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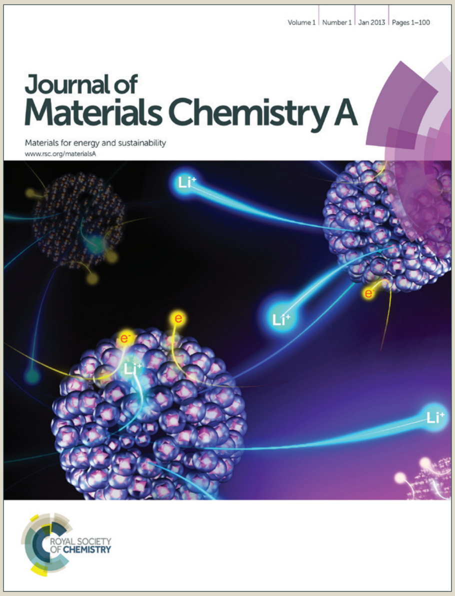

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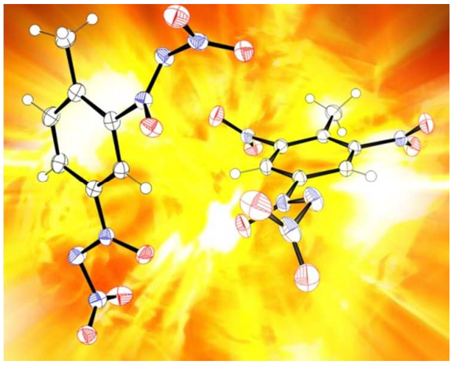
A Comparative Study of the Structure, Energetic Performance and Stability of Nitro-NNO-azoxy Substituted Explosives.

Yuan Wang, Shenghua Li , Yuchuan Li , Rubo Zhang, Dong Wang and Siping Pang**

Nitro-NNO-azoxy group: The unique structure that contains one nitro group, one N-oxide group and one azo-linkage, could improve the density, heat of formation, detonation velocity and detonation pressure of an explosive. Compared with nitro group, the nitro-NNO-azoxy group has a stronger energetic and electron-attracting property.



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ARTICLE TYPE

A Comparative Study of the Structure, Energetic Performance and Stability of Nitro-NNO-azoxy Substituted Explosives.

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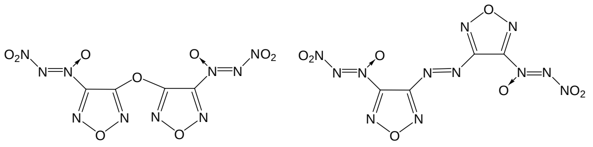
2,4-Di-nitro-NNO-azoxytoluene and 2,6-dinitro-4-nitro-NNO-azoxytoluene were synthesized as energetic compounds. Their structures and properties were studied by X-ray diffractometry, nuclear magnetic resonance and infrared spectroscopy. The differences between the nitro-NNO-azoxy and the nitro groups are discussed. The detonation properties as predicted using EXPLO5 indicate that the detonation velocity and pressure of 2,4-di-nitro-NNO-azoxytoluene increased by 21.7% and 74.3%, respectively, compared with 2,4-dinitrotoluene. Nucleus independent chemical shift analysis was used to investigate skeleton aromaticity and the effect of the nitro-NNO-azoxy and nitro groups on ring aromaticity. Electrostatic potential, bond dissociation energy, Mulliken charges and Wiberg bond order were estimated by density functional theory to establish the molecular electron distribution and their stabilities. The nitro-NNO-azoxy group has a stronger electron-withdrawing property than that of the nitro group.

Introduction

Energetic compounds are one of the most important organic components because of their unique energy storage and stability properties[1-3]. It is a challenge to design and synthesize novel energetic compounds with improved energetic performance and stability since propellants must transport increasing payloads and more powerful explosives are required. The performance of energetic compounds is linked closely to structure. In general, energetic compounds are composed of backbones and functional groups[4-6]. Only a few energetic compounds contain oxygen atoms in their backbones, and the oxygen balance is usually improved by introducing oxygen-rich groups. A nitro group is often introduced to improve the oxygen balance of an explosive. Other nitro-containing groups, such as the nitrato (ONO_2), nitramino ($NHNO_2$), geminal dinitro ($CH(NO_2)_2$) and trinitromethyl ($C(NO_2)_3$) groups are also introduced frequently into parent backbones to produce novel energetic derivatives with excellent detonation performance[7-10]. Recently, the introduction of N→O on nitrogen-heterocycles has been found to be useful to increase the energetic performance of energetic materials[11, 12]. However, these new oxygen-rich groups have drawbacks in that they may be difficult to synthesise or they may be sensitive to thermal conditions, impact and friction. Therefore, further research is required to develop new oxygen-rich groups.

