energetic materials. For the explosives with CHNO elements, the Kamlet–Jacobs empirical equations[17] and the nitrogen equivalent equation (NE equation)[18] were used to determine these parameters.

Kamlet–Jacobs empirical equations:

$$D = 1.01\,(NM^{0.5}Q^{0.5})^{0.5}(1 + 1.30\rho_o)$$

$$P = 1.55{\rho_o}^2\,NM^{0.5}Q^{0.5}$$

where D is the detonation velocity in km s^{-1}, P is the detonation pressure in GPa, N is moles of gaseous detonation products per gram of explosives, M is the average molecular weight of gaseous products, Q is the energy of explosion in J g^{-1} of the explosive and ρ_o is the crystal density in g cm^{-3}. N, M and Q are determined according to the largest exothermic principle, *i.e.*, for the explosives with CHNO elements, all the N atom converts into N_2, the O atom forms H_2O with the H atom first and the remainder forms CO_2 with the C atom. The remainder of the C atom will exist in solid state if the O atom does not satisfy full oxidation of the C atom. The remainder of the O atom will exist as O_2 if the O atom is superfluous.

Nitrogen equivalent equation (NE equation):

$$D = (690 + 1160\rho_0)\sum N$$

$$P = 1.092(\rho_0\sum N)2 - 0.574$$

$$\sum N = (100\sum x_iN_i)/M$$

in which D represents the detonation velocity of an explosive in m s^{-1}, ρ_0 represents the density of an explosive in g cm^{-3}, $\sum N$ represents the nitrogen equivalent of the detonation products, N_i is the nitrogen equivalent index of a certain detonation product, x_i is the mole number of a certain detonation product produced by one mole of the explosive.

Energetic properties

The energetic properties data of the compounds are listed in Table 1. When compared with compound **4**, it appears that introduction of an additional amino group in **5** and **6** increases the density but decreases the performance. A similar trend is observed for compounds **1**, **2**, and **3**. Oxygen balance (OB) is the number of moles of oxygen required by a compound in excess to the oxygen chemically bound within the molecule for complete combustion (negative OB) or excess number of moles of oxygen chemically bound within a molecule more than required for its complete combustion (positive OB). The sensitivity, strength, and stability of an explosive are all to some extent dependent upon the oxygen balance. Although all of the described compounds in this study have negative OB values, most of them have a better oxygen balance than TNT (−74%).

The enthalpy of formation is one of the most important parameters to be considered in the design of energetic materials. Compounds **1** to **6** have positive heats of formation. The calculated densities of the other compounds range between 1.89 and 1.91 g cm^{-3} and the experimental densities between 1.75 and 1.84 g cm^{-3}, as obtained by X-ray crystallographic analysis. The calculated detonation pressures (P) for the dinitroimidazole derivatives fall in the range of 31.36 to 32.82 GPa and the detonation velocities (D) are distributed from 8.28 to 8.48 km s^{-1}. All of those are close to the empirical calculation, 29.12 to 32.49 GPa and 8.11 to 8.44 km s^{-1}, respectively, predicted with the nitrogen equivalent equation.

X-ray crystallography

The colorless single crystals of title compounds were selected for X-ray diffraction analysis. The data were collected using a Nonius cad4 detector equipped with a graphite-monochromatic MoKα radiation (λ = 0.71073 Å) using a $\omega/2\theta$ scan mode at 293(2) K. The structure was solved by direct methods and expanded by difference Fourier techniques with SHELXL-97 program. The non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were added according to the theoretical models. The structure was refined by full-matrix least-squares techniques on F^2 with SHELXL-97. Crystallographic data for compounds **1**, **3**, **4**, **5** and **6** are summarized in Table 2. Selected bond lengths and angles for compounds are listed in the ESI.† Further information concerning the crystal-structure determinations in CIF format is available from the Cambridge Crystallographic Data Centre.[19] Compounds **1**, **3**, **4**, **5** and **6** are also characterized by a three-dimensional network.

The bonds of C(1)–N(3), C(3)–N(4) of the nitro groups in **1** are not coplanar with the imidazole ring and displaced by 0.019 Å and 0.027 Å from the imidazole ring, respectively. The 2- and 4-nitro groups are also twisted out of the imidazole plane by 6.20° and 12.35°, respectively. The bonds of C(5)–N(5), C(7)–N(6) and C(9)–N(7) of the nitro groups are not coplanar with the

