文章编号：1006-9941(2013)06-0726-04

# Synthesis and Properties of 1-(2′,4′,6′-Trinitrophenyl)-4,5-Dinitroimidazole

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**Abstract**: 1-(2′,4′,6′-Trinitrophenyl)-4,5- dinitroimidazole was prepared, and its thermal behavior was studied by DSC and TG. Results show that it is melting and decomposition temperatures are 228.98 ℃ and 339.73 ℃, respectively. And the mass loss due to overall reaction (200 – 440 ℃) is 98%. The structure of the compound belongs to the orthorhombic system, space group $P2_12_12_1$, $a$ = 8.2370 (16) Å, $b$ = 12.791(3) Å and $c$ = 12.916(3) Å. The calculated crystal density is 1.802 g · cm$^{-3}$, and the corresponding detonation velocity and pressure are 8296.48 m · s$^{-1}$ and 31.00 GPa.

**Key words**: organic chemistry; *N*-aryl-*C*-dinitroimidazole; structure; thermal behaviors; activation energy

**CLC number**: TJ55; O62 **Document code**: A **DOI**: 10.3969/j.issn.1006-9941.2013.06.007

## 1 Introduction

The new, insensitive, energetic materials that contain aromatic nitrogen-containing heterocyclic core units have attracted lots of attention due to their relatively high energetic performance, good oxygen balance, density, and other thermodynamic properties when compared to their carbon-only analogous aromatic compounds[1-5].

Imidazole derivatives with more than two nitro groups have been predicted to be high energetic, but insensitive explosives [6-10]. Cho et al. [6] reported that 1-methyl-2,4,5-trinitroimidazole was a promising candidate as an insensitive high explosive, with explosive performance comparable to hexogen (RDX). H. S. Jadhav and co-workers[3] reported the synthesis and characterization of *N*-methyl, *N*-ester and *N*-picryl derivatives of 2,4,5-trinitroimidazole using triiodoimidazole as substrate. R. Duddu and co-workers[7] developed a new, molten-state nitration method for the synthesis of 1-methyl-2,4,5-trinitroimidazole.

4,5-Dinitroimidazole crystallizes with two crystallographically unique molecules in the monoclinic space group $P21/n$ with unit cell parameters $a$ = 11.5360(8) Å, $b$ = 9.071(1) Å, $c$ = 11.822(1) Å, $Z$ = 8, and has a density of 1.781 g · cm$^{-3}$[11]. It is well known that insertion of picryl group into an organic compound increases the density of the compound[3]. The titled compound was first obtained by the reaction of picryl fluoride (expensive and difficult to obtain) with 4,5-dinitroimidazole in DMF in literature[12], and the impact sensitivity ($H_{50}$) was 50.2 cm. However, few studies were found on the thermodynamic properties of these imidazole derivatives. Therefore, 1-(2′,4′,6′-trinitrophenyl)-4,5- dinitroimidazole was synthisized by picry chloride, which was much cheaper than picryl fluoride. And the thermal behaviors and single crystal structure of the target compound was studied. Furthermore, the nitrogen equivalent equation (NE equation)[13] was used to predict its detonation velocity and pressure.

**Received Date**: 2012-08-17; **Revised Date**: 2012-12-22

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## 2 Experimental

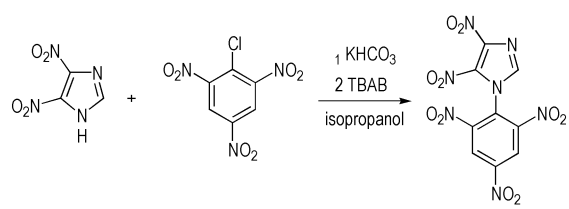
### 2.1 Materials and analytic instruments

4-Nitroimidazole was purchased from YanCheng Medical Chemical Factory. Picryl chloride was obtained according to Ref. [14]. 4,5- dinitroimidazole was obtained by nitration of 4-nitroimidazole[15]. Melting point was measured on a X-4 melting point apparatus and was uncorrected. The IR spectra was determined on Prestige-21 FTIR spectrophotometer. $^1$H NMR spectra was recorded on a Bruker Advance 500-MHz-NMR spectrometer. Differential Scanning Calorimetry (DSC) was carried out by Perkin-Elmer DSC-823e. Thermogravimetry (TG) was carried out using TGA/ SDTA851e simultaneous thermal analyzer.