We have become interested in the nitro-NNO-azoxy group, which has not been studied fully. Its unique structure that contains one nitro group, one N-oxide group and one azo-linkage, could improve the oxygen balance and heat of formation (HOF) of energetic compounds. The nitro-NNO-azoxy group was first reported by Churakov et al. in 1996[13]. After the first synthesis, Churakov modified the synthesis route by using tert-butyl-NNO-azoxy-benzenes as intermediates[14]. Bis-3,3'-(nitro-NNO-azoxy)-difurazanyl ether (**1**)[15], and bis-3,3'-(nitro-NNO-azoxy)-4,4'-azofurazan (**2**)[16] were then synthesized (see Scheme 1).

However, the nitro-NNO-azoxy group has not been studied thoroughly as an energetic functional group, and the influence of the group on the structural and energetic properties has not yet been clarified. Differences between the nitro-NNO-azoxy and nitro groups must still be explored. To investigate the above problems systematically, we designed two nitro-NNO-azoxy derivatives by substituting nitro groups of energetic compounds with nitro-NNO-azoxy groups, and studied their properties (see Scheme 2). Two traditional explosives, 2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (DNT), were selected since they are used widely and are obtained easily. Consequently, 2,4-di-nitro-NNO-azoxytoluene (**3**) and 2,6-dinitro-4-nitro-NNO-azoxytoluene (**4**) were synthesized and their structures were confirmed by mass spectrometry, ^{1}H nuclear magnetic resonance (NMR), ^{13}C NMR, infrared spectroscopy (IR) and elemental analysis. Changes in structural and performance features that resulted from the introduction of the new group onto the parent compounds are discussed in detail. X-ray diffractometry (XRD) and density functional theory (DFT) were used to reveal differences between the nitro-NNO-azoxy and nitro groups such as configuration and electrostatic potential (ESP)



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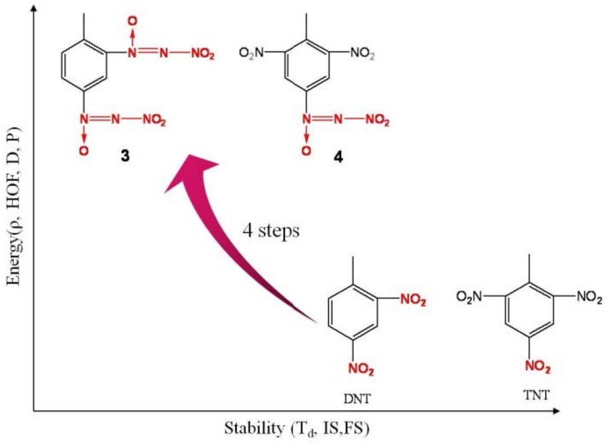
Scheme 1 Reported nitro-NNO-azoxy substituted furazan derivatives.



Scheme 1 Comparison of nitro-NNO-azoxy and nitro groups substituted with toluene.

Results and discussion

X-Ray crystallography

Single crystals of **3** and **4** suitable for crystal structure analysis were obtained by recrystallization from hexane and hexane/ethyl acetate 1:1, respectively, at room temperature. The molecular structures, as determined by XRD are shown in Figs 1 and 2. Some selected bond lengths are listed in Fig. 1. The N-NO$_2$ bond in the nitro-NNO-azoxy group has a standard N-N bond length of 1.47 Å[17], which is slightly shorter than the same bond in **1** (1.50 Å). In general, a shorter bond could result in increased stability. Dihedral angles of O1-N1-N2-N3 in the nitro-NNO-azoxy groups of **3** and **4** are less than 4°. The nearly planar conformation is quite common in azo compounds[18, 19]. A similar planar structure is also observed in the N-NO$_2$ segment and the two planes are almost perpendicular (the dihedral angle of O3-O2-O1-N1 is 86°). The dihedral angles between the O←N=N plane and the benzene ring, like O1-N1-C1-C6, range from 13° to 43°. The configuration indicates that the NNO-azoxy group and the ring do not share the same π system. The nitro-NNO-azoxy group tends to refrain from making a larger conjugated system with the ring. The packing diagram of two crystals shows that **3** packs in parallel layers, whereas **4** has a "V-shaped" packing. The XRD data and the parameters of compounds **3** and **4** are summarized in Table 1.

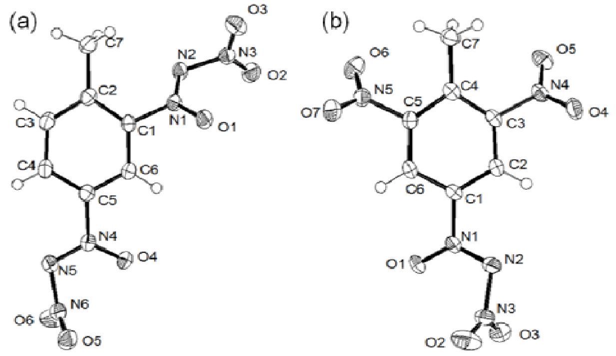


Fig. 1 Oak Ridge Thermal Ellipsoid Plot ORTEP representation of the molecular structure of **3** (a) and **4** (b). Displacement ellipsoids are shown at the 50% probability level. Selected bond length/Å: (a) C1-N1 1.47, N1-O1 1.24, N1-N2 1.28, N2-N3 1.47, N3-O2 1.21, N3-O3 1.21; (b) C5-N1 1.46, N1-O1 1.24, N1-N2 1.28, N2-N3 1.47, N3-O2 1.21, N3-O3 1.21, C1-N4 1.47, C3-N5 1.48.

