Stability Study of Poly Nitro Substituted Compounds of cis-syn-cis-2,6-Dioxodecahydro-lH,5H-Diimidazo[4,5-b:4',5'-e] Pyrazine

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Abstract. Due to their excellent performance both in density and high detonation velocity, poly nitro substituted cis-syn-cis-2,6-dioxodecahydro-lH,5H-diimidazo [4,5-b:4',5'-e] pyrazine derivatives (2-5) attract our focus. The stabilities study showed that the sensitivity of these compounds is increasing with more nitro groups substituted. Although compound 5 with six nitro groups exhibits the most excellent detonation velocity, it is very sensitive to friction and impact. As isomer to each other, compound 2 and 3 showed not only low sensitivity but also good thermal stability with similar detonation performance to RDX and HMX. It suggests that they are potential energetic materials.

1. Introduction
As weapon energy carrier, energetic materials must meet the requirements of high energy density, low sensitivity and good environmental adaptability [1]. Therefore, improving the energy density has always been the major goal of energetic materials research and development [2]. N-heterocyclic explosives have been one of the high energy density material (HEDM) researchers’ focuses because of the high formation heat and excellent oxygen balance [3]. However, Poly nitro N-hetero monocyclic compounds are difficult to enhance density and energy greatly due to their limited number of modified nitrogen atoms, such as RDX and HMX [4]. Therefore, many researchers have begun to design and synthesize fused aza-polynitrocyclic compounds. Binary, ternary or more aza-polycyclic skeleton can make molecular structure more compact, which increases molecular density[5]. High nitrogen content and multi-ring tension will improve energy itself, and the increase of modified nitrogen atoms can introduce more nitro groups or other energetic groups to further increase the molecular density and energy significantly [6]. Therefore, design and synthesis of fused aza-polynitrocyclic energetic compounds are important and promising way to prepare HEDM [7].

In 1990, Boyer and his colleagues publicly reported synthetic methods of HHTDD for the first time [8] and its performances such as density and detonation velocity have been reported [9]. In previous work[10], these poly nitro substituted compounds of cis-syn-cis-2,6-dioxodecahydro-lH,5H-diimidazo [4,5-b: 4',5'-e] pyrazine had been synthesized and characterized. All compounds exhibit high density and as good detonation velocity as RDX and HMX. We systematically studied the stabilities of these series compounds to evaluate their potential application as energetic materials.
2. Synthesis
As shown in Scheme 1, poly nitro products of 2, 3, 4, and 5 were controlled synthesized in one step of nitration. It was reported that two isomers of tetranitro substituted compounds 2 and 3 were synthesized as a mixture from nitration of 1 in 100% HNO\(_3\)/Ac\(_2\)O. It was found in our research that one isomer 2 was obtained at 0 °C for firstly 4 hours and the other one, compound 3, was detected at 25 °C for 30 h. It is speculated that the formation of isomer 3 was controlled by kinetics, while 2 was controlled by the thermodynamics of reaction [10]. So we realized controlled synthesis of 2 and 3 in fuming HNO\(_3\)/Ac\(_2\)O system respectively. It was failed to synthesis 4 with fuming HNO\(_3\)/ (CH\(_3\)CO)\(_2\)O by prolonging reaction time. It may be related to the capability of acetic anhydride to remove water is not strong enough [11]. So compound 4 was prepared in fuming HNO\(_3\)/ (CF\(_3\)CO)\(_2\)O system. Different from the nitration of intermediates in literature, compound 5 was nitrated directly from 1 in fuming HNO\(_3\)/ P\(_2\)O\(_5\) with yield of 35%. It is facile method.

![Scheme 1. Synthetic routes of 2, 3, 4, 5](image)

All compounds were thoroughly characterized by IR, \(^1\)H NMR and \(^13\)C NMR (acetone- \(d_6\)). To further confirm the structure, the 15N NMR spectra of compounds 2–5 were recorded in DMSO-\(d_6\) (Figure. 1) and the chemical shifts are given with respect to nitromethane (\(^{15}\)N) as an external standard. Compound 2 possess five well resolved resonances (δ -39.9 (N2), -45.6 (N1), -178.1 (N5), -198.8 (N4), -283.8 (N3)ppm). The signal of the secondary amino group (N3) was observed at the highest field as expected. Compound 3 possess seven well resolved resonances (δ -37.1 (N2), -46.6 (N1), -46.4 (N3), -178.2 (N5), -190.8 (N4), -206.2 (N6), -283.9 (N7)ppm). Compound 4 possess elevn well resolved resonances (δ -42.0 (N1), -45.3 (N5), -46.4 (N2), -52.8 (N3), -54.7 (N4), -177.1 (N6), -178.3 (N11), -179.3 (N7), -201.2 (N8), -204.2 (N10), -284.5 (N9)ppm). Compound 5 possess four well resolved resonances (δ -47.2 (N1), -54.4 (N2), -177.5 (N3), -205.1 (N4)ppm).
Figure 1. $^{15}$N NMR spectra of 2, 3, 4 and 5 in DMSO-d$_6$ with respect to CH$_3$NO$_2$ as an external standard.

3. Result and discussion.

3.1 Sensitivity of Energetic Materials

For energetic materials, density is one of the most important physical properties. [14] According to the Kamlet-Jacobs equation, the detonation velocity is proportional to the density, and the detonation pressure is proportional to the square of the density. Density can directly affect the detonation performance of explosives. We use the method of exhausting inert gas which is widely used in the world in recent years and is close to the density of single crystal. We use Ultra PYC1200e full automatic true density analyzer to test the true density at room temperature. With respect to 4 and 5, the densities are observed to be 1.88, 1.91 g/cm$^3$ respectively. Which outperform most currently used energetic materials. And densities of, 4 and 5 are significantly better than that of RDX (1.82 g/cm$^3$).