Table 1 Calculated energetic properties of dinitroimidazole derivatives

Compound	OB[a] [%]	HOF[b] [kJ mol^{-1}]	V [cm^3 mol^{-1}]	Density [g cm^{-3}]	D[c] [km s^{-1}]	P[d] [GPa]	Q[e] [J g^{-1}]
1	−41.19	251.9016	194.9999	1.892	8.27/8.11	31.26/29.12	1632.416
2	−41.67	213.3052	200.6145	1.914	8.32/—	31.81/—	1413.471
3	−42.11	180.4869	209.3913	1.906	8.27/8.44	31.36/32.49	1354.141
4	−41.19	277.1873	194.577	1.896	8.31/8.30	31.57/30.99	1497.748
5	−41.67	236.0061	202.3449	1.898	8.29/8.16	31.43/29.57	1427.600
6	−42.11	205.3951	209.7513	1.902	8.28/8.40	31.42/31.99	1369.06

[a] Oxygen balance. [b] Gas-phase HOF. [c] Detonation velocity: the left value is calculated by DFT, the right value is calculated by the NE equation. [d] Detonation pressure: the left value is calculated by DFT, the right value is calculated by the NE equation. [e] Chemical energy of detonation.

Table 2 Crystallographic and refinement data for some compounds

	1	3	4	5	6
CCDC	884547	888387	884548	884549	884546
Formula	$C_9H_3N_7O_{10}$	$C_9H_5N_9O_{10}$	$C_9H_3N_7O_{10}$	$C_9H_4N_8O_{10}$	$C_9H_5N_9O_{10}$
M_r [g mol^{-1}]	369.18	399.22	369.18	384.20	399.22
Temperature	293	293	293	293	293
Crystal system	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$P2_1/N$	$P2_1/N$	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
a (Å)	8.7000(17)	9.0830(18)	8.2370(16)	8.4941(7)	9.1580(18)
b (Å)	11.397(2)	11.395(2)	12.791(3)	12.7651(10)	12.318(3)
c (Å)	14.164(3)	14.089(3)	12.916(3)	13.3699(12)	12.862(3)
V (Å^3)	1403.1(5)	1439.3(5)	1360.8(5)	1449.7(2)	1450.9(5)
Z	4	4	4	4	4
Dc	1.748	1.842	1.802	1.760	1.828
R_1, wR_2 (observed reflections)	0.0508, 0.1398	0.0505, 0.1081	0.0608, 0.1465	0.0780, 0.1453	0.0535, 0.1381

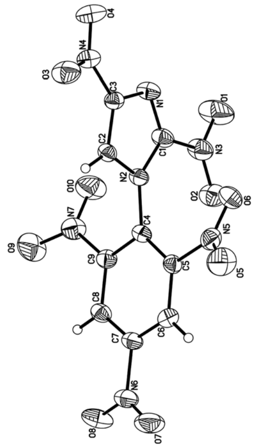
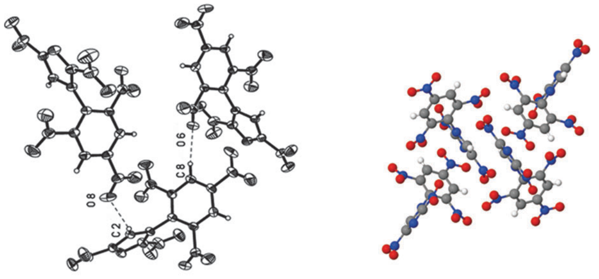


Fig. 1 Molecular structure of 1-(2,4,6-trinitrophenyl)-2,4-dinitroimidazole (**1**). Thermal ellipsoids are set to 50% probability.



(a) (b)

Fig. 2 (a) Hydrogen-bonding scheme in the crystal structure of compound **1**. Thermal ellipsoids are set to 50% probability. Symmetry operators: (a) −1/2 − *x*, 1/2 + *y*, 1/2 − *z* (b) −1/2 + *x*, 1/2 − *y*, −1/2 + *z*; (b) the spatial arrangement of four molecules in the unit cell of **1** viewed along the *a* axis.

Table 3 Hydrogen bonds present in compound **1**

D–H···A	d(D–H) [Å]	d(H···A) [Å]	d(D–H···A) [Å]	∠(D–H···A) [°]
C2–H2A···O8[a]	0.93	2.53	3.354(4)	147
C8–H8A···O6[b]	0.93	2.40	3.324(4)	173

[a] Symmetry operators: −1/2 − *x*, 1/2 + *y*, 1/2 − *z*. [b] Symmetry operators: −1/2 + *x*, 1/2 − *y*, −1/2 + *z*.

benzene ring and displaced by 0.013 Å, 0.017 Å and 0.028 Å from the benzene ring, respectively. And the corresponding nitro groups are also twisted out of the benzene plane by 28.22°, 6.40° and 29.25°, respectively. Furthermore, the angle of the imidazole plane and the benzene plane is 86.32° (Fig. 1).