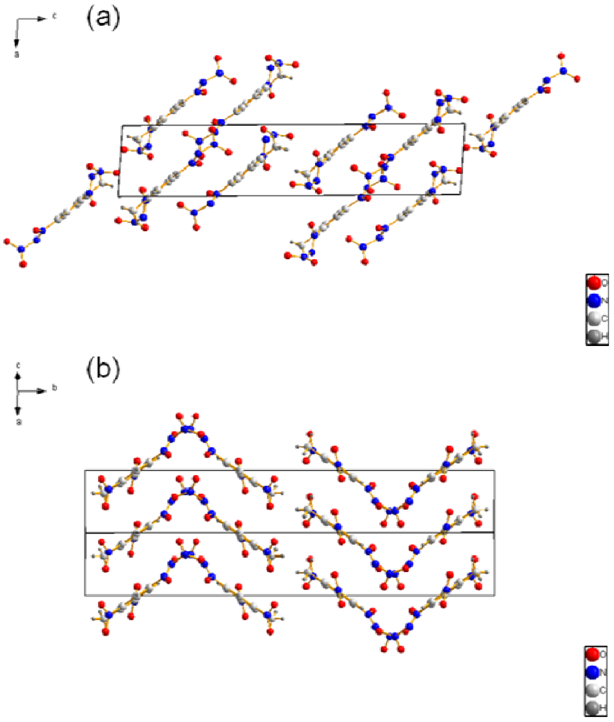


Fig. 2 Unit cell packing of **3** (a) and **4** (b).

Table 1 X-Ray data and parameters of compounds **3** and **4**.

	3	4
CCDC	1023014	1023015
Empirical formula	$C_7H_6N_6O_6$	$C_7H_5N_5O_7$
Formula mass	270.03	271.02
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P\ 2_1/n$
Z	4	4
a (Å)	5.3336(13)	5.2932(15)
b (Å)	7.9688(19)	29.236(8)
c (Å)	25.494(6)	6.907(2)
α (°)	90	90
β (°)	94.454(3)	98.746(4)
γ (°)	90	90
Volume (Å^3)	1080.3(5)	1056.4(5)
D_{calc} (g·cm^{-3})	1.661	1.705
Temperature (K)	153 (2)	153 (2)
F(000)	552	552
h, k, l	7, 10, 32	7, 37, 9
μ (cm^{-1})	0.147	0.155
$R_1[I > 2\sigma(I)]$	0.0393	0.0461
Reflections collected	9291	8887
Completeness to theta full (%)	0.994	0.998
wR_2 (all data)	0.1061	0.1290
S on F^2	0.999	1.003

Differential scanning calorimetry

T To determine the thermal behavior of the compounds, differential scanning calorimetry (DSC) measurements were carried out at 5°C·min^{-1} using dry oxygen-free nitrogen at 20 mL min^{-1}. As shown in Fig. 3, an endothermic peak is observed at 58.5°C, which indicates the melt of **3**. The exothermic peak at 139.5°C illustrates that **3** decomposed. It is likely that **4** melts at 114.0°C and decomposes at 137.0°C. Their decomposition temperature decreases compared with the parent compounds DNT (250°C) and TNT (295°C). This is presumably because the long nitrogen chain is more vulnerable to heat, and conjugation of the N-NO_2 bond in the chain is less stable than the C-NO_2 bond between the benzene ring and the nitro group. However, compared with previously reported benzene derivatives (85–110°C) and **2** (132°C)[13, 16], the decomposition temperature of 139.5°C of **3** makes it the most stable compound in this series. This provides a clue for the synthesis of new energetic nitro-NNO-azoxy compounds with better thermal stabilities.

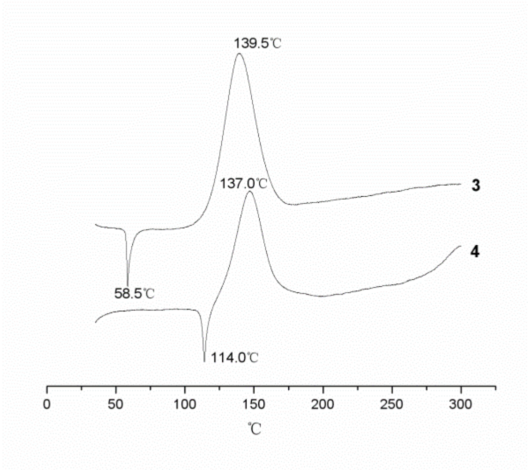


Fig. 3 DSC spectra of **3** and **4**.

