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A novel method to synthesize stable nitrogen-rich polynitrobenzenes with π -stacking for high-energy-density energetic materials

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Two nitrogen-rich energetic compounds with π -stacking, 1,1'dichloro-2,2',3,3',6,6'-hexanitro-5,5'-dihydroxyazobenzene (1) and 8-(2,4,6-triazido-3,5-dinitrophenyl)-8H-[1,2,3]triazolo[4',5':5,6]benzo [1,2-c:3,4-c']bis([1,2,5]oxadiazole) 1,4-dioxide (2), were prepared by a novel synthesis method, and their structures were determined by single-crystal X-ray diffraction analysis. The decomposition temperature of 1 is 336 °C and the 2 exhibits excellent heat of formation of 1160.5 kJ/mol (2.21 kJ/g). The condensation reaction of coupling of N=N bond and azido from 1 to 2 was proved to be an efficient method to synthesize benzotriazole. This synthetic strategy for benzotriazole may be arouse considerable interest in the area of organic synthesis.

In the past few decades, increasing research interest has been focused on the syntheses of the high density energetic materials (HEDMs). To acquire advanced HEDMs, many famous scientists such as Prof. Klapötke and Prof. Shreeve have devoted themselves to design and synthesize nitrogen-rich compounds with high energy.^{1, 2} For modern HEDMs, the high performance materials usually possess properties of good oxygen balance, superior thermal stability, high nitrogen content and density, predominant heat of formation, and release enormous energy during deflagration or explosion.3 Nitrogen-rich energetic materials functionalized with energetic groups (NO₂, NHNO₂, N₃, N=N, etc.) are rich in N-O, N-N, C-N, N=N bonds as well as extensive hydrogen bonds.4 The energy contains in these compounds is derived mostly from their high positive heats of formation, i.e. the energy is correlated to the number of nitrogen atoms in the compound.⁵ However, in explosives, the contradictory nature of high energy and stability, making the development of new HEDMs become an interesting and challenging problem.⁶⁻⁸ The nitrogen-rich energetic salts are the hottest topics

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In the area of energetic materials, most organic explosives with excellent performance are nitramine compounds, such as RDX, HMX et al. However, few organic compounds exhibit good balance between performance and sensitivity that can be used in military and civilian applications. Therefore, investigation on novel CHNO based explosives has significant meanings to material chemists throughout the world.

By analyzing the structures of reported in a large number of literatures about explosives so far, we can find out that the high performance organic energetic materials are mostly poly-nitro compounds. The presence of highly energetic group of azido group $(-N_3)$ and furoxan ring can increase the heats of formation. The macromonomer can be synthesized by small molecules through the N=N coupling reaction, and this method has been used to synthesize normal energetic materials. Meanwhile, the stability of nitro compounds can be improved by introducing the conjugate systems (Figure 1).

In a continuing effort to seek powerful and low sensitive HEDMs, we are interested in coupling aromatic compounds that



Figure 1 Advantages of poly-nitro compound with multi-nitro, multiazide and multi-oxidized furazan ring.

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contain nitro, azido, and furoxan group by N=N linker and fulfill the design strategies mentioned above. Herein, we synthesized 1,1'dichloro-2,2',3,3',6,6'-hexanitro-5,5'-dihydroxyazobenzene (1).which was connected by N=N to increase the stability. The organic compound 8-(2,4,6-triazido-3,5-dinitrophenyl)-8H-[1,2,3]triazolo[4', 5':5,6]benzo[1,2-c:3,4-c']bis([1,2,5]oxadiazole) 1,4-dioxide (2) was designed and synthesized by combining 1 and sodium azide via nucleophilic substitution and condensation reaction. These compounds were characterized by single-crystal X-ray diffraction, infrared spectroscopy, ¹H-NMR, ¹³C-NMR, elemental analysis, and DSC. This method was also proved to be a novel good reaction vields and high reaction selectivity method to synthesis benzotriazole. To understand its unique structure, the theoretical calculation was also used to investigate the unique structure of compounds 1 and 2.