### 2.2 Synthesis of 1-(2′,4′,6′-trinitrophenyl)-4,5- dinitroimidazole

A mixture of dinitroimidazole (0.32 g, 2.02 mmol), $KHCO_3$ (0.20 g, 2.00 mmol) and isopropanol (20 mL) was stirred at ambient temperature for 1h, followed by TBAB (0.12 g, 0.38 mmol), then picryl chloride (0.5 g, 2.02 mmol) added in small lots with stirring. The contents were kept stirring for 24 h at 85 ℃. The reaction mixture was filtered and washed with methanol to yield pure product.

Yield: 50%; m.p. 226 – 229 ℃; IR ($\upsilon_{max}$, cm$^{-1}$): 3121 (—CH), 3071 (—CH), 1620, 1538 (C—$NO_2$), 1496, 1467, 1350 (C—$NO_2$), 1338, 1309, 1233, 1186, 1095, 831, 723; $^1$H NMR (DMSO-$d_6$, 500 MHz) $\delta$: 9.3811 (s, 2H), 8.5897 (s, 1H).




**Scheme 1** Synthesis route of 1-(2′,4′,6′-trinitrophenyl)-4,5-dinitroimidazole

### 2.3 Thermal analysis

The enthalpy change and mass change measurements were made using about 0.6 mg sample in platinum-iridium thermocouples with the temperature ranging from 150 ℃ to 450 ℃ in static air against equal amount of calcined alumina. The heating rate was 10 ℃ · min$^{-1}$. Pt-Ir (Rh 10%) thermocouple assembly was used for $\Delta T$ and temperature measurement. For DSC studies, 0.6 ~0.7 mg sample was crimped in an aluminium cup which was heated against crimped blank cup at different heating rates, i.e. 10, 15, 20, 25 ℃ · min$^{-1}$. Activation energy of the compound was calculated using Ozawa[15] and Kissinger[16] methods.

## 3 Results and discussion

### 3.1 Crystal structure description of 1-(2′,4′,6′-trinitrophenyl)-4,5-dinitroimidazole

A perspective view of 1-(2′,4′,6′-trinitrophenyl)-4,5-dinitroimidazole molecule is shown in Fig. 1, and the three-dimensional packing diagram of 1-(2′,4′,6′-trinitrophenyl)-4,5-dinitroimidazole crystal cell is shown in Fig. 2. Its crystal structure belongs to the orthorhombic system, space group $P2_12_12_1$, $a$=8.2370 (16)Å, $b$=12.791(3)Å, $c$=12.916(3)Å, $Z$=4, $V$= 1360.8(5) Å$^3$, $d$=1.802 g · cm$^{-3}$. Further information concerning the crystal structure determinations in CIF format is available from the Cambridge Crystallographic Data Centre (CCDC-884548). The atomic coordinates, displacement parameters, selected bond distances and angles were listed in Tables 1-3, respectively. All results were obtained by Mercury program.

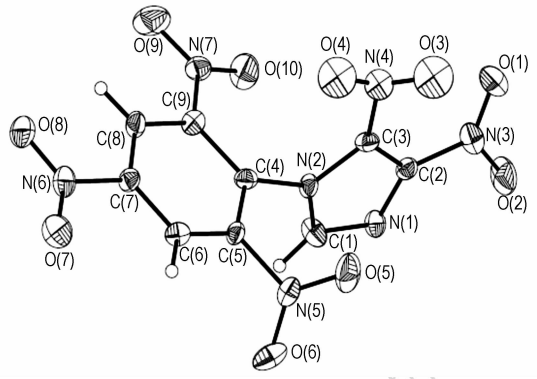



**Fig. 1** Molecular structure of 1-(2′,4′,6′-trinitrophenyl)-4,5-dinitroimidazole

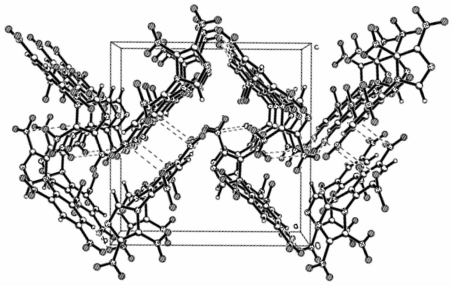


**Fig. 2** Packing diagram of 1-(2′,4′,6′-trinitrophenyl)-4,5-dinitroimidazole

**Table 1** Atomic coordinates ( ×10$^4$ ) and equivalent isotropic displacement parameters (Å$^2$) for 1-(2′,4′,6′-trinitrophenyl)-4,5- dinitroimidazole

