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Synthesis, Thermal Stability and Sensitivity of 2, 4-Dinitroimidazole

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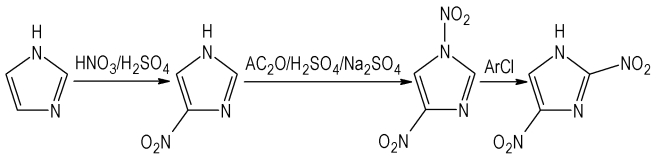
Pursuing new insensitive high explosive (IHE) is the main research hot-point in explosive field. Nitroimidazole compounds were mainly studied in the medicine chemistry in the past[1-2], seldom seen as the components of explosives and propellants. But now, several nitroimidazole compounds, such as 2, 4-dinitroimidazole (2, 4-DNI), 2, 4, 5-trinitroimidazole (2, 4, 5-TNI) and 1-methyl-2, 4, 5-trinitroimidazole (MTNI) etc are found to be the important intermediates of synthesizing new high explosives or itself possessing excellent explosive performances[3-5]. This paper introduces the synthesis, especially the experimental thermal stability, sensitivity and security of 2, 4-dinitroimidazole (2, 4-DNI).

2, 4-DNI were recrystallized with ethanol, and its molecular structure was characterized by B-E MS spectrometer, Nicolet 800 IR spectrometer (KBr), Bruker AVANCE-300 MHz NMR spectrometer and EA1108 elemental analysis instrument. The thermal stability and sensitivity experiments were carried out according to National Army Standard of People's Republic of China.

1 Synthesis and characterization of 2,4-DNI

Using imidazole as starting material, 2, 4-DNI was synthesized by three reaction steps(Scheme 1).



Scheme 1

1.1 Synthesis of 4-nitroimidazole (4-NI)

At about 25 ℃, 105.76 g (1.56 mol) imidazole was added to 171.0 mL H_2SO_4(98%), after stirring for 0.5 h, sulfuric acid salt of imidazole was obtained. After the mixed acid of 342.0 mL H_2SO_4(98%) and 99.5 mL fume nitric acid was dropwised slowly to the reaction mixture in icebath, it was stirred for another 2 h at 45 – 55 ℃, and then was put onto 4200 g crushed ice. The pH value of the solution was adjusted to 3.0 – 4.0 with concentrated ammonia. Then the precipitation was filtrated, washed with water. The collected solid was dried at 60 ℃ in vaccum for 4.0 – 5.0 h, and 83.2 g white powder solid was obtained with a yield of 47.3%, m. p.: 309.26 ℃. ^{1}H-NMR ($CDCl_3$, 300 MHz), δ: 7.85(s, 1H, C2H), 8.31(S, 1H, C5H), 13.25(br, 1H, NH); ^{13}C-NMR ($CDCl_3$, 300 MHz), δ: 120.270 (C5), 137.120(C2), 148.850(C4). IR(KBr, cm^{-1}), ν: 3355.8 (—NH), 1552.8, 1378.8 ($—NO_2$); MS (ESI): $M^+ + Na^+/z$ = 136.0. Anal. calcd for $C_3N_3O_2H_3$: C 31.86, N 37.17, H 2.65; found C 31.34 (31.59), N 35.93 (35.73), H 2.56 (2.72).

1.2 Synthesis of 1, 4-dinitroimidazole (1, 4-DNI)

At room temperature, 83.2 g (0.736 mol) 4-NI was dissolved in 191.5 mL AC_2O and cooled to 17 ℃. Then 60.8 mL fume nitric acid was added slowly. After it was stirred for another 5 mins at 17 ℃ hereinafter, 151.0 mL HAc was dropwised. It was reacted continuously for another 2.0 h at 17 ℃, and then stirred for overnight at room temperature. The reaction solution was put onto 3000 g crushed ice, and the precipitation was filtrated, washed with (3 × 500 mL) water, dried at 45 ℃ in vaccum for 16 h, 27.52 g white solid was obtained. The collectted filter liquor was extracted with methylene chloride, and methylene chloride was evaporated to obtain white solid 14.31 g. Thus, total 41.83 g 1, 4-DNI was obtained with a yield of 35.96%, m.p.: 92 – 93.6 ℃. ^{1}H-NMR ($CDCl_3$, 300 MHz), δ: 7.280(s, 1H, C2H), 8.394 – 8.530 (S, 1H, C5H); ^{13}C-NMR ($CDCl_3$, 300 MHz), δ: 112.933(C5), 130.143(C2), 145.0 (C4). IR (KBr, cm^{-1}), ν: 1642.39, 1557.78, 1383.67, 1331.66, ($—NO_2$); MS (ESI): $M^+ - H^-/z$ = 157.05, $M^+ + Na^+/z$ = 172.71; Anal. calcd for $C_3N_4O_4H_2$: C 22.78, N 35.44, H 1.27; found C 22.73 (22.65), N 34.97 (34.51), H 1.43 (1.38).