Table 1. Physical and detonation properties of the energetic materials (2–5) compared with those of RDX, HMX and CL-20.

| mat$^a$ | $\rho$ b g/cm$^3$ | $T_d$ c $^\circ$C | OB d % | D e m/s | P f GPa | Q g kJ·g | FS h N | IS i J |
|---------|------------------|-------------------|--------|---------|--------|---------|------|-------|
| 2       | 1.93             | 241               | -21.2  | 8987    | 37.48  | 6.05    | 324  | 5     |
| 3       | 1.86             | 225               | -21.2  | 8873    | 36.28  | 5.96    | 192  | 7.5   |
| 4       | 1.95             | 234               | -9.5   | 9405    | 41.58  | 6.55    | 80   | 1.0   |
| 5       | 2.04             | 228               | 0      | 9546    | 45.59  | 6.93    | 54   | 1.5   |
| RDX     | 1.91             | 204               | -21.6  | 8795    | 34.90  | 6.03    | 120  | 7.4   |
| HMX     | 1.80             | 280               | -21.6  | 9144    | 39.20  | 5.67    | 120  | 7.4   |
| CL-20   | 2.04             | 223               | -11.0  | 9600    | 43.00  | 6.31    | 54   | 4     |

$^a$ The results of RDX, HMX$^{[12]}$ and CL-20$^{[13]}$ were taken from references. $^b$ Density$^{[10]}$. $^c$ Thermal decomposition temperature under nitrogen gas (DSC, 5 $^\circ$C·min$^{-1}$). $^d$ Oxygen balance (C$_x$H$_y$O$_z$N$_d$, 1600(c-a-b)/M$_x$). $^e$ Detonation velocity (calculated). $^f$ Detonation pressure (calculated). $^g$ Detonation heat (calculated). $^h$ Impact sensitivity. $^i$ Friction sensitivity.

It showed that the impact sensitivity of 2 and 3 is much lower than 4 and 5 in table 1. The increase of nitro groups leads to an increase in energy, but this is at the expense of impact sensitivity. The impact sensitivity of 3 is comparable with that of HMX and RDX, and 2 is close to or even slightly better than CL-20. However, 4 and 5 will be classified as sensitive when compared to HMX, RDX and CL-20.
Friction sensitivity is measured according to GB/T 21566-2008 dangerous explosives friction sensitivity test method[14] by BAM Farf Hummer BFH-10 Friction sensitivity apparatus. Temperature, relative humidity, dosage and other conditions is same to impact sensitivity.

The friction sensitivities of 2, 3, 4 and 5 are increased in order. This is consistent with the conclusion that the increase of energetic group nitro group will reduce the stability of the molecule. The friction sensitivity of 2 and 3 is lower than that of HMX and RDX, while FS of 3 and 4 is comparable with that of CL-20.

It has been reported [15] that the ε-HNIW impact sensitivity decreases with the decrease of the particle size, and the friction sensitivity increases with the decrease of the particle size. So the SEM image was showed in Figure. 2. It can be seen that the compounds 2, 3 and 4 are in the form of random polyhedrons. The particle sizes are clearly inconsistent and many small particles are scattered around the large particles. Compound 5 exhibits partial agglomeration.

Figure 2. SEM image of compound 2 (a), 3 (b), 4 (c) and 5 (d)

3.2 Thermal stability of Energetic Materials

The thermal properties of the compounds 2, 3, 4 and 5 were determined by differential thermal gravity (DTG) (Figure.3).
As shown in Figure 2, decomposition temperature of 2, 3, 4 and 5 are between 220-245°C. Their decomposition temperature decreased in accordance with the order 2, 4, 5. That is to say, this corresponds to the order in which the number of nitro groups increases. While heat release decreases in reverse turn. 3 appears abnormal perform. 2 has the highest decomposition temperature in these four energetic materials. Thermal behavior of 2 contains a violent exothermic process, releasing instantaneous heat 7.49kJ/g, and decomposition temperature is 241.52 °C. From TGA tests we find that a weak loss peak of 2 exists from 94 to 101 °C with weight loss rate 3.3%, which could be the result of water weightlessness. Compared with 2, 4 and 5 have relatively low decomposition temperature but release more instantaneous heat, especially instantaneous heat of 5 can be up to 11.29kJ/g [16]. They all showed good thermal stability when compared to RDX and CL-20.

Figure 3. DTG of 2 (a), 3 (b), 4 (c) and 5 (d). Aluminum sample cells are used and take empty aluminum sample cell as reference. Sample dosage is about 1mg, temperature interval is from 40 to 450 °C. Heating rate is 10 °C/min with nitrogen gas atmosphere at 50mL/min flow rate.

Figure 4. DSC curves of 2, 3, 4 and 5 at a heating rate of 5 °C/min.
Thermal stabilities were determined by differential scanning calorimetric (DSC) measurements at a heating rate of 5 °C/min. Compound 5 exhibits the lowest decomposition temperature of 216 °C and 4 melts at 140 °C while decomposing at 225°C. The others have moderate thermal stabilities exceeding 250°C. Of these, 3 has the highest decomposition temperature of 254°C, which is higher than that of its isomer 2 (250°C). (figure 4.)

4. Conclusion
In this work, we report the stability of poly nitro substituted compounds of cis-syn-cis-2, 6-dioxodecahydro-1H,5H-dimidazo-[4,5-b: 4',5'-e] pyrazine. Although the density and detonation velocity of 4 and 5 are excellent, they are not suitable as explosives because of their high impact sensitivity. Compound 2 and 3 are better in density, sensitivity, detonation pressure and detonation velocity, so they are promising energetic materials application in the field of propellants.

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