

# Synthesis and Detonation Properties of 5-Amino-2,4,6trinitro-1,3-dihydroxy-benzene

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5-Amino-4,6-dinitro-1,3-dihydroxy-benzene (**6**) was synthesized through the ring-opening reaction of macrocyclic compound **4** with the aid of VNS (vicarious nucleophilic substitution of hydrogen) reaction conditions. The mechanism of ring opening of macrocyclic compound **4** was studied. 5-Amino-2,4,6-trinitro-1,3-dihydroxy-benzene (**8**) was obtained after the nitration of **6** in KNO<sub>3</sub> and concentrated sulfuric acid. The thermal stability, sensitivity, and other detonation performances of **6** or **8** were compared to commercially used 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) or 1,3,5-trinitrotriazacyclohexane (RDX), respectively. All target compounds were characterized by using

## 1. Introduction

The synthesis of high-energy and high-density materials is one of the important research and development aspects of energetic materials. Development of modern energetic materials is significant in materials science research. Driven by increasing demands from both military and civilian applications, the structural design of energetic molecules has to meet diverse standards, for example, performance properties, environmental compatibility, as well as safety concerns.<sup>[1-4]</sup> Synthesis of energetic materials based on a benzene backbone has had a long tradition since the discovery of 2,4,6-trinitrotoluene (TNT).<sup>[5,6]</sup> Owing to its important property as a melt-castable explosive, it is still in use nowadays, even though it is highly toxic to the environment.<sup>[7]</sup> Multi-nitro (or multi-hydroxyl) and multi-amino aromatic explosives are important members in the family of explosives, owing to strong intramolecular hydrogen bonds between alternating amino and nitro groups. 1,3,5-triamino-2,4,6trinitrobenzene (TATB) has a remarkably higher density of 1.930 g cm<sup>-3</sup>, originating primarily from the hydrogen-bonding interactions by virtue of additional amino functionalization. TNPG (1,3,5-trinitro-2,4,6-phloroglucinol) also has a remarkably

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single-crystal X-ray diffraction, NMR spectroscopy, elemental analysis, and differential scanning calorimetry. The sensitivities were determined by using BAM methods (drop-hammer and friction tests). Performance parameters, including heats of formation and detonation properties, were calculated by using Gaussian 03 and EXPLO5 v6.01 programs, respectively. It is worth pointing out that compound **8** has a remarkable measured density of 2.078 g cm<sup>-3</sup> at 298 K. In addition, compound **8** is more insensitive than RDX (compound **8**: *IS* = 11 J; RDX: *IS* = 7 J; *IS* is the impact sensitivity).

high density of 2.170 g cm<sup>-3</sup>, for the same reason. For many applications, TATB ( $H_{50}$  = 320 cm) shows a meager performance and is too insensitive to detonation. Similarly, one obvious weaknesses of TNPG is that it is too strongly acidic for direct use in military or civilian applications, although it has a better impact sensitivity value ( $H_{50}$  = 27 cm) than TATB. Therefore, alternatives with a better detonation performance, such as less toxic properties, weaker or no acidity, lower sensitivities towards external stimuli like impact, friction, and electrostatic discharge, and safer synthesis, are desired.

It is worth pointing out that we originally intended to prepare compound 5 according to the principle of vicarious nucleophilic substitution of hydrogen (i.e. the VNS reaction) by treatment of 4-amino-4H-1,2,4-triazole (ATA) and compound 4 with sodium methanol in dimethyl sulfoxide (DMSO) solution (Scheme 1). Compound 5 was expected to be a substitute for tetranitrodibenzo-1,3a,4,6a-tetrazapentalene (TACOT) as a type of heat-resistant explosive, because its thermal decomposition temperature was predicted to exceed the that of TACOT (the other calculated detonation performances of compound 5 were much better than those of TACOT). However, compound 5 was not obtained from the reaction. Rather, the solution that was obtained from the reaction was treated with 6 M HCl and purified by column chromatography to obtain compounds 6 and 7. It was unexpected to obtain compounds 6 and 7, because the conditions for the ring-opening reaction of the macrocyclic compound are usually very demanding and have not been reported thus far.

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Scheme 1. Synthesis of compound 6.

### 2. Results and Discussion

#### 2.1. Synthesis

Compound **4** was successfully synthesized by employing compound **3** as a common precursor. Compound **3** was prepared by using a similar synthetic route in a single step by reacting 1,5-difluoro-2,4-dinitrobenzene and resorcinol under basic conditions (Scheme 1).<sup>[8-9]</sup> First, 1,3-dichlorobenzene was transformed into 1,5-difluoro-2,4-dinitrobenzene in 93 % yield. Compound **4** was obtained by nitration of compound **3**. The operation processes of the three reactions are very simple, and postprocesses are also simple (see the Supporting Information).

