Synthesis and Characterization of a Thermally and Hydrolytically Stable Energetic Material based on N-Nitrourea

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Abstract: The novel primary explosive tetranitrodiglycoluril (TNDGU) was synthesized from glycoluril dimer. It was fully characterized by using NMR (^{1}H, ^{13}C), IR spectroscopy, and elemental analysis. X-ray diffraction revealed that the crystals of TNDGU belong to triclinic system with space group $P\bar{1}$. The thermal behavior of TNDGU was studied using DSC methods. TNDGU exhibited good thermal stability with a decomposition temperature of 284.8 °C. TNDGU was also more resistant to hydrolysis compared to other nitrourea analogues. Additionally, density, enthalpy of formation, detonation velocity (VOD), and detonation pressure of TNDGU were predicted and it was found that TNDGU is a potential powerful explosive with a calculated density of 1.93 g cm^{-3}, a detonation velocity of 8305 m s^{-1} and low sensitivity to electric discharge.

Keywords: Tetranitrodiglycoluril · Synthesis · Characterization · Explosive · Nitrourea

1 Introduction

Synthesis of explosives with outstanding comprehensive performance is a major goal in the development of high energy density materials (HEDM) [1–7]. Heterocyclic explosives with N—NO$_2$ group(s) are of huge industrial and military importance because of the high formation heat, high density, and excellent oxygen balance [8–14]. Especially, N-nitroureas are very attractive because mono-nitroureas and di-nitroureas proved to have a good explosive performance [15]. In general, explosives with nitrourea groups usually have high densities (> 1.90 g cm^{-3}) [16–19] and the intramolecular hydrogen bonding within the nitrourea framework can dramatically reduce the impact sensitivity. Due to their potential use as HEDM, numerous cyclic N-nitroureas, like the well-known 1,3,4,6-tetranitroglycouril (TNGU) (Scheme 1), which was first reported by Boileau et al. [20] in 1984, were synthesized. TNGU is a powerful explosive with a crystal density of 2.04 g cm^{-3} and a detonation velocity of 9150 m s^{-1} [21]. However, TNGU is unstable in water [22], which limits its practical applications. Pagoria and co-workers [23] synthesized 2,4,6,8-tetranitro-2,4,6,8-tetraazabicyclo[3.3.0]octane-3-one (K-55) and 2,4,6-trinitro-2,4,6,8-tetraazabicyclo[3.3.0]octane-3-one(HK-55) with densities of 1.91 g cm^{-3} and 1.905 g cm^{-3}, respectively, and a low shock sensitivity. Additionally, other N-nitrourea analogues, such as K-56 [24], HK-56, TNPDU [25] and K-6 [26], were synthesized. Among these HEDMs, 2,6-dioxo-1,3,4,5,7,8-hexanitrodecahydro-1H,5H-diimidazo pyrazine (HHTDD) [27,28] (Scheme 1) has a density of 2.07 g cm^{-3}, which is the highest density recorded for C,H,N,O explo-

sives. The calculated VOD of HHTDD is 9700 m s^{-1}. However, the practical applications of most of the above compounds are limited because they are hydrolytic unstable. Obviously, the hydrolytic instability is related to the powerful electron-withdrawing groups in the molecule. The electropositive carbon atom could be easily attacked by water and as a result of hydrolysis, the electron-withdrawing nitro group could increase the positive electricity of carbon atom. Therefore, studies on new cyclic and caged HEDMs with N-nitrourea functionality but hydrolytic stability are still desperately needed.