Further investigation on hydrogen bonds within the crystal structure of compound **1** shows that three intermolecular interactions including the formation of two intermolecular hydrogen bonds, that is C8–H8A···O6 and C2–H2A···O8, could be observed (Fig. 2a and Table 3). Considering the withdrawing effect of two nitro groups on both sides of C(8E)–H, this hydrogen atom behaves as an approximately naked proton, and can easily form a hydrogen bond with the nitro group of another molecule, so is C(2E)–H. The spatial arrangement of four molecules in the unit cell is presented in Fig. 2(b), as viewed along the *a* axis.

The bonds of C(9)–N(8), C(8)–N(9) of the nitro groups in **3** are displaced by 0.042 Å and 0.068 Å from the imidazole ring and the 2- and 4-nitro groups are twisted out of the imidazole plane by 2.59° and 8.84°, respectively. The bonds of C(1)–N(1), C(3)–N(3) and C(5)–N(5) of the nitro groups are displaced by 0.068 Å, 0.126 Å and 0.157 Å from the benzene ring and the corresponding nitro groups are twisted out of the benzene plane by 25.71°, 7.60° and 33.72°, respectively. The bonds of C(2)–N(2) and C(4)–N(4) of the amino groups are also displaced by 0.039 and 0.153 Å from the benzene ring, and the corresponding amino groups are twisted out of the benzene plane by 3.05 and 4.95°, respectively. Furthermore, the angle of the imidazole plane and the benzene plane is 86.39° (Fig. 3).

Further investigation on hydrogen bonds within the crystal structure of compound **3** shows that four intermolecular interactions including the formation of four intermolecular hydrogen bonds, that is N2–H2B···O2, N4–H4A···O1, N2–H2A···O2 and N4–H4B···O5, could be observed (Fig. 4a). And intramolecular hydrogen bonds formed between NH_2 and 4′-NO_2 are stronger than 2′(6′)-NO_2 (Table 4) because NH_2 and 4′-NO_2 groups are nearly coplanar with the benzene plane compared with 2′(6′)-NO_2. The spatial arrangement of four molecules in the unit cell viewed along the *a* axis is presented in Fig. 4(b).

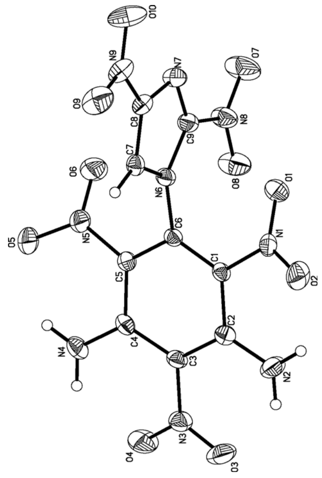


Fig. 3 Molecular structure of 1-(3,5-diamino-2,4,6-trinitrophenyl)-2,4-dinitroimidazole (**3**). Thermal ellipsoids are set to 50% probability.

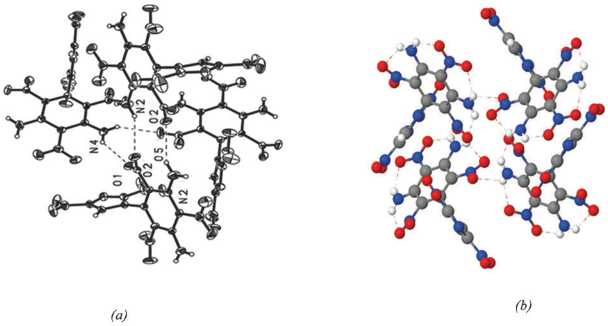


Fig. 4 (a) Hydrogen-bonding scheme in the crystal structure of compound **3**. Thermal ellipsoids are set to 50% probability. Symmetry operators: (a) −*x*, 1 − *y*, 1 − *z*; (b) −1/2 + *x*, 1/2 − *y*, 1/2 − *z*; (c) −*x*, −*y*, 2 − *z*; (b) the spatial arrangement of four molecules in the unit cell of **3** viewed along the *a* axis.

Table 4 Hydrogen bonds present in compound **3**

D–H···A	*d*(D–H) [Å]	*d*(H···A) [Å]	*d*(D–H···A) [Å]	∠(D–H···A) [°]
N2–H2A···O3	0.86	1.89	2.531(4)	130
N2–H2B···O2	0.86	1.98	2.610(4)	129
N2–H2B···O2[a]	0.86	2.54	3.326(3)	152
N4–H4A···O4	0.86	1.91	2.534(3)	128
N4–H4A···O1[b]	0.86	2.20	2.828(3)	130
N4–H4B···O5	0.86	1.97	2.619(4)	131
N4–H4B···O5[c]	0.86	2.59	3.354(3)	149

[a] Symmetry operators: −*x*, 1 − *y*, 1 − *z*. [b] Symmetry operators: −1/2 + *x*, 1/2 − *y*, 1/2 − *z*. [c] Symmetry operators: −*x*, −*y*, 2 − *z*.