Sensitivity

The impact sensitivity (IS) and friction sensitivity (FS) of **3** and **4** were determined according to general methods. The ISs of **3** and **4** are 5 J and 15 J, respectively. Both compounds are classified as “sensitive” explosives[20]. The results indicate that **4** has a similar IS to its parent compound TNT (IS = 15 J), whereas **3** is more sensitive towards impact than DNT (measured IS > 40 J). The IS is not affected significantly when one nitro group is substituted by a nitro-NNO-azoxy group. However, it decreases significantly when the two nitro groups are replaced by nitro-NNO-azoxy groups. The FSs for **3** and **4** are 120 N and 160 N, respectively. These compounds are less stable than DNT (FS > 360 N) and TNT (FS = 353 N)[21]. Detailed sensitivity information is given in the Electronic Supplementary Information (ESI†).

Density, heat of formation and detonation properties

Density and HOF are important parameters used to predict the detonation performance of an explosive[22]. Their precise values play a significant role in obtaining accurate results. The crystal densities of **3** and **4** measured at 153 K are 1.661 g·cm^{-3} and 1.705 g·cm^{-3}, which is higher than the measured values of DNT (1.559 g·cm^{-3}, 173 K) and TNT (1.704 g·cm^{-3}, 123 K) at low temperature[23, 24]. The nitro-NNO-azoxy group is more powerful than the nitro group in improving the density. An increase of 0.1 g·cm^{-3} was obtained when both nitro groups were replaced with nitro-NNO-azoxy groups. To obtain more reliable results for detonation performance, the low temperature densities are converted to those at room temperature by using Sun’s method[25]. Densities used for the calculation of the detonation performance of **3** and **4** are 1.63 g·cm^{-3} and 1.67 g·cm^{-3}, respectively.

HOFs were estimated by isodesmic reaction and molecule optimization was accomplished by using the Gaussian 03 program package[26]. The calculation was carried out using the density functional theory (DFT) B3LYP method [27, 28] and the 6-311++G(d,p) basis set[29, 30]. Vibrational analysis confirmed that the structures obtained correspond to the minima on their potential energy hypersurfaces. To guarantee the accuracy, the solid-phase HOF was calculated by subtracting the heat of sublimation (ΔH_s) from the gas-phase HOF by Politzer’s method[31, 32]. The calculated HOFs of the title compounds are summarized in Table 2. More HOF calculation details are shown in the ESI†.

$$\Delta \mathrm{H(Solid)} = \Delta \mathrm{H(Gas)} - \Delta \mathrm{H(Sublimation)} \quad (1)$$

$$\Delta \mathrm{H(Sublimation)} = \mathrm{a(SA)}^2 + \mathrm{b}\sqrt{\sigma^2_{\mathrm{Tot}}\nu} + \mathrm{c} \quad (2)$$

ΔH(Solid), ΔH(Gas) and ΔH(Sublimation) refer to the solid-phase HOF, gas-phase HOF and heat of sublimation, respectively; a, b, and c are fitting parameters, respectively; SA is the molecular surface area; σ^2_{Tot} is the total variance of the calculated ESP on the molecular surface and ν is a balance parameter.

The calculated HOFs of **3** and **4** are 415.7 $kJ \cdot mol^{-1}$ and 55.4 $kJ \cdot mol^{-1}$, respectively, and are higher than those of DNT and TNT. The HOF of toluene (50.1 $kJ \cdot mol^{-1}$) decreased when toluene was nitrated, and increased when the nitro-NNO-azoxy groups were introduced. According to our calculations, when one nitro group is displaced by one nitro-NNO-azoxy group in TNT, an increment of 135.9 $kJ \cdot mol^{-1}$ in HOF is obtained. The phenomenon is more evident when the nitro groups in DNT are displaced completely by nitro-NNO-azoxy groups. Compare with DNT, **3** obtains an extra 480 $kJ \cdot mol^{-1}$ in HOF. The nitro-NNO-azoxy group enhances the HOF in the skeleton more positively than the nitro group. The azo and N-N bonds are the main contributors[33, 34].

Table 2 Properties of title compounds.

compound	$\rho/g \cdot cm^{-3}$	OB/%	N/%	HOF/$kJ \cdot mol^{-1}$	D/$km \cdot s^{-1}$	P/GPa	Tm/°C	Td/°C	IS/J	FS/N
3	1.63	-65.2	31.1	415.7	7.78	24.4	58.5	139.5	5	120
4	1.67	-56.1	25.8	55.4	7.64	23.9	114	137	15	160
DNT [a]	1.52	-114.3	15.4	-64.3 [c]	6.39	14.0	70	250	40	360
TNT [b]	1.65	-74	18.5	-80.5 [c]	6.88	19.5	80.4	295	15	353

[a] Record of 2,4-dinitrotoluene in the GESTIS Substance Database from the IFA, accessed on 9. October 2007. [b] Reference [35]. [c] Reference [36].