It is worth pointing out that we originally intended to prepare compound **5** according to a known procedure (VNS method) by treatment of compound **4** with ATA and sodium methanol in DMSO solution. However, compound **5** was not obtained from the reaction (Scheme 1). The mixture was purified by virtue of a silica gel column and we verified that a new compound, 5-amino-4,6-dinitro-dibenzene-1,3-diol (**6**), and another compound, 4,6-dinitrobenzene-1,3-diol (**7**), were obtained. Then, compound **6** was nitrated with a mixture of KNO<sub>3</sub> and concentrated sulfuric acid to get the new compound 5amino-2,4,6-trinitro-1,3-dihydroxy-benzene (**8**) (Scheme 2).



Scheme 2. Synthesis of compound 8.

#### 2.2. Single-Crystal X-ray Structure Analysis

A crystal of 8·H<sub>2</sub>O, suitable for single-crystal X-ray diffraction, was obtained by dissolving 8 in a mixed solvent of methanol and ethyl acetate. The sums of the dihedralangles of compound 8: [ (C2–C1–O1–H1A) = 233.89°, (C1–C2–N1–O2) = 240.43°, ≩(N1–O2–H1A) = 103.06°, ≩(O1–H1A–O2) = 139.42°, the sum of the six angles of the hexagon is 716.8° (233.89° + $240.43^{\circ} + 103.06^{\circ} + 139.42^{\circ} = 716.8^{\circ});$ **∢**(C3–C2–N1–O3) =  $(C2-C3-N2-H4A) = 232.51^{\circ}$ , 238.04°, (O3-N1-H4A) =  $101.61^{\circ}$ , (O3–H4A–O4) = 147.03°, the sum of the six angles of 147.03,  $\bigstar$  (H4A»1-O3»1-N»1) = 101.61°, the sum of the six angles of the hexagon is 719.19°], which should reflect that the two C-NO<sub>2</sub> (2-NO<sub>2</sub>, 6-NO<sub>2</sub>) groups, two C-OH groups, the C-NH<sub>2</sub> group, and benzene ring are nearly coplanar with four torsion angles, which are less than  $3.2^{\circ}$  (720–716.8° =  $3.2^{\circ}$ ). In addition, the sums of the remaining dihedral angles of compound 8 [(C3)-C4-N3-O5)=61.68° or (C3)-C4-N3-O5»1) = 118.32°], which should reflect the degree of molecular twist, are 61.68°. Thus, two planes are formed in compound 8, and have an angle  $(180-118.32^\circ=61.68^\circ)$  between the plane of C4–O5–N3–O5»1 and the plane of aromatic ring. Four intramolecular hydrogen bonds are formed between the two hydroxyl groups, one amino group, and the two nitro groups in compound 8. The intramolecular H-O distances are O2-H1A = H4A…O3 = 1.863 Å, H4A»1…O3»1 = 1.863 Å, 1.802 Å. and O2»1···H1A»1 = 1.802 Å, respectively. 5-Amino-2,4,6-trinitro-1,3dihydroxy-benzene monohydrate (8·H<sub>2</sub>O) crystallizes in the triclinic space group P-1 with six molecules per unit cell (Figure 1 b), and has a single-crystal density of 1.960 g cm<sup>-3</sup> (when compound 8 does not contain crystalline water, its measured density is 2.078 g cm<sup>-3</sup>) at 298 K. A molecule of water is connected to three molecules of compound 8 by hydrogen bonds. Two oxygen atoms of the nitro group in compound 8 (not formed into the intramolecular hydrogen bonds) are connected through intermolecular hydrogen bonds with two different water molecules, respectively. The length of the intermolecular hydrogen bond is 5.659 Å (N–O…H–O).

A crystal of compound **6**, suitable for single-crystal X-ray diffraction, was successfully obtained by dissolving **6** in ethanol and letting ethyl acetate (EA) diffuse into the solution. Compound **6** crystallizes in the triclinic space group *P*-1 with six molecules per unit cell (Figure 2 b). It has a single-crystal density of 1.916 g cm<sup>-3</sup> at 173 K.