The bonds of C(2)–N(3), C(3)–N(4) of the nitro groups in 4 are displaced by 0.119 Å and 0.037 Å from the imidazole ring and the 4- and 5-nitro groups are also twisted out of the imidazole plane by 12.43° and 35.11°, respectively. The bonds of C(5)–N(5), C(7)–N(6) and C(9)–N(7) of the nitro groups are displaced by 0.001 Å, 0.074 Å and 0.093 Å from the benzene ring and the corresponding nitro groups are twisted out of the benzene plane by 61.95°, 2.07° and 7.43°, respectively. Furthermore, the angle of the imidazole plane and the benzene plane is 77.51° (Fig. 5).

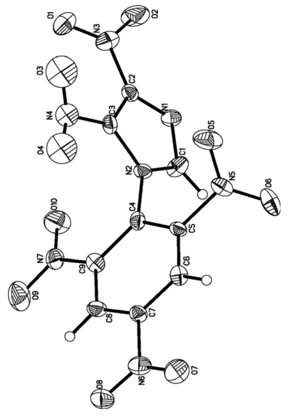


Fig. 5 Molecular structure of 1-(2,4,6-trinitrophenyl)-4,5-dinitroimidazole (**4**). Thermal ellipsoids are set to 50% probability.

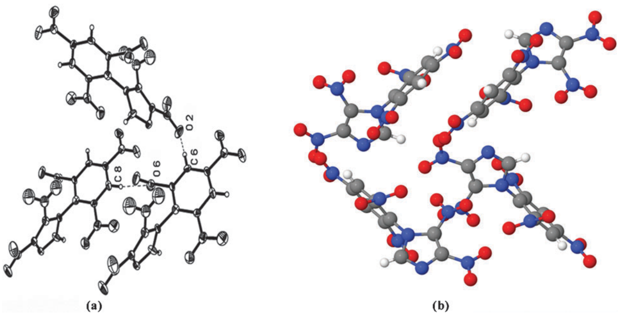


Fig. 6 (a) Hydrogen-bonding scheme in the crystal structure of compound **4**. Thermal ellipsoids are set to 50% probability. Symmetry operators: (a) 2 − *x*, 1/2 + *y*, 3/2 − *z*; (b) −1 + *x*, *y*, *z*; (b) the spatial arrangement of four molecules in the unit cell of **4** viewed along the *a* axis.

Further investigation on hydrogen bonds within the crystal structure of compound **4** shows that three intermolecular interactions including the formation of two intermolecular hydrogen bonds, that is C6–H6A···O2 and C8–H8A···O6, could be observed (Fig. 6a and Table 5). The spatial arrangement of four molecules in the unit cell viewed along the *a* axis (Fig. 6b) is different from **1** because 4-NO_2 of imidazole formed a hydrogen bond not 2-H of it. The bigger angle of 2′-NO_2 with the benzene plane (61.95°) may be another reason.

The bonds of C(2)–N(3), C(3)–N(4) of the nitro groups in 5 are displaced by 0.043 Å and 0.107 Å from the imidazole ring and the 4- and 5-nitro groups are twisted out of the imidazole plane by 1.93° and 35.49°, respectively. The bonds of C(5)–N(5), C(7)–N(6) and C(9)–N(8) of the nitro groups are displaced by 0.004, 0.025 and 0.015 Å from the benzene ring and the corresponding

Table 5 Hydrogen bonds present in compound **4**

D–H···A	*d*(D–H) [Å]	*d*(H···A) [Å]	*d*(D–H···A) [Å]	∠(D–H···A) [°]
C6–H6A···O2[a]	0.93	2.45	3.348(8)	162
C8–H8A···O6[b]	0.93	2.45	3.373(7)	169

[a] Symmetry operators: 2 − *x*, 1/2 + *y*, 3/2 − *z*. [b] Symmetry operators: −1 + *x*, *y*, *z*.

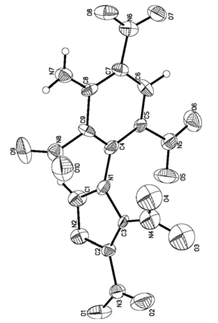


Fig. 7 Molecular structure of 1-(3-amino-2,4,6-trinitrophenyl)-4,5-dinitroimidazole (**5**). Thermal ellipsoids are set to 50% probability.

nitro groups are also twisted out of the benzene plane by 6.18°, 3.73° and 89.12°, respectively. The bonds of C(8)–N(7) of the amino group is also displaced by 0.038 Å from the benzene ring, and twisted out of the benzene plane by 1.85°. Furthermore, the angle of the imidazole plane and the benzene plane is 80.79° (Fig. 7).