The detonation velocity and pressure of the title compounds were calculated using EXPLO5 v 6.01 with a rectified density and HOF[37]. As expected, with a better density, oxygen balance, nitrogen content and HOF, **3** and **4** achieved better detonation performance than their corresponding nitro-compounds. The new nitro-NNO-azoxy energetic group improves the energetic performance, especially for the disubstituted **3**, with its performance compared with DNT being as follows: 0.11 $g \cdot cm^{-3}$ increase in density; 49.1% increase in oxygen balance; additional 480 $kJ \cdot mol^{-1}$ HOF; and most importantly, 1.39 $km \cdot s^{-1}$ and 10.4 GPa increase in detonation velocity and pressure, respectively. The nitro-NNO-azoxy group therefore enhanced every energetic level parameter. However, as shown in Table 2, adverse effects also result. In **3**, for example, the decomposition temperature drops by 110°C after substitution. There is a simultaneous decrease in IS and FS of 35 J and 240 N, respectively. Thus, the nitro-NNO-azoxy group could improve the energetic performance of a compound but weakened its heat and mechanical stability. To explain the origin of the instability of the nitro-NNO-azoxy group, a series of computations were carried out that addressed structural and electronic differences between the nitro-NNO-azoxy and nitro groups.

Nucleus independent chemical shift

The nucleus independent chemical shift (NICS) is a useful tool to describe compound aromaticity or the magnetic properties of a structure. The original definition of the NICS is the negative value of the absolute magnetic shielding computed at ring centers[38, 39]. The NICS(1) concept is more practical for illustration of the *π*-electron structure character since it is defined as an NICS of 1 Å above the ring plane. However, NICS(1) is still based on the total isotropic shielding value[40, 41]. $NICS(1)_{zz}$ was therefore proposed to reflect contributions arising from the *zz* component of the shielding tensor[39, 42]. Larger negative values imply a stronger molecule aromaticity. $NICS(1)_{zz}$ is believed to offer an improved interpretation of aromaticity with fewer errors.

To compare the aromatic differences that result from the substitution of the nitro and nitro-NNO-azoxy groups, the $NICS(1)_{zz}$ values of **3**, **4**, DNT, TNT and toluene were calculated using the GIAO/B3LYP/6-311++G** method. The results are summarized in Table 3.

Table 3 $NICS(1)_{zz}$ values of title compounds.

	3	**4**	DNT	TNT	Toluene
$NICS(1)_{zz}$/ ppm	-24.2309	-23.0447	-24.5468	-23.0761	-27.8042

The $NICS(1)_{zz}$ values of **3** and **4** are higher than those of DNT and TNT even though the increases are not very evident. Both **3** and **4** have a slightly weaker aromaticity than DNT and TNT, respectively. Compared with toluene, the four other compounds have high NICS values, which means that the aromaticity of the benzene ring decreases after the H atoms are substituted by electron-withdrawing groups. The nitro-NNO-azoxy group has a stronger ability than the nitro group to weaken the aromaticity of the toluene skeleton.

To investigate the shielding distribution of the *zz* component 1 Å above the plane, the NICS of 125000 points around the molecule was computed using the same method. Color-filled shielding maps were sketched using Multiwfn v 3.3.4[43] (see Fig. 4). The colors range from -45 to +40 ppm with dark blue denoting extremely anti-shielding regions and red denoting shielding regions. The white regions have shielding values larger than 40 ppm. Since shielding and NICS share the same value of opposite sign, a darker red color in the figure means that the structure has better aromaticity. The scale on the right refers to the shielding of a *zz* component. The curves in the maps are contour lines.

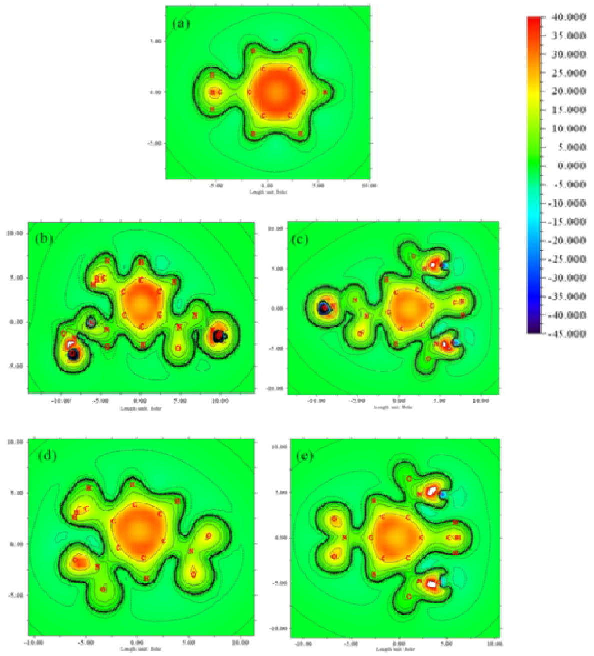


Fig. 4 Shielding maps of toluene (a), **3** (b), **4** (c), DNT (d) and TNT (e).

Fig. 4a shows that the ring is filled with red, which means that toluene has a strong and uniform aromaticity. The dark red color is well distributed on the six carbon atoms, and the contour line on these atoms is a regular hexagon. Nevertheless, results of other compounds in the study are different from those of toluene. The contour line on the carbon atoms has a "nut-like" shape. The red areas have decreased in size compared with toluene, especially for the positions connected with an electron-withdrawing group. These groups not only affect the magnetic property of the center, but also that of the periphery. The red on the ring of **3** is less uniformly distributed than that of DNT. The strong electron-withdrawing property and the chain configuration of the nitro-NNO-azoxy group probably result in a less regular magnetic field spread. The results of **4** and TNT did not differ much, mainly because **4** has only one nitro-NNO-azoxy group and the effect is limited.