The synthesis of the first two steps is similar to the method of Mehilal *et al.*¹¹ However, the product of the third synthesis step, 1,1'-dichloro-2,2',3,3',6,6'-hexanitro-5,5'-dihydroxyazobenzene (1), is confirmed to a completely novel compound. Interestingly, the nitro groups are replaced by the hydroxyls and the synthesis of 1 is shown in Scheme 1. The light yellow product was obtained with a high yield of 90 %.

As the chlorine substituents, hydroxyl groups, and the nitro groups that near the N=N group are very lively and easy to react with azido group via nucleophilic substitution. Inspired by the synthesis method reported by Li and Lü,¹² a new simple synthesis route for the formation of compound **2** has been proposed (Scheme 2). The compound **1** was treated with NaN₃ in acetic acid solution to synthesize the pure compound **2**. It is interesting to find that furazan formation only occurs on one aryl ring. We had considered this issue and conducted further exploration. We propose possible product structures (**3**) and optimize the structure with Gaussian. It was found that the product is planar structure, and it is difficult to change the conformation again on the basis of compound **2**.

The structures of **1** and **2** were determined by FT-IR, ¹H-NMR and ¹³C-NMR spectroscopy, elemental analysis as well as





Scheme 2 Synthesis of 2 from 1

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Figure 2 (a) The molecular structure of 1, (b) The planarity of 1, (c) The stacking crystal structure of 1

single crystal X-ray diffraction analysis. The spectrum of 13 C NMR indicates that the compound **2** may be a symmetric isomer. The spectral information, crystallographic data and refinement details can be found in the electronic supplementary information.

Crystals of 1 and 2 suitable for single-crystal X-ray diffraction were obtained by slow evaporation method, and 1 was from its acetone solution and 2 was from acetic acid solution at room temperature, respectively. The obtained results of 1 show that it crystallizes in the monoclinic space group P21/c and a calculated density of 1.933 g/cm³ at 153 K. Its high density may be attributable to intensive zig-zag packing mode and Cl atom as well as hydrogen bon ds. The molecular structure of 1, perpendicular and lateral views of the rings demonstrated the planarity of the unit, have been shown in Figure 2. The molecular unit contains two aromatic rings of which are linked by N=N forms a center symmetric structure (Figure 2(a)). Except the oxygen atoms in the nitro, all atoms are coplanar (Figure 2(b)). The length of the N=N bond that connects the aromatic rings is 1.265(3) Å, which is longer than the normal N=N bond (1.25 Å). The length of the C-N bond that connects the aromatic rings is 1.401(3) Å, which is shorter than the normal C-N single bond (1.490 Å). This phenomenon may be attributed to the conjugation effect. The stacking crystal structures of 1 show that the molecules are staggered and vertical arrangement thus ensured the molecular accumulation intensive (Figure 2(c)).

Compound 2 crystallizes in the orthorhombic space group Pbca



Figure 3 (a) A view of the molecular unit of compound 2. (b) The single vertical arrangement of the molecular unit of compound 2. (c) The stacking crystal structure of compound 2. (d) The π - π stacking structure of compound 2.