Further investigation on hydrogen bonds within the crystal structure of compound **5** shows that three intermolecular interactions including the formation of two weak intermolecular hydrogen bonds, that is N7–H7B···N2, could be observed (Fig. 8a and Table 6). And in this case, we find that it is the 3-N of imidazole owing lone pair electrons that formed an intramolecular hydrogen bond with NH_2 of another molecule, and the spatial arrangement of four molecules in the unit cell (Fig. 8b) is looser than in compound **4** due to the nearly vertical angle of 2′-NO_2 on the NH_2 side with the benzene plane (89.12°) which does not form a hydrogen bond with NH_2.

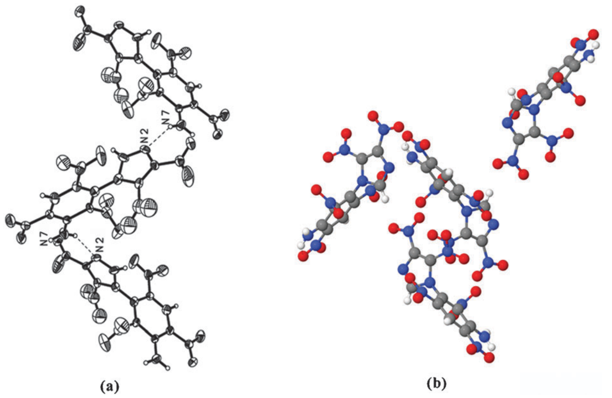


Fig. 8 (a) Hydrogen-bonding scheme in the crystal structure of compound **5**. Thermal ellipsoids are set to 50% probability. Symmetry operators: (a) 1/2 − *x*, −*y*, −1/2 + *z*; (b) the spatial arrangement of four molecules in the unit cell of **5** viewed along the *a* axis.

Table 6 Hydrogen bonds present in compound **5**

D–H···A	*d*(D–H) [Å]	*d*(H···A) [Å]	*d*(D–H···A) [Å]	∠(D–H···A) [°]
N7–H7A···O8	0.86	2.04	2.639(11)	126
N7–H7B···N2[a]	0.86	2.30	3.097(11)	153

[a] Symmetry operators: 1/2 − *x*, −*y*, −1/2 + *z*.

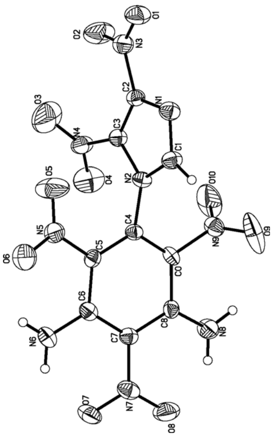


Fig. 9 Molecular structure of 1-(3,5-diamino-2,4,6-trinitrophenyl)-4,5-dinitroimidazole (**6**). Thermal ellipsoids are set to 50% probability.

The bonds of C(2)–N(3), C(3)–N(4) of the nitro groups in **6** are displaced by 0.016 Å and 0.014 Å from the imidazole ring and the 4- and 5-nitro groups are also twisted out of the imidazole plane by 0.69° and 33.5°, respectively. The bonds of C(5)–N(5), C(7)–N(7) and C(9)–N(9) of the nitro groups are displaced by 0.079 Å, 0.088 Å and 0.009 Å from the benzene ring and the corresponding nitro groups are also twisted out of the benzene plane by 14.83°, 12.42°, and 73.34°, respectively. The bonds of C(6)–N(6) and C(8)–N(8) of the amino groups are also displaced by 0.117 and 0.048 Å from the benzene ring, and twisted out of the benzene plane by 3.85 and 1.93°, respectively. Furthermore, the angle of the imidazole plane and the benzene plane is 77.19° (Fig. 9).

Further investigation on hydrogen bonds within the crystal structure of compound **6** shows that four intermolecular interactions including the formation of three intermolecular hydrogen bonds, that is N6–H6B···O9, N8–H8A···O4 and N8–H8B···N1, could be observed (Fig. 10a and Table 7). The spatial arrangement of four molecules in the unit cell (Fig. 10b) is the same as in **4** but more compact than in **4** due to the intermolecular and intramolecular hydrogen bonds formed between NH_2 and NO_2. And it is looser than in **3** due to the approximate vertical angle of 2′-NO_2

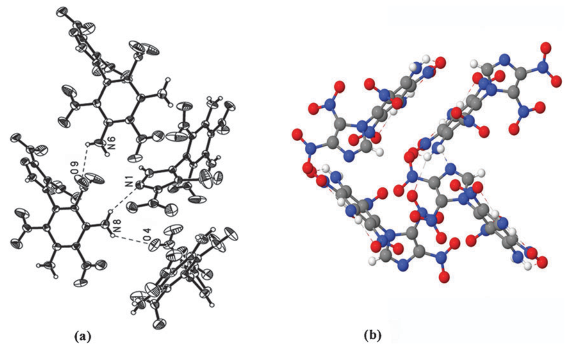


Fig. 10 (a) Hydrogen-bonding scheme in the crystal structure of compound **6**. Thermal ellipsoids are set to 50% probability. Symmetry operators: (a) 1 + *x*, *y*, *z*; (b) 1/2 − *x*, 1 − *y*, 1/2 + *z*; (c) −*x*, 1/2 + *y*, 3/2 − *z*; (b) the spatial arrangement of four molecules in the unit cell of **6** viewed along the *a* axis.

