



A new family of insensitive energetic copolymers composed of nitro and nitrogen-rich energy components: Structure, physicochemical property and density functional theory

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ABSTRACT

A series of nitro-containing energetic copolymers, HD-DNSA (**1**), G-DNSA (**2**), AG-DNBA (**3**), TZ-DNSA (**4**), 5-ATZ-DNSA (**5**) and 4-ATZ-DNSA (**6**) (DNSA, 3,5-dinitrosalicylic acid; HD, hydrazine; G, guanidine; AG, amino guanidine; TZ, 1H-1,2,4-triazole; 5-ATZ, 5-amino-tetrazole; 4-ATZ, 4-amino-1,2,4-triazole) are successfully synthesized based on intermolecular interactions. All compounds are structurally characterized by powder and single crystal X-ray diffractions, infrared spectrum (IR) and elemental analyses. Thermogravimetric analysis (TG), differential scanning calorimetry (DSC) and density functional theory (DFT) calculations show that compounds **1–6** present favorable thermal stabilities. Moreover, all compounds feature good detonation properties and low sensitivities, representing potential energetic materials and promising alternatives to traditional explosives.

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1. Introduction

Energetic materials represent a class of compounds with plenty of stored chemical energy in their molecular structures, which are usually applied in civil and military areas [1–7]. Although an increasing number of new monomer explosives have been reported, there are rarely satisfactory on the coexistence of safety-power [8,9]. As well known, an incorporation of numerous explosives benefits for improving the density and detonation performance, the aggregates of excess energetic groups into a limited backbone leads to decreased sensitivity to mechanical stimulation [10,11]. It has thus aroused more attention and intense research interest to explore a more suitable strategy to synthesize of the energetic materials with high-energy and low-sensitivity [12]. The energetic copolymers prepared *via* intermolecular interactions are promising alternatives, in which the energetic units could be molecule-arranged and tailored according to the requirements of energy and sensitivity [13–19]. The prominent scientists, Klapotke [20–24] and Shreeve [25–31] have made a great contribution

in the field of energetic materials that many energetic salts with excellent properties have been synthesized through intermolecular interactions. Recently, Zhou et al., synthesized a series of energetic salts of 3-Nitro-1-(2H-tetrazol-5-yl)-1H-1,2,4-triazol-5-amine (HANTT) that displayed good thermal stability and low sensitivity [32]. As a unique class of energetic materials, energetic copolymers with multi-components often perform lower vapor pressure, higher density, better thermal stability and more convenient synthetic method [33–36].

As reported, nitrogen-rich compounds possess high heats of formation which are directly attributable to an abundance of inherently energetic N–N and C–N bonds in the molecule, and provide the hydrogen-bond donor and acceptor tend to form extensive intermolecular hydrogen-bonding [37]. Therefore, nitrogen-rich compounds are usually served as the preferred energetic units in the construction of energetic materials [38,39]. Beyond that, the nitro group is more active than other energetic groups (amidogen, etc) because of the integrated properties including more rapid release of energy, higher bond dissociation energy, greater density, and more appropriate oxygen balance and nitrogen content [40–42], thereby, polynitroarenes with explosive performance have been widely investigated and used in civil as well as military applications, in which the rigid aromatic rings are conducive to improving the structural stability and insensitivity [43]. It is antici-

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pated that combination of nitrogen-rich unit and nitro group would result in energetic copolymers with low-sensitivity.

In the present work, six energetic salts, HD-DNSA (**1**), G-DNSA (**2**), AG-DNBA (**3**), TZ-DNSA (**4**), 5-ATZ-DNSA (**5**) and 4-ATZ-DNSA (**6**) (DNSA, 3,5-dinitrosalicylic acid; HD, hydrazine; G, guanidine; AG, amino guanidine; TZ, 1H-1,2,4-triazole; 5-ATZ, 5-amino-tetrazole; 4-ATZ, 4-amino-1,2,4-triazole) have been synthesized and structurally characterized. Compounds **1–6** consist of the active NO₂ group and conjugated system, which present stabilized structures due to the existence of large amounts of intermolecular interactions. Sensitivity tests show that the title compounds are insensitive to external stimuli. In addition, the detonation properties are investigated, indicating that **1–6** display the potential of energetic materials.

2. Experimental

General caution: 3,5-dinitro salicylic acid and the title compounds are energetic materials and tend to explode under the intense friction and impact stimulation. Although no difficulties were experienced in the synthesis of these materials, proper protective measures should be taken, especially when the compounds are prepared on a large scale.

2.1. Materials and instruments

All solvents and chemicals (>99% purity) were obtained from commercial sources and used without further purification unless otherwise stated.

Fourier transform infrared spectroscopy (FT-IR) analysis was performed on a Bruker Vector-33 Fourier transform infrared spectrometer (Bruker Spectrospin, Karlsruhe, Germany) with spectrum range of 4000–500 cm⁻¹. IR spectra were recorded on samples dispersed in KBr pellets. Thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) were performed on a Netzsch STA 449C instrument and a CDR-4P thermal analyzer of Shanghai Balance Instrument factory, respectively. The temperature range for the heating curve was 33–500 °C, and the sample was heated at a rate of 5 °C min⁻¹ under a dry oxygen-free nitrogen atmosphere.

Elemental analyses were performed on a Vario EL III analyzer fully automated trace element analyzer. The sensitivity to impact stimuli was determined by fall hammer apparatus applying standard staircase method using a 2 kg drop weight, and the results were reported in terms of height for 50% probability of explosion (*h*_{50%}) [44]. The friction sensitivity was determined on a Julius Peter apparatus by following the BAM method [45].