1,4-Dinitroglycouril (DINGU) (Scheme 1), as an insensitive energetic material, slowly decomposes in boiling water [29,30]. Therefore, a new strategy is required to synthesize new N-nitrourea compounds, in which the carbon atom of urea framework is not easily attacked by water. To the best of our knowledge, tetranitrodiglycoluril (TNDGU) is still an unexplored compound (Scheme 1). Herein, the explosive performances of TNDGU were calculated based on its opti-
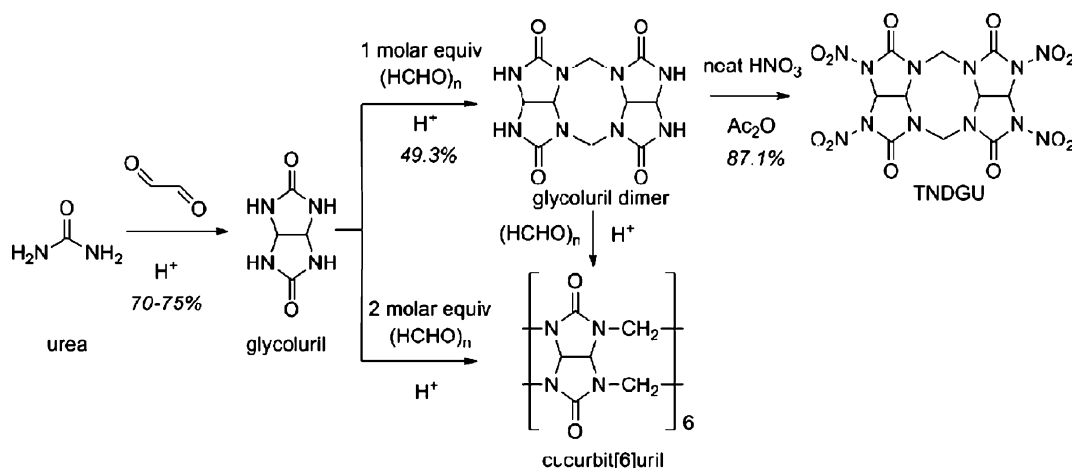
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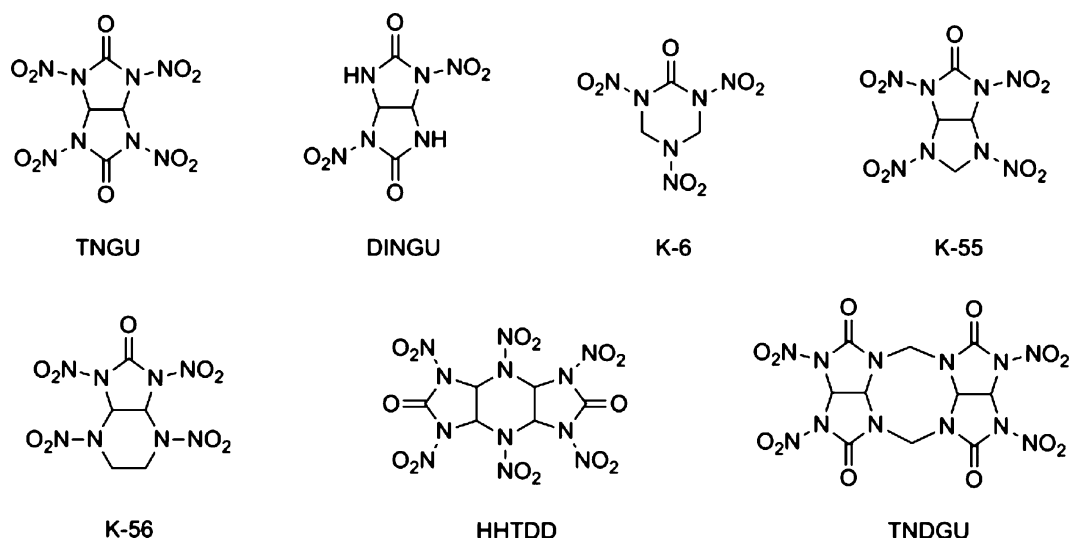
Scheme 1. Some N-nitroureas and TNDGU.

Scheme 2. Synthesis of TNDGU and cucurbit[6]uril.

mized geometry. The theoretically calculated density and VOD values are similar to that of many widely used energetic materials, such as 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), and DINGU, and higher than that of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). In addition, it has been found that TNDGU hardly decomposes in water at room temperature within 7 d. In this study, the novel, thermal and hydrolytic stable TNDGU was synthesized (as shown in Scheme 2) and fully characterized.

2 Experimental Section

2.1 Materials and Methods

All the reagents and chemicals were purchased without further purification. IR spectra were obtained with a Perkin-Elmer 1600 FT-IR instrument with KBr pellets. NMR spectra were recorded with a Bruker Avance II 400 MHz spectrometer (TMS as an internal standard). Elemental analysis was carried out with a Vario EL (Elementar Analysensysteme GmbH). The thermal analysis was performed with a Shimadzu DSC-60 (Japan) instrument with different heating rates (5, 10, 15, 20 and 25 $K min^{-1}$) in nitrogen atmosphere.

The sensitivity to impact stimuli was determined by using a falling hammer apparatus according to GJB7723A-97 of China. The weight of the hammer was 5000 ± 5 g and the results were reported in terms of height for 50% probability of explosion (H_{50}) of sample. The friction sensitivity of the compound was determined by using explosion probability method according to GJB772A-97 of China. Sensitivity of TNDGU to electric discharge was measured according to GJB178.8A of China.