The 5-amino,4,6-dinitro,1,3-dihydroxyl groups and benzene ring are nearly planar, owing to consecutive hydrogen-bond interactions. The sums of dihedral angles [ $\downarrow$ (C6–C1–O1–H1c) = 232.82°,  $\downarrow$ (C1–C6–N3–O6) = 238.47°,  $\downarrow$ (N3–O6–H1C–O1) = 247.55°, the sum of the six angles of the hexagon is 718.84°;  $\downarrow$ (H2C–O2–C3–C4) = 228.66°,  $\downarrow$ (C3–C4–N1–O3) = 238.19°,  $\downarrow$ (N1–O3–H2C–O2) = 252.74°, the sum of the six angles of the hexagon is 719.59°;  $\downarrow$ (H2B–O5–N3–C6) = 224.22°,  $\downarrow$ (N3–C6–C5–N2) = 242.22°,  $\downarrow$ (C5–N2–H2B–O5) = 253.1°, the sum of the six angles of the hexagon is 719.59°;  $\downarrow$ (H2A–N2–C5–C4) = 240.7,  $\downarrow$ (C5–C4–N1–O4) = 242.02, N1–O4–H2A–N2 =

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Figure 1. a) Single-crystal X-ray structure of 8. b) Packing diagram of 8.

235.34, the sum of the six angles of the hexagon is 718.06°)], which should reflect that the two C–NO<sub>2</sub> (2-NO<sub>2</sub>, 6-NO<sub>2</sub>) groups, two C–OH groups, the C–NH<sub>2</sub> group, and benzene ring are nearly coplanar with three torsion angles, are less than 2°. The two nitro groups lie within the ring plane fixed by the intermolecular and the lengths of three hydrogen bonds are 1.7632 Å (O1-H1c···O6), 1.728 Å (O2-H2c···O3), and 1.8412 Å (*N*-H2B···O5).

A crystal of 4,6-dinitro-1,3-dihydroxy-benzene (7), suitable for single-crystal X-ray diffraction, was successfully obtained by dissolving 7 in ethanol and letting the ethanol slowly evaporate into the air. The unit cell of 7 crystallizes in the triclinic space group P-1 with six molecules per unit cell (Figure 3b). It has a single-crystal density of 1.824 g cm<sup>-3</sup> at 173 K. The sums of dihedral angles [ ≩ (H1A–O1–C1–C6) = 231.32°, ≩ (N2–O6–  $H1A-O1) = 248.09^{\circ}; \Rightarrow (C1-C6-N2-O6) = 239.87^{\circ}, \text{ the sum of}$ 239.92°; ≩(H2A–O2–C3–C4) = 229.77°; ≩(N1–O3–H2A–O2) = 250.23°; the sum of the six angles of the hexagon is 719.92], which should reflect that the two C-NO<sub>2</sub> (4-NO<sub>2</sub>, 6-NO<sub>2</sub>) groups, two C-OH groups group, and benzene ring are nearly coplanar with two torsion angles, are less than 2°. The lengths of the two hydrogen bonds are 1.865 Å (O3-H2A) and 1.860 Å (O6--H1A). As can be seen in the crystal structure given in





Figure 2. a) Single-crystal X-ray structure of 6. b) Packing diagram of 6.



Figure 3. a) Single-crystal X-ray structure of 7. b) Packing diagram of 7.

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Figure 3, the two C–NO<sub>2</sub>, two hydroxyl groups, and benzene ring are nearly coplanar. Two nitro and two hydroxyl groups lie within the ring plane and are fixed by intermolecular hydrogen bonds.

#### 2.3. Physicochemical Properties

ture of 8·H<sub>2</sub>O.

The phase transition and thermal stabilities of all compounds were determined by using differential scanning calorimetry (DSC). With the exception of  $8 \cdot H_2O$ , its thermal decomposition temperature is only 205 °C, which is lower than that of compound **6** (291 °C). Being non-coplanar is one of the important reasons for the decrease in thermal decomposition temperature (Table 1). The thermal decomposition temperatures are ar-