Table 7 Hydrogen bonds present in compound **6**

D–H···A	d(D–H) [Å]	d(H···A) [Å]	d(D–H···A) [Å]	∠(D–H···A) [°]
N6–H6A···O7	0.86	1.89	2.551(8)	132
N6–H6B···O6	0.86	1.96	2.580(8)	128
N6–H6B···O9[a]	0.86	2.45	2.911(7)	114
N8–H8A···O8	0.86	1.93	2.540(8)	127
N8–H8A···O4[b]	0.86	2.46	3.145(7)	137
N8–H8B···O9	0.86	2.51	3.015(8)	118
N8–H8B···N1[c]	0.86	2.35	3.146(7)	154

[a] Symmetry operators: $1 + x, y, z$. [b] Symmetry operators: $1/2 - x, 1 - y, 1/2 + z$. [c] Symmetry operators: $-x, 1/2 + y, 3/2 - z$.

with the benzene plane (73.34°) which does not form a hydrogen bond with adjacent NH_2 but can form an intermolecular hydrogen bond with NH_2 of another molecule, making it different from **5**.

Forming intermolecular hydrogen bonds in different ways leads to different spatial arrangements of four molecules in the unit cell. For compound **1**, hydrogen atoms of imidazole and benzene form intermolecular hydrogen bonds with $-NO_2$ on the benzene ring of another molecule. For **3**, NH_2 on the benzene ring only forms intermolecular hydrogen bonds with $-NO_2$ on the benzene ring of another molecule. For **4**, 4-NO_2 of imidazole formed hydrogen bonds with H on the benzene ring of another molecule. For **5**, NH_2 only formed intermolecular hydrogen bonds with N owing lone pair electrons on the imidazole ring of another molecule. For **6**, an amino group formed intermolecular hydrogen bonds both with 3-N owing lone pair electrons on the imidazole ring of another molecule and 5-NO_2 on the imidazole ring of the third molecule, and the 2′-NO_2 which has an approximately vertical angle with the benzene plane forms intermolecular hydrogen bonds with NH_2 of the fourth molecule.

The results showed that when $-NH_2$ groups are introduced into the benzene ring, the spatial arrangement of four molecules in the unit cell has changed. It also indicates that the densities are increased when two amino groups are introduced (Table 2, compounds **1** and **3**, **4** and **6**), due to the formation of intermolecular and intramolecular hydrogen bonds, but decreased when one amino group is introduced (Table 2, compounds **4** and **5**), due to the nearly vertical angle of NO_2 on the NH_2 side with the benzene plane which does not form hydrogen bonds with NH_2.

The thermal stabilities of the related compounds were studied by differential scanning calorimetry (DSC) at a heating rate of 10 °C min^{-1} (Fig. 11 and 12). For **1** and **4**, no amino groups inside, they all have a melting point, but for **2**, **3**, **5** and **6**, substituents including either 1 or 2 amino groups inside, there are only exotherm peaks. All of the derivatives decomposed between 250 and 350 °C, and their thermal stability decreased as the number of amino groups increased, this is unexpected as the substituted combination of amino and nitro groups can stabilize the molecule.

Overall, based upon their performance parameters, these compounds are especially promising candidates for energetic materials and are all thermally stable, since they all decomposed at high temperatures.

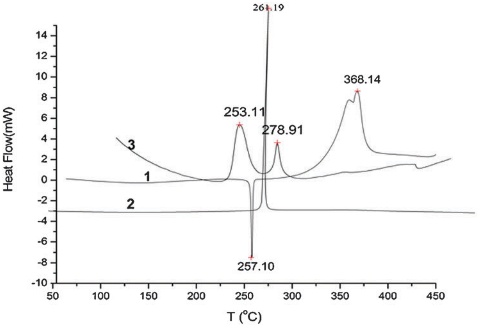


Fig. 11 DSC thermograms of compounds **1–3** (**2,4-DNI** derivatives, heating rate: 10 °C min^{-1}).