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2.2 Synthesis

2.2.1 Preparation of Glycoluril Dimer

A mixture of paraformaldehyde (0.300 g, 10 mmol), glycoluril (1.42 g, 10 mmol) and conc. H_2SO_4 (10 mL) was heated at 90 °C for 18 h. The precipitate was isolated by filtration, washed with methanol and dried overnight under high vacuum. About 0.76 g of crude white solid (yield 49.3%) was obtained. IR (KBr): $\tilde{v} = 3602$, 3219, 1761, 1704, 1494, 1469, 1331, 1245, 1190, 1110, 960, 885, 754, 722 cm^{-1}.

2.2.2 Preparation of Tetranitrodiglycoluril

Glycoluril dimer (1 g, 3.25 mmol) was added to pure HNO_3 (20 mL) and the mixture was cooled down to 0 °C. Afterwards Ac_2O (10 mL) was added portion-wise into the solution over 30 min at 0–10 °C. The mixture was stirred at room temperature for additional 8 h. The acidic solution was poured into ice water with vigorous stirring, and a faint yellow precipitate formed. After several minutes, the slightly yellow solid was separated, washed with ice water and dried overnight under high vacuum. Finally, 1.38 g of white solid (yield 87.1%) was obtained with the following characterization data: IR (KBr): $\tilde{v} = 3014$, 1787, 1600, 1451, 1270, 1225, 1068, 980, 833, 801, 739 cm^{-1}. ^{1}H NMR (400 MHz, DMSO-d_6): $\delta = 7.15$ (d, 2 H), 5.68 (m, 4 H), 4.78 (d, 2 H). ^{13}C NMR (150 MHz, DMSO-d_6): $\delta = 148.0$ (–CO–, 4C), 67.37 (–CH–, 2C), 67.09 (–CH$_2$–, 2C), 52.03 (–CH–, 2C). $C_{10}H_8N_{12}O_{12}$: calcd. C: 24.6; N: 34.43; H: 1.65%; found: C: 24.67; N: 32.83; H: 2.19%.

3 Results and Discussion

3.1 Synthesis of TNDGU

Since hexameric macrocycle cucurbit[6]uril (CB[6]) was synthesized by Mock [31] in 1981 through the condensation of glycoluril and formaldehyde, many attentions to its unique structure has been aroused. For example, Huang [32] synthesized and characterized glycoluril oligomers(2–6), and compared its synthetic conditions with that of cucurbit[n]uril(CB[n]). And it was found that, compared to CB[n] from a 1:2 molar ratio of glycoluril to formaldehyde, glycoluril dimer was mainly produced through the condensation of glycoluril with a little more than 1 molar equiv. of formaldehyde (Scheme 2).

Herein, glycoluril was prepared from condensation of urea with 40% glyoxal/water solution with a yield of 70–75%. TNDGU was synthesized from the condensation of glycoluril with paraformaldehyde in the presence of catalytic concentrated sulfuric acid, followed by the N-nitration of glycoluril dimer by using a mixture of nitric acid and acetic anhydride. It is a competitive route to synthesize TNDGU due to the low-cost raw materials and convenient handle process, although the yield of glycoluril dimer is not high (<50%) with the main impurity CB[6]. The direct N-nitra-

tion of amino groups of the glycoluril dimer is successful due to the inherent low basicity of the secondary amino. The yield of N-nitration is relatively high by using the mixture of nitric acid and acetic anhydride. TNDGU is resistant to hydrolytic destruction and exhibits better hydrolytic stability than its analogues.

IR, ^{1}H NMR, and ^{13}C NMR spectra were used to confirm the structure of TNDGU. In the IR spectrum, the bands at 3014, 1787, 1600, and 1270 cm^{-1} correspond to methylene bridge, carbonyl and nitro groups, respectively. In the ^{1}H NMR spectrum, the signals at $\delta = 7.15$ ppm and 4.78 ppm correspond to the hydrogen atoms on the glycoluril rings and the signal at $\delta = 5.68$ ppm corresponds to hydrogen atoms on the methylene bridge. The signal at $\delta = 148.0$ of the ^{13}C NMR spectrum corresponds to the carbonyl carbon and other signals are at $\delta = 67.37$ ppm, 67.09 ppm and 52.03 ppm.

3.2 SEM and X-ray Crystallography Studies

TNDGU is a white crystalline solid with a density of 1.93 g cm^{-3}, which was obtained by using gas pycnometers method on an US Ultra PYC 1200e Density Tester. This experimental density (1.93 g cm^{-3}) is in accordance with the calculated value listed in Table 5. As shown in the SEM images (Figure 1), these rod-type crystals with sharp edges have a smooth and integrated particle surface, which might contribute to its high density. The particle sizes are in range of 5–20 μm with loose agglomerates.