Electrostatic potentials

Determination of an ESP is an efficient way to relate compound stability to outer stimulations[44]. Murray et al. showed that there is a link between ESP, IS and the C-NO_2/N-NO_2 bond dissociation energy (BDE) of an energetic compound[45]. The ESP at any point r is given in the following equation.

$$V(r)=\sum_A \frac{Z_A}{|R_A-r|}-\int\frac{\rho(r')dr'}{|r'-r|} \quad (3)$$

Where Z_A is the charge on nucleus A, located at R_A, and ρ(r) is the molecule's electronic density. ESP was computed based on the optimized structures of the title compounds. Fig. 5 shows the ESPs for the 0.001 electron/bohr^3 isosurfaces of electron density evaluated at the B3LYP/6-311++G(d,p) level. The colors range from -0.015 to +0.04 hartrees with dark blue denoting extremely electron-deficient regions ($V(r) \geq 0.04$), red denoting electron-rich regions ($V(r) \leq -0.015$) and yellow denoting neutral regions.

As shown in Fig. 5, the four calculated compounds have a strongly positive center and negative periphery. This is a common phenomenon for traditional explosives such as HMX and CL-20[8]. Because only two electron-withdrawing groups exist on the ring, the ESP of **3** and DNT is divided into three parts. The blue part on the left refers to an electron-deficient region, whereas the red part on the right represents an electron-rich region. The cyan part in the middle is a transition region. In contrast with compound **3** and DNT, **4** and TNT show electron-deficient skeletons surrounded by electron-rich groups. Since electron-withdrawing groups are attached to the toluene ring, the blue color in the middle of **4** is darker than that of **3**. The same result is also observed in TNT and DNT. We are more concerned with differences caused by replacing the nitro group with the nitro-NNO-azoxy group. Fig. 5b and 5d shows that the prolonged nitrogen chain leads to an enhancement of the electron-rich part at the bottom of the molecule. Furthermore, the blue color over the middle of **4** is darker than that of TNT. These phenomena indicate that the electron-withdrawing capability of the nitro-NNO-azoxy group is stronger than that of the nitro group, which concurs with the results of $NICS(1)_{zz}$. The charge distribution on the surface of **4** is more scattered than that on TNT. Generally, such as structure is not conducive to the stabilization of one molecule. The ESP figures of **3** and DNT depict the phenomenon clearly. Compared with DNT, the red part of **3** is distributed irregularly and the blue color on the left is darkened. In terms of ESP, the nitro-NNO-azoxy group could not perform better than the nitro group in stabilizing the molecules. This is probably another way to illustrate why the nitro-NNO-azoxy group derivatives have a relatively lower stability.

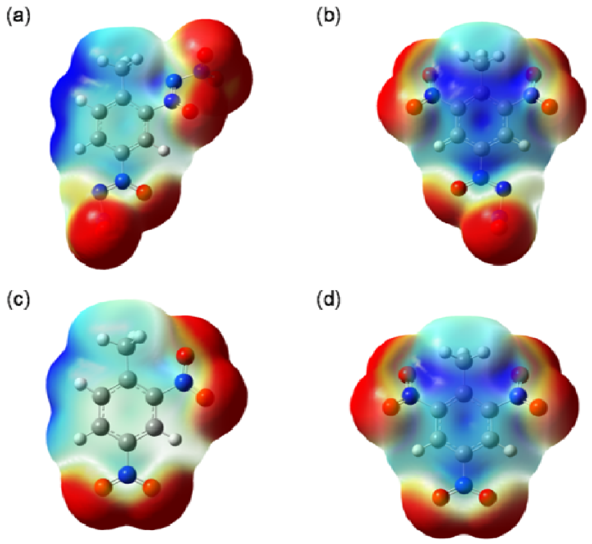


Fig. 5 ESPs of **3** (a), **4** (b), DNT (c) and TNT (d). Red: negative, orange: slightly negative, yellow: neutral, green: slightly positive, light blue: positive, dark blue: very positive.

Bond dissociation energy

To test the firmness of the N-NO_2 and N→O bonds in the nitro-NNO-azoxy group and the C-N bond between the ring and the group, the corresponding bond dissociation energies were calculated according to the following equation[46]:

$$A\text{-}B\ (g) \rightarrow A\bullet\ (g) + B\bullet\ (g)$$

The BDE values of the C-N bonds between the ring and the nitro-NNO-azoxy group are large whereas the N-NO_2 BDE is relatively small (Table 4). BDE values larger than 280 kJ·mol^{-1} indicate that the connection between the ring and the group is strong and firm. The C-NNO bonds in **3** or **4** share similar BDE values with the C-NO_2 bonds in the same position of DNT or TNT, which indicates that the two groups have a close stability in terms of linking with the skeleton. BDE values larger than 500 kJ·mol^{-1} for N→O BDE imply that the bond is stable. However, the BDEs of N-NO_2 range from 130-140 kJ·mol^{-1}, and the N-NO_2 bond is deemed to be the vulnerable bond for the title compounds. To stabilize the nitro-NNO-azoxy containing compounds, N-NO_2 bond deactivation should be considered.