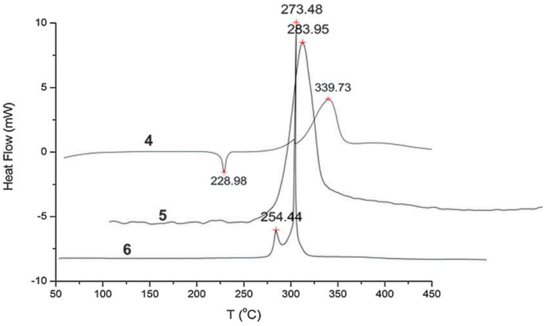


Fig. 12 DSC thermograms of compounds **4–6** (**4,5-DNI** derivatives, heating rate: 10 °C min^{-1}).

Conclusion

In summary, we have synthesized a number of dinitroimidazole derivatives using simple, scalable methods without the need for complicated purification procedures. Single-crystal X-ray measurements were accomplished for compounds **1**, **3**, **4**, **5** and **6** and deliver insights into their structural characteristics. All of these derivatives have a relatively high decomposition temperature (250 to 350 °C), and their thermal stability decreased as the number of amino groups increased.

Experimental section

Caution

The titled compounds are energetic materials and tend to explode under certain conditions. Appropriate protective measures (safety glasses, face shields, leather coat, ear plugs and earthing equipment and person) should be taken during the synthesis, test and measurement processes, especially when these compounds are prepared on a larger scale.

Materials and instruments

The starting materials used in the present study were of AR grade and purchased from the trade. 2,4-Dinitroimidazole (**2,4-DNI**) was prepared from commercially available 4-nitroimidazole with the total yield of 83% by following the method of Cho *et al.*,[5] and 4,5-dinitroimidazole (**4,5-DNI**) was obtained by nitration of 4-nitroimidazole with the yield of 75%.[20] Picryl chloride (**a**), 3-chloro-2,4,6-trinitro-benzenamine (**b**) and 5-chloro-1,3-diamino-2,4,6-trinitrobenzene (**c**) were obtained according to ref. 1. Melting point was measured on a X-4 melting point apparatus and was uncorrected. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) were recorded on a Bruker Avance Spectrometer (TMS as an internal standard). High-resolution mass spectra were recorded on a Finnigan TSQ Quantum ultra AM mass spectrometer. Elemental analysis was carried out on a Perkin-Elmer instrument.

The synthesis of the starting compounds (Scheme 1)

2,4-Dinitroimidazole (2,4-DNI). Yield: 82%; m.p. 264–266 °C; ^{1}H NMR (DMSO-d_6): δ 8.46 (s, 1H).

4,5-Dinitroimidazole (4,5-DNI). Yield: 72%; m.p. 187–189 °C (188–189 °C[20]); ^{1}H NMR (DMSO-d_6): δ 7.97 (s, 1H).

Picryl chloride (a). Yield: 72%; m.p. 80–82 °C; ^{1}H NMR ($CDCl_3$): δ 8.87 (s, 1H).

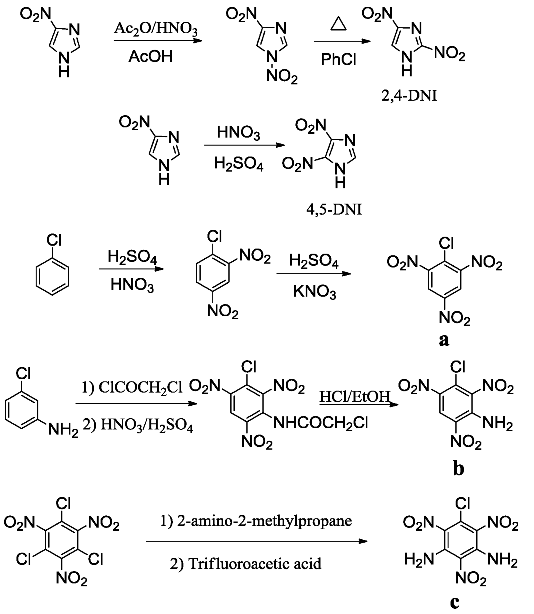
3-Chloro-2,4,6-trinitro-benzenamine (b). Yield: 76%; m.p. 184–185 °C; ^{1}H NMR (DMSO-d_6): δ 8.96 (s, 1H), 8.57 (s, 2H).

5-Chloro-1,3-diamino-2,4,6-trinitrobenzene (c). Yield: 40%; m.p. 250–253 °C; ^{1}H NMR (DMSO-d_6): δ 8.60 (s, 1H).