1.3 Synthesis of 2, 4-dinitroimidazole (2, 4-DNI)

23.43 g (0.15mol) 1, 4-DNI was added to 468.6 mL chlorobenzene at room temperature, then the reaction system was heated to 125 ℃ and reacted for 3.5 – 4.0 h . After it was cooled to room temperature, the precipitation of 2, 4-DNI was filtrated, washed with water. The collectted filter liquor was evaporated to give another 2, 4-DNI solid. After being dried in vaccum at 60 ℃ for 6.0 h, total 19.34 g 2, 4-DNI was obtained with a yield of 82.5%, m.p.: 271 – 271.5 ℃. ^{1}H-NMR IR ($CDCl_3$, 300 MHz), δ: 7.281(s, 1H, C5H),

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7.821 (br, 1H, NH); ^{13}C-NMR ($CDCl_3$, 300 MHz), δ: 125.214(125.264)(C5), 147.552(C2), 150.011(C4). Anal. calcd for $C_3N_4O_4H$: C 22.78, N 35.44, H 1.27; found C 22.65 (23.40), N35.07 (34.94), H1.47 (1.53).

2 Thermal stability of 2,4-DNI

The purity of samples was 97.2% (HPLC). According to the DSC experiments results as shown in Table 1, using Ozawa method as shown in equation (1) to calculate the thermal decomposition apparent active energy E, E is 242.9 kJ·mol^{-1} with the related coefficent of 0.976.

Table 1 DSC eigenvalue of 2,4-DNI

heat rate/℃·min^{-1}	2.5	5	10	20	40
peak temperature/℃	277.2	280.9	285.6	293.6	305.0

$$\frac{d(\lg\beta)}{d(1/T)} = -0.4567\frac{E}{R} \quad (1)$$

Using Kissinger method as shown in equation (2) to calculate the thermal decomposition apparent activation energy E, E is 246.06 kJ·mol^{-1} with the related coefficent of 0.975.

$$\frac{d(\ln\frac{\Phi}{T_p^2})}{d(1/T_p)} = -\frac{E}{R} \quad (2)$$

According to DSC evaluating stability standard method of GJB772A-97502.1, T_{pi} of 2, 4-DNI was calculated by equation (3):

$$T_{pi} = T_{PO} + b\beta_i + c\beta_i^2 + d\beta_i^3 \quad (3)$$

Where T_{pi} is the peak temperature of the heat rate β_i, K; T_{PO} is peak temperature of the heat rate of zero, ℃; β_i is the heat rate, K·min^{-1}; b, c, d is constant. The T_{Pi} of 2, 4-DNI is 271.9 ℃.

TG experiments showed that 2, 4-DNI is stable up to 200 ℃, to begin to decomposite at 230 ℃. The thermal decomposition reaction go to be some stable after 300 ℃, stop after 370 ℃, and the hole weight loss of 2,4-DNI is 73.27% with residual of about 26%.

According to GJB772A-97 method 502.2, the VST value tested of 2,4-DNI is 0.71 mL/5 g/100 ℃/48 h, very good.

3 Sensitivity and security of 2,4-DNI

The mechanical sensitivity of 2, 4-DNI is shown in Table 2. 2, 4-DNI is insensitive or possessing low sensitivity, better than HMX and RDX, approaching to TATB or TNT. Electrostatic discharge sensitivity is V_{50} = 3.65 kV, E_{50} = 0.203 J, ideal. According to GJB772A-97 method 606.1,5S-delayed explosion temperature is 322 ℃, good.

Table 2 The mechanical sensitivity of 2, 4-DNI

explosive	impact sensitivity[1] /%	friction sensitivity[2] /%
HMX	100	100
RDX	80±8	76±8
2,4-DNI	0	14
TATB	0	0

Note: 1) 10 kg drop hammer, 25 cm; 2) 90°, 1.5 kg switch hammer, 3.92 MPa.

4 Conclusions

Nitroimidazole heterocyclic compound 2, 4-dinitroimidazole (2, 4-DNI) was synthesized, and its molecular structure was characterized by IR, MS, ^{1}H-NMR, ^{13}CNMR and elemental analysis. The experimental thermal stability, sensitivity and security of 2,4-DNI show that 2,4-DNI is stable, better than RDX and other nitramine explosives, has low mechanical sensitivity approaching to TATB or TNT and good electrostatic sensitivity. So, it will be one insensitive or low sensitivity high explosive has promising applications in many insensitive munitions (IM) in future.

Key words: insensitive high explosive; 2, 4-dinitroimidazole; synthesis; thermal property; sensitivity

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