Table 4 Selected bond dissociation energies of title compounds.

	3[a]	**3**[b]	**4**	DNT[c]	TNT[c]
C-N/kJ·mol^{-1}	283.9	299.3	289.9	299.1	289.6
N-NO_2/kJ·mol^{-1}	134.6	140.1	138.2		
N→O/kJ·mol^{-1}	551.7	557.3	555.9		

[a] Values refer to the group connected with C1 in compound **3**. [b] Group connected with C5 in compound **3**. [c] BDEs of C5-NO_2 in DNT and TNT.

Mulliken charges and Wiberg bond order

To illustrate how electrons are distributed on different atoms, the Mulliken charges and Wiberg bond order of the two compounds were calculated. Mulliken charges may reflect the electron distribution on different atoms whereas the Wiberg bond order indicates bond stability[47]. Both analyses methods can be used to investigate the interactions between atoms in the nitro-NNO-azoxy group. Selected values are shown in Table 5.

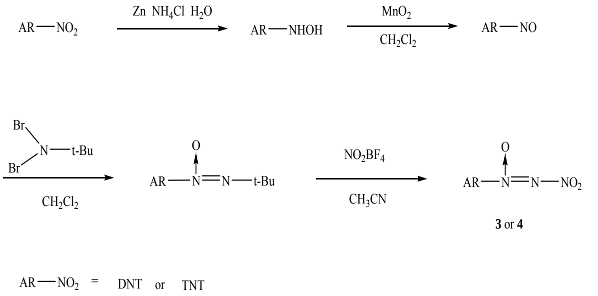
Table 5 Selected Mulliken atomic charges and Wiberg bond orders of title compounds.

		3	**4**	DNT	TNT
Mulliken atomic charges	C1	0.223	0.181	0.206	0.182
	C2	0.202	0.189	0.182	0.190
	C3	-0.211	0.185	-0.205	0.182
	C4	-0.119	-0.136	-0.122	-0.141
	C5	0.298	0.304	0.269	0.264
	C6	-0.150	-0.143	-0.174	-0.141
	O1	-0.395	-0.416		
	O2	-0.318	-0.313		
	O3	-0.323	-0.314		
	N1	0.161	0.155		
	N2	-0.132	-0.113		
	N3	0.566	0.569		
Wiberg bond orders	C-NNO	0.918	0.927		
	N1-O1	1.428	1.424		
	N1-N2	1.472	1.469		
	N2-N3	0.869	0.868		
	N3-O2	1.563	1.560		
	C1-NO_2		0.913	0.927	0.914
	C3- NO_2		0.913		0.914
	C5- NO_2			0.927	0.921

The N3 in the nitro group is positively charged since it is connected with two electron-withdrawing O atoms. Nevertheless, the nitro group, which is treated as an individual part, is a negatively charged moiety. Interestingly, the charge on N2 is negative, with two O atoms and the N2 that stretches the N3 in a different direction. The N-NO_2 bond therefore becomes the weakest bond in the molecule. This is also seen from the Wiberg bond order of N2-N3, which is the lowest value in the molecule. The Wiberg bond orders for N1-N2 and N1-O1 are 1.47 and 1.43, respectively, and lie between the single and double bonds. The π-electron is delocalized on the three atoms, which makes the bonds firm and stable. These results agree with the BDE conclusions. The Mulliken charges for the O1-N1-N2-N3 structure are characteristic of alternately distributed positive and negative values. The O1 stabilized the nitro-NNO-azoxy group and is crucial. The total Mulliken charge of atoms in the nitro-NNO-azoxy group (-0.43) is larger than that of the nitro group (-0.36). After being affected by the strong electron-attracting property of the nitro-NNO-azoxy group, C1 and C5 on compound **3** possess higher charges than those of DNT. Similarly, the charge of C5 on compound **4** (0.304) is higher than that of TNT (0.264). This is because the nitro-NNO-azoxy group has a stronger electron-attracting property than that of the nitro group. The bond order of the C-NNO bond on **3** or **4** and the C-NO_2 bond on DNT or TNT in the same place did not show much difference. The rebalance of electrons between the ring and the group made the C-NNO bond as stable as the C-NO_2 bond.

Experimental

The synthesis method of **3** and **4** is shown in Scheme 3.



Scheme 3 Synthesis methods used in the study.

2,4-Dihydroxaminotoluene: DNT (3 g, 16.5 mmol), dichloromethane (18 mL), Ethanol (75 mL) and water (18 mL) were added to a 250 mL three-necked flask followed by zinc powder (27 g, 412.8 mmol). A dropwise solution of 3 g (56.1 mmol) ammonium chloride and 30 mL water was added to the vigorously stirred mixture under nitrogen. The reaction was maintained at 15°C in an ice bath for 30 min. $MgSO_4$ was used to remove residual water after the reaction. The precipitate was filtered, washed with dichloromethane and a solution of 2,4-dihydroxaminotoluene was obtained. The solution was concentrated to 50 mL using a rotary evaporator.