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with a crystal density of 1.877 g/cm³ at 153 K. The asymmetric unit of 2 is presented in Figure 3. The connection structure of two aromatic rings occurred conformational change. Further functionalization one of the two benzene rings by construction of the furoxan rings and construction of the benzotriazole after nucleophilic substitution (Figure 3(a)). It is interesting to find that all the functional group atoms perfectly situate the plane of the ring of benzotriazole, which nearly mutually-perpendicular with another benzene ring plane (Figure 3(b)). The bond lengths show nitrogennitrogen bonds of N12-N13 and N13-N14 range in 1.33-1.35 Å, which are consistent with bond lengths characteristic of aromatic nitrogen-nitrogen bonds (1.35 Å). The azido groups on the benzene ring present disordered arrangement and are all outside the plane. The stacking crystal structure of 2 shows the benzene rings with azido groups parallel to each other by face-to-face. Meanwhile, the molecules are staggered and vertical arranged in different directions, classifying the whole crystal to arrange wave-like-type stacking (Figure 3c)). These arrangements of π - π stacking (Figure 3(d)) facilitate the formation of stable conjugated systems, increasing the stability of this molecular. The distances between benzene ring centroids of compound 2 (4.01 Å), approximately belong to typical geometrical parameters of aromatic π - π interactions (3.65-4.00 Å).¹³ The high density of this compound can be rationalized in terms of the intensive packing mode.

Based on the experimental observations, we suggest the following plausible mechanism (Scheme 3). Superficially, the annulation reaction implementation is by N=N reacted with $-NO_2$ group, however, actually come true by nucleophilic substitution and condensation reaction. Initially, the product I is probably formed. Obviously, the $-N_3$ is a deficient electron group and the azo group is a rich electron group that can provide electron, the azo group reacts with the adjacent $-N_3$ to form an intermediate III, the compound **2** was obtained in good yield through thermal decomposition in the acetic acid.

Thermal stability, which needs first to be concerned, is a significant element, because the application of energetic materials will be limited by an unacceptably low decomposition temperature. The thermal decomposition temperature of compounds 1 and 2 were determined by differential scanning calorimetry (DSC) measurements with a heating rate at 5 °C/min (Table 1). Not surprisingly, the 1 exhibited excellent thermal stabilities with



Scheme 3 Proposed mechanism for the formation of 2

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decomposition temperature of 336°C and showed a sharp exothermic decomposes at 153.0°C and 165.1°C with two intense exothermic signals, which implicates the rapid decomposition of the compound in two steps (see Fig. S9†). Apparent activation energies (Ea), determined by Kissinger's method¹⁴ and Ozawa's method,¹⁵ are 126.1 and 155.4 kJ/mol, respectively (see Table S13†), which further illustrate the moderate activity of thermo-kinetic of the two compounds.

The enthalpy of formation $(\Delta_f H)$ of **1** and **2** were calculated by Gaussian 09 (Revision D.01) suite program 30, and were estimated to be -190.2 kJ/mol (-0.34 kJ/g) and 1160.5 kJ/mol (2.21 kJ/g), respectively (Table 1). Compound **2** has high positive enthalpies of formation due to the large number of N–N, N-O bonds and two furazan backbones. Compare with current used explosives, the heat of formation of compound **2** is much higher.

With the data of room-temperature density and heats of formation, the detonation properties¹⁶ of **1** and **2** was evaluated by using EXPLO 5 6.01 program. As it can be seen in Table 1, the calculated detonation velocity of compound **1** is 8082 m/s, and detonation pressure is 30.8 GPa. The calculated detonation velocity of compound **2** is 8094 m/s, and detonation pressure is 26.5 GPa. The value of detonation velocity of compound **2** dramatically exceeds TNT (6881 m/s) but lower than RDX (8748 m/s). Obviously, although the compounds **1** and **2** have high density and high enthalpy of formation, the detonation pressure is relatively low. This may due to the presence of the benzene rings generally have a low detonation velocity and detonation pressure.¹⁷

The testing impact sensitivity (IS) and friction sensitivity (FS) values are listed in Table 1. Of the two newly prepared compounds, compound 1 can be deemed as thermally-stable insensitive high explosives. The compound 2 exhibits similar sensitivity to RDX, suggesting compound 2 can serve as promising candidates for HEDM.