| Table 1. Physical properties of some of the compounds discussed.   |   |                                   |                           |  |  |                          |                                 |  |  |  |  |
|--|---|-----------------------------------|---------------------------|--|--|--------------------------|---------------------------------|--|--|--|--|
| Cmpd   | $ ho^{\scriptscriptstyle{[a]}}$ [g cm $^{\scriptscriptstyle{-3}}$ ] | $D^{(b)}$<br>[m s <sup>-1</sup> ] | P <sup>[c]</sup><br>[GPa] | $\Delta H_{ m fm}^{ m [d]}$<br>[kJ mol <sup>-1</sup> ] | T <sub>DSC</sub> <sup>[e]</sup><br>[C] | IS <sup>[f]</sup><br>[J] | <i>FS</i> <sup>[g]</sup><br>[N] |  |  |  |  |
| 4  | 1.750   | 7865                              | 28.9                      | 618  | 375                                    | 42                       | 160                             |  |  |  |  |
| 6  | 1.916   | 7697                              | 30.7                      | -305   | 291                                    | 30                       | 240                             |  |  |  |  |
| 7  | 1.824   | 7363                              | 24.2                      | -295   | 302                                    | 24                       | 240                             |  |  |  |  |
| 8  | 2.078 <sup>[h]</sup>  | 8750                              | 36.5                      | -285   | 205 <sup>[i]</sup>                     | 11                       | 120                             |  |  |  |  |
| RDX  | 1.816   | 8748                              | 34.9                      | 80   | 204                                    | 7                        | 120                             |  |  |  |  |
| TATB   | 1.930   | 7606                              | 31                        | 75   | 350                                    | >50                      | 350                             |  |  |  |  |
| нмх  | 1.905   | 9144                              | 39.5                      | 104  | 280                                    | 7                        | 120                             |  |  |  |  |
| [a] Single-crystal density. [b] Detonation velocity (calculated with EXPLO5 v6.01). [c] Detonation pressure (calculated with EXPLO5 v6.01). [d] Heat of formation. [e] Decomposition temperature. [h] Measured density. [h] Eriction constituity. [l] Decomposition temperature temperature temperature temperature temperature. |   |                                   |                           |  |  |                          |                                 |  |  |  |  |

ranged from large to small [350 (TATB) > 302 (7) > 291 (6) >  $280(HMX) > 205(\mathbf{8} \cdot \mathbf{H}_2 \mathbf{O}) \cong 204 \,^{\circ} \mathbf{C}$  (RDX)]. At the same time, their densities are arranged from large to small [2.078 (9) > 1.930 (TATB) > 1.916 (6) > 1.90 (HMX) > 1.824 (7) > 1.816 g cm<sup>-3</sup> (RDX); except for the density for compound 9, which is a measured density, those of the others are the single-crystal densities]. Thus, the enhanced inter- and intramolecular interactions in the molecule give rise to compact packing and smaller volume, which are conducive to improving the density and stability of these materials. It is noteworthy that compound  ${\bf 8}$  has an impressive measured density of 2.078 g cm<sup>-3</sup> at 298 K, which is higher than those for the currently used energetic materials, such as RDX (1.816 g cm<sup>-3</sup>) and cyclo-1,3,5,7-tetramethylen-ene-2,4,6,8-tetranitramine (HMX, 1.91 g cm<sup>-3</sup>). In addition, the lowest density compound studied here (among compounds 6–8), that is, compound 7 (1.824 g cm<sup>-3</sup>), has a higher density than that of RDX (1.816  $g cm^{-3}$ ).

To evaluate the energetic properties, computation of the heats of formation were performed by using the Gaussian 03 suite of programs (Supporting Information). The calculated detonation velocities are arranged from large to small: HMX (9320 ms<sup>-1</sup>) > RDX (8748 ms<sup>-1</sup>)  $\cong$  **8** (8746 ms<sup>-1</sup>) > **6** (7697 ms<sup>-1</sup>) > TATB (7606 ms<sup>-1</sup>) > **7** (7363 ms<sup>-1</sup>). The forma-

tion enthalpy of compound **8** is similar to that of RDX. The formation enthalpy of compound **6** is higher than that of TATB.

In addition to the heat of formation, detonation properties as well as impact and friction sensitivities play a major role in new energetic materials. With experimental densities and calculated values for heats of formation in hand, the detonation pressures (*P*) and velocities (*D*) were calculated by using EXPLO5 v6.01 (see the Supporting Information). The calculated detonation pressures and velocities lie in the ranges from 24.2 to 36.5 GPa, and from 7363 to 8746 m s<sup>-1</sup>. Compound **8** exhibits the highest detonation properties (*P*=36.5 GPa; *D*= 8750 m s<sup>-1</sup>) among compounds **6–8**, which are significantly superior to the highly explosive RDX (*P*=34.9 GPa; *D*= 8748 m s<sup>-1</sup>). In addition, the detonation velocity ratio of compound **6** (*D*=7697 m s<sup>-1</sup>) is higher than that of TATB (7606 m s<sup>-1</sup>), but the detonation pressure of compound **6** (*P*= 27.2 GPa) is lower than that of TATB (31.0 GPa).