| atom | *x* | *y* | *z* | *U*(equiv.) |
|---|---|---|---|---|
| N(1) | 0.9477(6) | 0.0154(3) | 0.6332(4) | 0.0322(11) |
| O(1) | 0.8534(7) | 0.0756(5) | 0.3788(4) | 0.0688(16) |
| C(1) | 0.8856(9) | 0.0613(5) | 0.7157(4) | 0.0398(15) |
| N(2) | 0.8011(6) | 0.1491(4) | 0.6888(3) | 0.0282(10) |
| C(2) | 0.8948(7) | 0.0723(4) | 0.5533(4) | 0.0298(12) |
| O(2) | 1.0283(7) | −0.0315(4) | 0.4378(4) | 0.0644(15) |
| N(3) | 0.9248(7) | 0.0366(4) | 0.4489(4) | 0.0423(13) |
| C(3) | 0.8000(7) | 0.1535(4) | 0.5832(4) | 0.0309(12) |
| O(3) | 0.7799(9) | 0.2691(6) | 0.4560(6) | 0.099 |
| N(4) | 0.7193(8) | 0.2420(5) | 0.5268(5) | 0.052 |
| C(4) | 0.7104(7) | 0.2125(4) | 0.7616(4) | 0.0304(13) |
| O(4) | 0.6547(8) | 0.2913(5) | 0.5738(5) | 0.092 |
| N(5) | 0.9739(6) | 0.2953(4) | 0.8023(4) | 0.0356(12) |
| C(5) | 0.7983(7) | 0.2851(4) | 0.8200(4) | 0.0278(12) |
| O(5) | 1.0197(7) | 0.3243(4) | 0.7166(4) | 0.0664(16) |
| O(6) | 1.0630(5) | 0.2763(4) | 0.8759(4) | 0.0549(13) |
| N(6) | 0.4878(7) | 0.3991(4) | 0.9911(4) | 0.0412(12) |
| C(6) | 0.7278(7) | 0.3470(4) | 0.8933(4) | 0.0305(13) |
| O(7) | 0.5708(7) | 0.4582(4) | 1.0413(4) | 0.0558(13) |
| N(7) | 0.4441(6) | 0.1257(4) | 0.7288(4) | 0.0403(12) |
| C(7) | 0.5662(7) | 0.3372(4) | 0.9086(4) | 0.0305(12) |
| O(8) | 0.3429(6) | 0.3901(4) | 1.0020(3) | 0.0556(13) |
| C(8) | 0.4709(7) | 0.2672(5) | 0.8544(4) | 0.0359(14) |
| O(9) | 0.2974(7) | 0.1272(5) | 0.7475(5) | 0.0696(16) |
| C(9) | 0.5393(7) | 0.2029(4) | 0.7805(4) | 0.0310(13) |
| O(10) | 0.5062(7) | 0.0623(4) | 0.6728(4) | 0.0639(15) |

**Table 2** Selected bond lengths (Å) of 1-(2′,4′,6′-trinitrophenyl)-4,5- dinitroimidazole

| bond | length/Å | bond | length/Å |
|---|---|---|---|
| N(1)—C(1) | 1.319(7) | C(3)—N(4) | 1.500(8) |
| N(6)—O(7) | 1.207(7) | N(1)—C(2) | 1.337(7) |
| O(3)—N(4) | 1.098(7) | N(6)—O(8) | 1.207(7) |
| O(1)—N(3) | 1.190(7) | N(4)—O(4) | 1.024(7) |
| N(6)—C(7) | 1.477(7) | C(1)—N(2) | 1.366(7) |
| C(4)—C(5) | 1.398(8) | C(6)—C(7) | 1.352(8) |
| N(2)—C(3) | 1.366(7) | C(4)—C(9) | 1.436(8) |
| N(7)—O(10) | 1.201(7) | N(2)—C(4) | 1.449(7) |
| N(5)—O(6) | 1.224(7) | N(7)—O(9) | 1.233(7) |
| C(2)—C(3) | 1.356(8) | N(5)—O(5) | 1.227(6) |
| N(7)—C(9) | 1.426(7) | C(2)—N(3) | 1.445(7) |
| N(5)—C(5) | 1.470(7) | C(7)—C(8) | 1.382(8) |
| O(2)—N(3) | 1.227(7) | C(5)—C(6) | 1.364(8) |
| C(8)—C(9) | 1.380(8) | | |