The structure of TNDGU was also confirmed by X-ray crystallography, and the crystals were obtained from 98% fuming nitric acid and water system. X-ray data for the colorless crystals of TNDGU were obtained at 153(2) K with an AFC10/Saturn724+ diffractometer with Mo-K_α radiation ($\lambda = 0.071073$ nm), a graphite monochromator and the ϕ and Ω scan modes ($1.92° < \theta < 26.50°$). The absorption was corrected semi-empirically from equivalents. Structures were solved by direct methods and refined by full-matrix least-squares on F^2 (SHELXL-97).

Crystallographic data for TNDGU: triclinic, $P\bar{1}$, $a = 1.16828(18)$ nm, $\alpha = 78.214(3)°$, $b = 1.5184(2)$ nm, $\beta = 86.955(5)°$, $c = 2.9032(4)$ nm, $\gamma = 89.071(4)°$, $V = 5.0343(13)$ nm^3, $Z = 8$, calculated density = 1.93 g cm^{-3}, ab-

Figure 1. SEM images of TNDGU.

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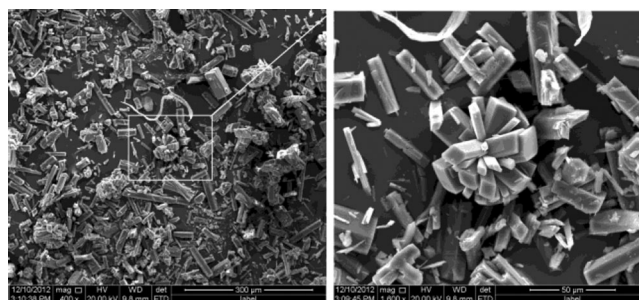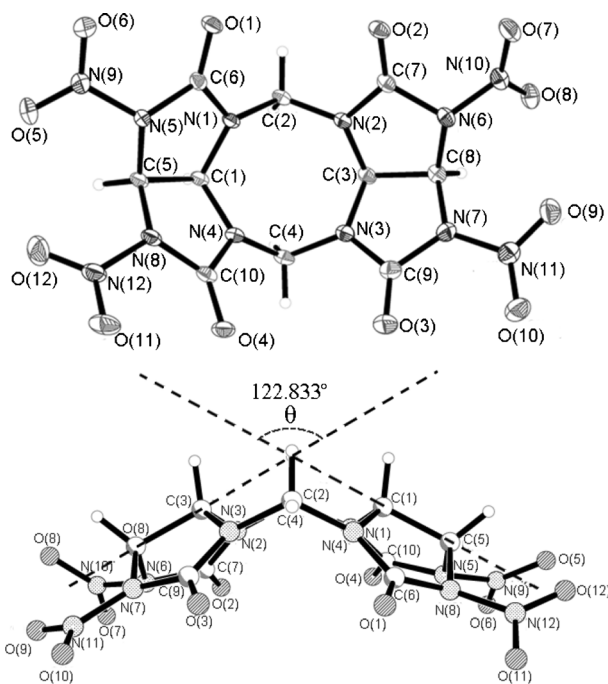

Figure 2. Molecular structure and arrangement of TNDGU.

sorption coefficient = 0.145 mm^{-1}, $F(000) = 2564$, crystal size = 0.53 × 0.42 × 0.12 mm. The structure and geometry of TNDGU are shown in Figure 2 and selected interatomic distances and angles are summarized in Table 1 and Table 2.

The X-ray analysis showed that TNDGU had a C-shaped arrangement, and the curvature was mainly restricted to a single plane. The angle between the adjacent glycoluril

Table 1. Bond lengths [nm] of TNDGU.