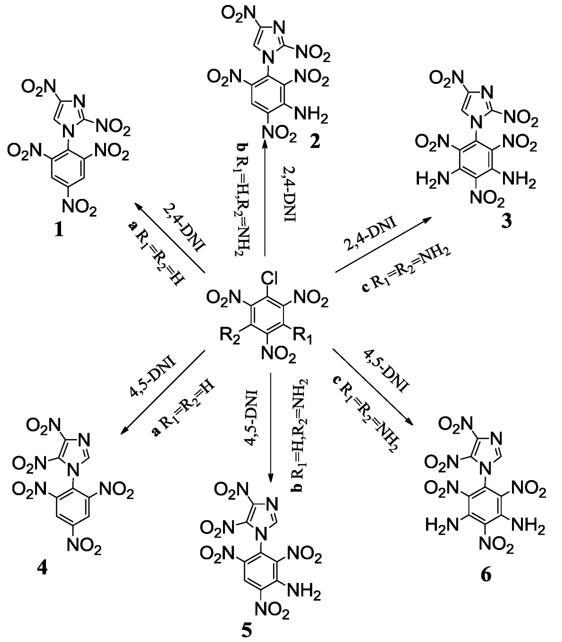
A general procedure for the preparation of *N*-aryl-C-nitroimidazoles (Scheme 2)

A mixture of dinitroimidazole (**2,4-DNI** or **4,5-DNI**, 0.32 g, 2.02 mmol), $KHCO_3$ (0.2 g, 2 mmol) and isopropanol (20 mL) was stirred at ambient temperature for 1 h, followed by TBAB (tetrabutyl ammonium bromide, 0.12 g, 0.38 mmol), then chloronitroarene (**a**, **b**, **c**, 2 mmol) was added in small lots with stirring. The contents were stirred for 24 h at 85 °C The reaction mixture was filtrated and washed with water and then methanol to yield pure products:

1-(2,4,6-Trinitrophenyl)-2,4-dinitroimidazole (1). Yield: 57%; m.p. 238–241 °C (237–240 °C[12]); ^{1}H NMR (DMSO-d_6): δ 9.06 (s, 2H), 8.99 (s, 1H).



Scheme 1 Synthesis scheme of reagents and substrates.



Scheme 2 Synthesis scheme of dinitroimidazole derivatives.

1-(3-Amino-2,4,6-trinitrophenyl)-2,4-dinitroimidazole (2). Yield: 50%; m.p. 260–263 °C; ^{1}H NMR (DMSO-d_6): δ 8.92 (s, 2H), 9.12 (s, 1H), 9.16 (s, 1H); ^{13}C NMR (DMSO-d_6): δ 125.45, 126.39, 127.14 127.50 127.78, 128.42, 132.46, 135.19, 140.84, 141.14, 143.60; anal. calcd for $C_9H_4N_8O_{10}$: C, 28.14; H, 1.05; N, 29.17%; found: C, 28.22; H, 1.08; N, 29.21%. MS (ESI) *m*/*z*: 382.84 (M-H).

1-(3,5-Diamino-2,4,6-trinitrophenyl)-2,4-dinitro-imidazole (3). Yield: 78%; m.p. 251–253 °C; ^{1}H NMR (DMSO-d_6): δ 8.40 (s, 4H), 9.10 (s, 1H). ^{13}C NMR (DMSO-d_6) δ: 121.60, 121.91, 124.76, 126.44, 129.31, 141.58, 143.35; anal. calcd for $C_9H_5N_9O_{10}$: C, 27.08; H, 1.26; N, 31.58%; found: C, 27.11; H, 1.31; N, 31.62%. MS (ESI) *m*/*z*: 397.81 (M-H).

1-(2,4,6-Trinitrophenyl)-4,5-dinitroimidazole (4). Yield: 65%; m.p. 226–229 °C (220–223 °C[12]); ^{1}H NMR (DMSO-d_6): δ 9.38 (s, 2H), 8.59 (s, 1H).

1-(3-Amino-2,4,6-trinitrophenyl)-4,5-dinitro-imidazole (5). Yield: 61%; m.p. 282–284 °C; ^{1}H NMR (DMSO-d_6): δ 8.57 (s, 1H), 8.92 (s, 2H), 9.15 (s, 1H); ^{13}C NMR (DMSO-d_6): δ 125.52, 126.17, 127.56, 129.09, 130.53, 132.56, 136.44, 138.44, 140.93; anal. calcd for $C_9H_4N_8O_{10}$: C, 28.14; H, 1.05; N, 29.17%; found: C, 28.22; H, 1.08; N, 29.21%. MS (ESI) *m*/*z*: 382.84 (M-H).

1-(3,5-Diamino-2,4,6-trinitrophenyl)-4,5-dinitro-imidazole (6). Yield: 84%; m.p. 271–274 °C; ^{1}H NMR (DMSO-d_6): δ 8.35 (s, 4H), 8.55 (s, 1H). ^{13}C NMR (DMSO-d_6) δ 1221.81, 122.73, 127.17, 131.16, 136.07, 137.91, 140.69, 141.47, 146.18; anal. calcd for $C_9H_5N_9O_{10}$: C, 27.08; H, 1.26; N, 31.58%; found: C, 27.11; H, 1.31; N, 31.62%. MS (ESI) *m*/*z*: 397.79 (M-H).

Acknowledgements

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