**Table 3** Selected bond angles (°) of 1-(2′,4′,6′-trinitrophenyl)-4,5-dinitroimidazole

| bond | angle/(°) | bond | angle/(°) |
|---|---|---|---|
| C(1)—N(1)—C(2) | 104.7(4) | C(2)—C(3)—N(2) | 104.4(5) |
| N(1)—C(1)—N(2) | 111.0(5) | C(2)—C(3)—N(4) | 134.0(5) |
| C(1)—N(2)—C(3) | 106.9(5) | N(2)—C(3)—N(4) | 121.3(5) |
| C(1)—N(2)—C(4) | 123.9(5) | C(6)—C(5)—N(5) | 118.4(5) |
| C(3)—N(2)—C(4) | 128.4(5) | C(4)—C(5)—N(5) | 119.0(5) |
| N(1)—C(2)—C(3) | 112.7(5) | C(8)—C(7)—N(6) | 117.7(5) |
| N(1)—C(2)—N(3) | 119.5(5) | C(8)—C(9)—N(7) | 120.8(5) |
| C(3)—C(2)—N(3) | 127.3(5) | N(7)—C(9)—C(4) | 121.3(5) |

### 3.2 Thermal properties

There are one endothermic peak and one exothermic peak in the DSC curve of 1-(2′,4′,6′-trinitrophenyl)-4,5-dinitroimidazole (Fig. 4) according to the two obvious mass-loss stages in the TG-DTG curves (Figure 3). The endothermic peak (with peak temperature of 228.98 ℃) in the DSC curve indicates the melting of the compound, which can be confirmed by the first mass-loss stage (in the temperature range of 200 – 230 ℃) in the TG-DTG curves with mass-loss of 6%. The exothermic peak (with peak temperature of 339.73 ℃) represents the decomposition processes of 1-(2′,4′,6′-trinitrophenyl)-4,5- dinitroimidazole, according to the second mass-loss stage (in the temperature range of 230 – 330 ℃) in the TG-DTG curves with mass-loss of 87%, the mass loss due to overall reaction (200 –440 ℃) is 98%. In order to determine the energy of activation, the DSC studies have been carried out at four different heating rates, i.e. 10, 15, 20, 25 ℃ · min$^{-1}$. The temperatures of decomposition were shown with the heating rate in Table 4. The energy of activation was calculated using Ozawa and Kissinger equations and it is found to be 146.32 kJ · mol$^{-1}$ and 143.53 kJ · mol$^{-1}$, respectively, with an excellent linear correlation.

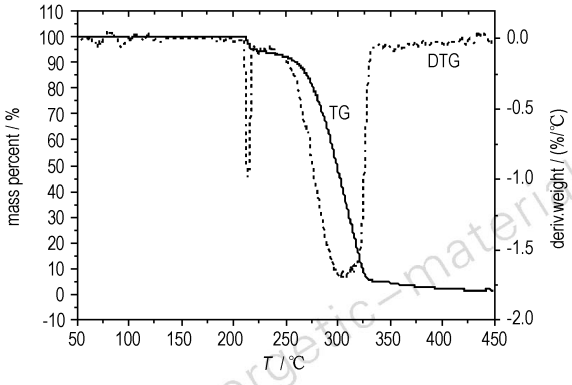



**Fig. 3** TG/DTG curves of 1-(2′,4′,6′-trinitrophenyl)-4,5- dinitroimidazole

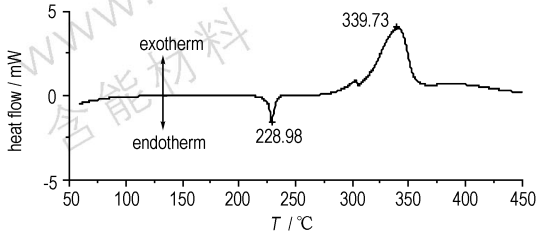



**Fig. 4** DSC curves of 1-(2′,4′,6′-trinitrophenyl)-4,5- dinitroimidazole

**Table 4** Activation energy according to maximal exothermic peaks at different heating rates

| | heating rate/℃ · min$^{-1}$ | | | | activation energy/kJ · mol$^{-1}$ | |
|---|---|---|---|---|---|---|
| | 10 | 15 | 20 | 25 | Kissinger[16] | Ozawa[15] |
| maximal peak /℃ | 339.73 | 347.58 | 354.18 | 358.73 | 143.53 | 146.32 |