Impact and friction sensitivity measurements were made by using a standard BAM Fallhammer and a BAM friction tester. Not surprisingly, compound 8, with an impact sensitivity (IS) of 11 J and friction sensitivity (FS) of 240 N, is more insensitive to RDX with an IS of 7 J and FS of 120 N, but it is more sensitive than TATB with an IS of 50 J and FS of 350 N. In addition, the IS (30 J) and FS (240 N) of compound 6 are lower than those of TATB, but are larger than those of RDX, although the detonation properties of compound 6, including detonation velocity, detonation pressure, and even density, are similar to TATB. Oxygen balance (OB) is another important index to evaluate the deficiency or excess of oxygen in a molecule required to convert all carbon into carbon monoxide and all hydrogen into water. The OB value of compound 8 is -36.92%. Compound 8 has an excellent OB value of -36.92%, which is better than that of TATB (-55.81%).

#### 2.4. Reaction Mechanism of Compound 6

It is believed that the amination of compound 4 proceeds in accordance with the VNS mechanism.<sup>[9-12]</sup> In the presence of a strong base, deprotonation of 4-amino-4H-1,2,4-triazole (ATA) occurs, resulting in the formation of 4-amino-4H-1,2,4-triazole imide (ATAI). The latter is added onto the aromatic ring of compound  ${\bf 4}$  in the middle of the two nitro groups to give the corresponding ó-adduct. When the ó-adducts are acted upon by a base, deprotonation with simultaneous elimination of 1,2,4-triazole takes place to obtain intermediate 12. A more stable intermediate 13 or 14 is obtained, because of the repulsive effect of the electronic cloud of the 5-NH<sub>2</sub> group. According to the same mechanism, intermediate 15 is obtained. Intermediate 15 is hydrolyzed with an aqueous solution of 6 M hydrochloric acid to obtain compounds 6 and 7. (Scheme 3). When the aqueous solution of 6 m hydrochloric acid is replaced by an aqueous solution of acetic acid, compounds 6 and 7 are still obtained (Table 2). Compound 4 is synthesized after the nitration of 3 in nitrosonitric acid and concentrated sulfuric acid; thus, it is stable and the ring-opening reaction does not occur in strong acid. Similarly, compound 4 is also

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Scheme 3. Reaction mechanism to obtain compound 6.

| Table 2. Relationship between the concentration of acid and the yield of compound 6 or 7. |       |       |       |       |       |       |  |  |  |  |
|---|-------|-------|-------|-------|-------|-------|--|--|--|--|
| Cmpd.   | 12 м  | 6м    | 3м    | 10 м  | 5м    | 5м    |  |  |  |  |
|   | НСІ   | HCl   | HCl   | HOAc  | HOAc  | HNO₃  |  |  |  |  |
| Yield of <b>6</b> [%]   | 81.33 | 81.08 | 80.92 | 81.06 | 81.01 | 81.12 |  |  |  |  |
| Yield of <b>7</b> [%]   | 75.23 | 75.16 | 76.01 | 75.47 | 75.34 | 75.27 |  |  |  |  |

stable and a ring-opening reaction does not occur in alkaline conditions if 4-amino-4*H*-1,2,4-triazole (ATA) is not added.

## 3. Conclusions

From this experimental study the following conclusions can be drawn. 5-Amino-2,4,6-trinitro-1,3-dihydroxybenzene can be synthesized in three steps in high purity and on a large scale. The molecular structures of **6**, **7**, and **8** were determined by



using single-crystal X-ray diffraction. The values of the detonation velocity and thermal decomposition temperature of 5amino-2,4,6-trinitro-1,3-dihydroxybenzene is similar to that of RDX, but its values of impact sensitivity, detonation pressure, and the measured density (2.078 g cm<sup>-3</sup>) are much higher than those of RDX. All of these show that 5-amino-2,4,6-trinitro-1,3dihydroxybenzene is a more promising energetic material than RDX. It can also be found that compound **6** displays an excellent performance for energetic materials. The values of the density, detonation velocity, and detonation pressure of the compound **6** are equivalent to those of TATB. However, the sensitivities of compound **6** lie between RDX and TATB; thus, it is more sensitive and easy to explode than TATB. In addition, the ring-opening reaction mechanism of macrocyclic compound **4** has also been studied.

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## **Conflict of Interest**

The authors declare no conflict of interest.

**Keywords:** benzene backbone • energetic materials • macrocyclic compound • mechanism • VNS reaction

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## **FULL PAPERS**





Synthesis and Detonation Properties of 5-Amino-2,4,6-trinitro-1,3dihydroxy-benzene



**Off with a bang!** 5-Amino-4,6-dinitro-1,3-dihydroxy-benzene (**6**) is synthesized through a ring-opening reaction of macrocyclic compound **4** with the aid of VNS (vicarious nucleophilic substitution of hydrogen) reaction conditions.

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