2,4-Dinitrosotoluene: Activated MnO_2 (150 g) and 250 mL dichloromethane were added to a 500 mL three-necked flask. A dropwise solution of 2,4-dihydroxaminotoluene was added to the stirred mixture under nitrogen and at ambient temperature. Thirty minutes after the solution had been added, the MnO_2 was filtered off and the solution was concentrated to 50 mL.

2,4-Di-tert-butyl-NNO-azoxytoluene: Under nitrogen, N,N-dibromo-tert-butylamine (8 g, 35.1 mmol) was added to the vigorously stirred 2,4-dinitrosotoluene solution at room temperature. After one hour, the solution was evaporated in a rotary evaporator and the residue passed through a silicagel column to yield 2,4-di-tert-butyl-NNO-azoxytoluene (3.14 g, 65.1%, three steps).

2,4-Di-nitro-NNO-azoxytoluene: 2,4-Di-tert-butyl-NNO-toluene (4.4 g, 15 mmol) was dissolved in 50 mL dry acetonitrile, to which 5 g (37.5mmol) NO_2BF_4 was added in a nitrogen atmosphere. The solution was stirred for 5 h at 0°C, poured into 200 mL water, and extracted with dichloromethane three times. The solvent was removed and 2,4-di-nitro-NNO-azoxytoluene (2.13 g, 52.3%), a yellow solid, was obtained after passing it through a silicagel column. (Found: C, 31.26; H, 2.47; N, 30.65; O, 35.62; calc. for $C_7H_6N_6O_6$: C, 31.12; H, 2.24; N, 31.11; O, 35.53). *m/z* 270, 180, 91. ^1H NMR: (400 MHz, acetone-d_6 Me_4Si) δ 2.58 (3H, s, Me), 7.91-7.93 (1H, m, Ph), 8.48-8.50 (1H, m, Ph), 8.88 (1H, m, Ph), ^{13}C NMR: (400 MHz, acetone-d_6 Me_4Si) δ 22.93 (1C, Me), 114.99 (1C, Ph), 124.18 (1C, Ph), 131.45 (1C, Ph), 139.81 (1C, Ph), 145.63 (1C, Ph). IR KBr ν/cm^{-1} 1617, 1484, 1275, 860, 828, 710, 576.

2,6-Dinitro-4-nitro-NNO-azoxytoluene could be synthesized in a similar way and only half the moles of zinc powder, ammonium chloride, N,N-dibromo-tert-butylamine and NO_2BF_4 were needed. Yield 38.6%, yellow solid. (Found: C, 30.52; H, 1.96; N, 26.07; O, 41.45; calc. for $C_7H_5N_7O_8$: C, 31.01; H, 1.86; N, 25.83; O, 41.30) *m/z* 181, 165, 89. ^1H NMR: (400 MHz, acetone-d_6 Me_4Si) δ 2.72 (3H, s, Me), 9.04 (2H, s, Ph) ^{13}C NMR: (400 MHz, acetone-d_6 Me_4Si) δ 15.77 (1C, Me), 110.71 (1C, Ph), 122.70 (2C, Ph), 134.72 (1C, Ph), 152.70 (2C, Ph). IR KBr ν/cm^{-1} 3090, 1603, 1536, 1487, 1352, 1272, 909, 852, 723. All spectra of **3** and **4** are shown in the ESI†.

Conclusions

2,4-Di-nitro-NNO-azoxytoluene and 2,6-dinitro-4-nitro-NNO-azoxytoluene were designed and synthesized. Differences between the nitro-NNO-azoxy and nitro groups were compared systematically. The structures of the two new compounds were determined by mass spectrometry, IR, NMR, elemental analysis and XRD. Their intramolecular interactions were studied by investigating their crystal structures and their electron distribution properties were obtained by calculating their NICS, ESP, BDE, Mulliken atomic charges and Wiberg bond order. Substitution of the nitro-NNO-azoxy group could enhance the energetic levels of the toluene system such as density, HOF, detonation velocity and pressure. The nitro-NNO-azoxy derivatives also have an adverse effect in terms of lower decomposition temperature, higher impact and friction sensitivities than the traditional nitro-containing counterparts. The nitro-NNO-azoxy group has a stronger electron-withdraw capability than the nitro group. Its higher electronegativity makes the nitro-NNO-azoxy group more able to influence the aromaticity and electron distribution of the benzene ring than the nitro group. The BDE and Wiberg bond order results indicate that the N-NO_2 bond is the most vulnerable. The comprehensive performance of the nitro-NNO-azoxy group proves it is a competitive energetic group for designing new compounds with high energetic levels. We anticipate that the results from this paper could contribute to further studies of compounds of this kind.

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† Electronic Supplementary Information (ESI) available: spectra of compounds **3** and **4**, details of HOF calculations. See DOI: 10.1039/b000000x/

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