### 3.3 Characterization of detonation velocity and pressure

Detonation velocity ($D$, m · s$^{-1}$) and detonation pressure ($p$, GPa) are the most important targets of the detonation characteristics of energetic materials. The detonation velocity and pressure of an explosive can be predicted with the nitrogen equivalent equation (NE equation) shown as Eq. (1) – (3)[13].

$$D = (690 + 1160\rho_0) \sum N \quad (1)$$

$$p = 1.092(\rho_0 \sum N)^2 - 0.574 \quad (2)$$

$$\sum N = (100 \sum x_i N_i)/M \quad (3)$$

where $\rho_0$ represents density of an explosive, g · cm$^{-3}$, $\sum N$ represents nitrogen equivalent of the detonation products, $N_i$ is nitrogen equivalent index of certain detonation product, $x_i$ is the mole number of certain detonation product produced by a mole explosive.

The detonation products produced by general explosives together with their nitrogen equivalent indexes are listed in Table 6. According to the order of $H_2O$—CO—$CO_2$ in forming detonation products, the detonation products of 1-(2′,4′,6′-trinitrophenyl)-4,5- dinitroimidazole are calculated as follows:

$C_9H_3N_7O_{10} = 1.5H_2O + 8.5CO + 0.5C + 3.5N_2$

According to Eq. (3), in which M = 369.18, $\rho_0$ = 1.802 g · cm$^{-3}$, total nitrogen equivalents of 1-(2′,4′,6′-trinitrophenyl)-4,5-dinitroimidazole are obtained through the nitrogen equivalent indexes of the detonation products in Table 6.

$$\sum N = 100 \times (1.5 \times 0.54 + 8.5 \times 0.78 + 0.5 \times 0.15 + 3.5 \times 1)/369.18 = 2.984$$

$$D = (690 + 1160\rho_0) \sum N = (690 + 1160 \times 1.802) \times 2.984 = 8296.48 \text{ m} \cdot \text{s}^{-1}$$

$$p = 1.092(\rho_0 \sum N)^2 - 0.574 = 1.092 \times (1.802 \times 2.984)^2 - 0.574 = 31.00 \text{ GPa}$$

As indicated above, the calculated detonation velocity and pressure of 1-(2′,4′,6′-trinitrophenyl)- 4,5- dinitroimidazole are 8296.48 m · s$^{-1}$ and 31.00 GPa, respectively.

**Table 6** Nitrogen equivalents of different detonation products

| detonation products | nitrogen equivalent index |
|---|---|
| $N_2$ | 1 |
| $H_2O$ | 0.54 |
| CO | 0.78 |
| $CO_2$ | 1.35 |
| $O_2$ | 0.5 |
| C | 0.15 |
| HF | 0.577 |
| $CF_4$ | 1.507 |
| $H_2$ | 0.290 |
| $Cl_2$ | 0.876 |

## 4 Conclusions

1-(2′,4′,6′-Trinitrophenyl)-4,5-dinitroimidazole was obtained by the reaction of picryl chloride with 4,5-dinitroimidazole under $KHCO_3$/TBAB catalytic system, and its melting and decomposition temperatures are 228.98 ℃and 339.73 ℃ and the mass loss of overall reaction (200 ~440 ℃) is 98%. The calculated crystal density is 1.802 g·cm$^{-3}$, and the corresponding detonation velocity and pressure are 8296.48 m·s$^{-1}$ and 31.00 GPa, respectively.

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# 1-(2′,4′,6′-三硝基苯基)-4,5-二硝基咪唑的合成与性能


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**摘　要:** 合成出1-(2′,4′,6′-三硝基苯基)-4,5-二硝基咪唑,研究了其热性能和晶体结构。其熔解温度为228.98 ℃,分解温度为339.73 ℃,热重变化范围为200 ~440 ℃, 总共失重98%; 其晶体属于斜方晶系,空间群为 $P2_12_12_1$, 晶胞参数为: $a$ = 8.2370 (16)Å, $b$ =12.791(3)Å, $c$ =12.916(3)Å, $Z$ =4 , $V$ =1360.8(5)Å$^3$, $d$ =1.802 g·cm$^{-3}$. 根据晶体密度计算的爆速和爆压分别为8296.48 m·s$^{-1}$和31.00 GPa。



**关键词:** 有机化学; *N*-芳基-*C*-二硝基咪唑; 结构; 热性能; 活化能

**中图分类号:** TJ55; O62　　**文献标识码:** A　　**DOI:** 10.3969/j.issn.1006-9941.2013.06.007