It has been found that analyses of the molecular orbitals provides valuable information on its electronic structure, and then helps us understand molecular reactivity and other molecular properties.²⁰ The imbalance between positive and negative regions determined the stability of energetic material. The regions of

Table 1. Physical Properties	of 1 and 2 Compared	with Those of TNT
and RDX		

	Tda	N ^b	D c	$\Delta_{\rm f} {\rm H}^{\rm d}$	V _D ^e	P ^f	IS ^g	FS ^h
1	336	20.3	1.892	-190.2	8082	30.8	15	192
				(-0.34)				
2	153	48.1	1.837	1160.5	8094	26.5	6.6	96
				(2.21)				
TNT	240	18.5	1.65	-115	6881	19.5	15	353
				(-0.26)				
RDX	210	37.8	1.82	80	8748	34.9	7.4	120
				(0.36)				

^a Thermal decomposition temperature (°C). ^b Nitrogen content (%). ^c The room-temperature densities was calculated by the volume expansion equation $\rho_{_{296K}} = \rho_{_{T}} / (1 + \alpha_v (298 - T)); \, \alpha_v = 1.5 \times 10^{-4} K^{-1}$. ^{1B} d Calculated heat of formation [kJ/mol (kJ/g)]. ^e Detonation velocity (m/s). ^f Detonation pressure (GPa). ^gImpact sensitivity (J). ^h Friction sensitivity (N). Properties of TNT and RDX are taken from ref. ^{3, 13,19}

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Figure 4 HOMO, LUMO, and ESP of compounds 1 and 2. Color coding for ESP are from red (negative) to blue (positive).

stronger positive potential indicate the high impact sensitivity in theory.²¹ Figure 4 illustrates HOMO, LUMO, and ESP of compounds 1 and 2.

It can be seen that the whole chemical bonds in compound **1** participate in HOMO and LUMO levels, indicating that the balance of the electrons in the molecule, make sure the stabilization of the skeleton framework. Meanwhile, the ESP indicates that the negative charges are concentrated in the N=N bond, which corresponds to the change in the bond length. Inspection of compound **2**, the whole chemical bonds participate in HOMO or LUMO levels, the large difference in energy between these two orbits indicates the stability of the substance. The ESP indicates that the charges tend to average, neither very positive nor very negative potential except few positive potential distributes on the C–NO₂ moiety or azide group. This very positive potential from which indicates the instability of a compound, indicating the possible trigger bond may appear here and contribute to its thermal stability.¹³

In conclusion, two conjugated nitrogen-rich organic compounds with good property were constructed and confirmed by single crystal X-ray diffraction. Structurally speaking, the formation of hydroxyl in the compound 1 may be produced by Stephenson reduction reaction. The compound 1 possesses good oxygen balance and superior thermal stability, can be considered as a potential thermally stable insensitive explosive. The compound 2 possesses good nitrogen content, moderate decomposition temperatures, acceptable sensitivities, excellent positive heat of formation at 1160.5 kJ/mol (2.21 kJ/g) and ascendant density of 1.837 g/cm³ that are higher than RDX. Theoretical performances of detonation velocity and detonation pressure are 8094 m/s and 26.5 GPa, respectively. Furthermore, computational results of HOMO, LUMO and ESP also support the superiority of the compounds 1 and 2. The presence of nitro, azide group, and the oxidized furazan ring simultaneously in this molecule promote its detonation performance. Meanwhile, the benzene ring and oxidized furazan ring increase its thermal stability as well as reduce sensitivity. The larger multi-nitro, multi-azide and multi-oxidized furazan ring compound 2 with π - π stacking of benzene ring, and macrocyclic aromatic conjugation system can be confirmed as a new green HEDM. Furthermore, the hitherto unknown nitrogen rich CNO-compound 2 has been synthesized by coupling of N=N bond and azido, which can also be considered as a novel method with high yield to synthesize benzotriazole. In the

recent literature, to the best of our knowledge there is no report related to the method. It suggests the future chemistry and medicine applications might be interested in this method as synthesis of benzotriazole.

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Conflicts of interest

There are no conflicts to declare.

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