The phase purity of the bulk samples was verified by powder X-ray diffraction (PXRD) measurements performed on a Rigaku RU200 diffractometer at 60 kV and 300 mA with Cu K_α radiation ($\lambda = 1.5406 \text{ \AA}$) with a scan speed of 5° min⁻¹ and a step size of 0.02° in 2θ . The calculations were carried out using the Gaussian 03 suite of programs [46]. The crystal asymmetric units of the compounds were selected as the initial structure, and the DFT-B3LYP/6-31+G(d) method was used to optimize the structure of the compounds and compute their frequencies. Vibration analysis indicates that the optimized structure are in accordance with the minimum points on the potential energy planes, which means no virtual frequencies, proving that the obtained optimized structures are stable.

2.2. Single crystal X-ray diffraction

The single-crystal X-ray diffraction data of the crystals were collected on a Bruker Smart Apex CCD diffractometer equipped with graphite monochromatized Mo K_α radiation ($\lambda = 0.71073 \text{ \AA}$) using ω and ϕ scan modes. The structures were solved by the direct methods using the SHELXS-97 [47] and refined by means

of full-matrix least-squares procedures on F² with SHELXL-97 program [48]. All non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were placed in calculated positions and constrained to ride on their parent atoms. Selected crystallographic data and structural refinement details of **1–6** are summarized in Table 1. Selected bond lengths and bond angles of **1–6** are listed in Table S1 (in Supporting information). The hydrogen-bonding distances and angles are summarized in Table S2 (in Supporting information).

2.3. Preparation of 1–6

2.3.1. Preparation of 1

DNSA (0.3 mmol) was dissolved in 5 mL of a 1:9 mixture of hydrazine and water with stirring for 20 min. Then the resulting solution was sealed into a Teflon-lined bomb and heated at 90 °C for 3 days. After a gradual cooling at room temperature 25 °C, yellow block crystals of **1** were obtained in a yield of 76% (based on DNSA). Anal. (%) Calcd. For C₇H₈N₄O₇ (260.17): C, 32.29; H, 3.07; N, 21.52. Found: C, 32.32; H, 3.11; N, 21.56. IR (KBr, cm⁻¹): 3361 m, 3073 m, 2688 w, 1704 m, 1605 m, 1469 m, 1340 s, 1289 w, 1160 m, 1090 m, 973 m, 796 w, 708 w.

2.3.2. Preparation of 2

Guanidine carbonate (0.3 mmol) was dissolved in boiling water (5 mL) and stirred for 20 min. Then the Guanidine aqueous solutions and DNSA (0.3 mmol) were sealed into a Teflon-lined bomb and heated at 70 °C for 3 days. After a gradual cooling to room temperature 25 °C, yellow block crystals of **2** were obtained in a yield of 81% (based on DNSA). Anal. (%) Calcd. For C₈H₉N₅O₇ (287.20): C, 33.43; H, 3.13; N, 24.37. Found: C, 33.46; H, 3.17; N, 24.41. IR (KBr, cm⁻¹): 3484 s, 3389 s, 3190 s, 1663 m, 1533 m, 1454 m, 1340 s, 1283 m, 1175 m, 1081 m, 932 m, 745 m, 609 m.

2.3.3. Preparation of 3

The salt was prepared following the procedure for **2** from DNSA (0.3 mmol) and amino guanidine bicarbonate (0.3 mmol) to give yellow plates crystals in a yield of 74% (based on DNSA). Anal. (%) Calcd. For C₈H₁₀N₆O₇ (302.22): C, 31.76; H, 3.31; N, 27.79. Found: C, 31.82; H, 3.36; N, 27.82. IR (KBr, cm⁻¹): 3484 s, 3383 s, 3214 m, 2883 w, 1676 s, 1575 w, 1520 w, 1441 w, 1311 s, 1175 m, 1081 m, 989 w, 932 w, 745 m, 708 m, 587 m.

2.3.4. Preparation of 4

DNSA (0.3 mmol) and TZ (0.3 mmol) were dissolved in acetonitrile (10 ml) with stirring at 70 °C. The resulting solution was filtered and kept at room temperature for crystallization. After five days, yellow block crystals of **4** were obtained in a yield of 79% (based on DNSA). Anal. (%) Calcd. For C₉H₇N₅O₇ (297.20): C, 36.34; H, 2.36; N, 23.55. Found: C, 36.37; H, 2.39; N, 23.59. IR (KBr, cm⁻¹): 3427 m, 3117 m, 3045 w, 2902 w, 2782 w, 1663 w, 1612 w, 1520 m, 1447 m, 1353 s, 1274 s, 1167 m, 1039 m, 945 m, 903 m, 798 w, 701 m, 638 m, 552 m.

2.3.5. Preparation of 5

A mixed aqueous ethanol (6 mL, 1:1) of DNSA (0.3 mmol) and 5-ATZ (0.3 mmol) was heated in a Teflon-lined bomb at 70 °C for 3 days, slowly cooled to room temperature 25 °C. Yellow block crystals of **5** were obtained in a yield of 81% (based on DNSA). Anal. (%) Calcd. For C₈H₇N₇O₇ (313.21): C, 30.65; H, 2.23; N, 31.29. Found: C, 30.68; H, 2.26; N, 31.34. IR (KBr, cm⁻¹): 3598 m, 3504 m, 3095 m, 2540 w, 1862 m, 1698 m, 1605 s, 1540 s, 1447 m, 1347 m, 1252 m, 1167 m, 1090 m, 923 m, 844 w, 701 s.

2.3.6. Preparation of 6

Following the same synthetic procedure of **5**, yellow block crystals of **6** were obtained through the replacement of 4-ATZ with

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