O(1)—C(6)	0.1208(3)	N(4)—C(4)	0.1452(3)
O(2)—C(7)	0.1204(3)	N(5)—N(9)	0.1413(3)
O(3)—C(9)	0.1203(3)	N(5)—C(6)	0.1427(3)
O(4)—C(10)	0.1199(3)	N(5)—C(5)	0.1454(3)
O(5)—N(9)	0.1215(3)	N(6)—N(10)	0.1419(3)
O(6)—N(9)	0.1207(3)	N(6)—C(7)	0.1445(3)
O(7)—N(10)	0.1214(3)	N(6)—C(8)	0.1456(3)
O(8)—N(10)	0.1221(3)	N(7)—N(11)	0.1387(3)
O(9)—N(11)	0.1223(3)	N(7)—C(9)	0.1421(3)
O(10)—N(11)	0.1206(3)	N(7)—C(8)	0.1454(3)
O(11)—N(12)	0.1216(3)	N(8)—N(12)	0.1399(3)
O(12)—N(12)	0.1199(3)	N(8)—C(10)	0.1431(3)
N(1)—C(6)	0.1353(3)	N(8)—C(5)	0.1462(3)
N(1)—C(1)	0.1447(3)	C(1)—C(5)	0.1549(3)
N(1)—C(2)	0.1452(3)	C(1)—H(1)	0.10000
N(2)—C(7)	0.1354(3)	C(2)—H(2A)	0.099
N(2)—C(3)	0.1449(3)	C(2)—H(2B)	0.099
N(2)—C(2)	0.1452(3)	C(3)—C(8)	0.1546(3)
N(3)—C(9)	0.1359(3)	C(3)—H(3)	0.10000
N(3)—C(3)	0.1450(3)	C(4)—H(4A)	0.099
N(3)—C(4)	0.1455(3)	C(4)—H(4B)	0.099
N(4)—C(10)	0.1364(3)	C(5)—H(5)	0.10000
N(4)—C(1)	0.1450(3)	C(8)—H(8)	0.10000

Table 2. Bond angles [°] of TNDGU.

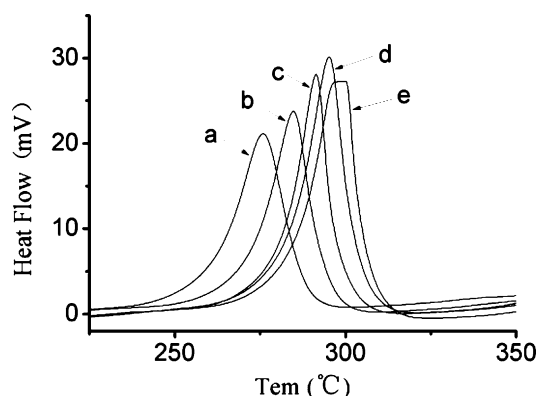|			
C(6)—N(1)—C(1)	114.19(18)	N(1)—C(2)—N(2)	113.23(18)
C(6)—N(1)—C(2)	121.38(19)	N(1)—C(2)—H(2A)	108.9
C(1)—N(1)—C(2)	122.65(19)	N(2)—C(2)—H(2A)	108.9
C(7)—N(2)—C(3)	114.67(19)	N(1)—C(2)—H(2B)	108.9
C(7)—N(2)—C(2)	120.57(19)	N(2)—C(2)—H(2B)	108.9
C(3)—N(2)—C(2)	123.16(19)	H(2A)—C(2)—H(2B)	107.7
C(9)—N(3)—C(3)	114.6(2)	N(2)—C(3)—N(3)	114.14(18)
C(9)—N(3)—C(4)	120.9(2)	N(2)—C(3)—C(8)	103.61(18)
C(3)—N(3)—C(4)	123.65(19)	N(3)—C(3)—C(8)	104.37(19)
C(10)—N(4)—C(1)	114.36(19)	N(2)—C(3)—H(3)	111.4
C(10)—N(4)—C(4)	120.93(19)	N(3)—C(3)—H(3)	111.4
C(1)—N(4)—C(4)	123.17(19)	C(8)—C(3)—H(3)	111.4
N(9)—N(5)—C(6)	118.56(18)	N(4)—C(4)—N(3)	112.70(19)
N(9)—N(5)—C(5)	118.93(19)	N(4)—C(4)—H(4A)	109.1
C(6)—N(5)—C(5)	111.32(18)	N(3)—C(4)—H(4A)	109.1
N(10)—N(6)—C(7)	114.79(19)	N(4)—C(4)—H(4B)	109.1
N(10)—N(6)—C(8)	117.81(18)	N(3)—C(4)—H(4B)	109.1
C(7)—N(6)—C(8)	111.27(19)	H(4A)—C(4)—H(4B)	107.8
N(11)—N(7)—C(9)	124.7(2)	N(5)—C(5)—N(8)	110.78(19)
N(11)—N(7)—C(8)	119.6(2)	N(5)—C(5)—C(1)	103.86(17)
C(9)—N(7)—C(8)	114.1(2)	N(8)—C(5)—C(1)	102.61(18)
N(12)—N(8)—C(10)	118.55(19)	N(5)—C(5)—H(5)	112.9
N(12)—N(8)—C(5)	117.77(19)	N(8)—C(5)—H(5)	112.9
C(10)—N(8)—C(5)	112.21(18)	C(1)—C(5)—H(5)	112.9
O(6)—N(9)—O(5)	126.9(2)	O(1)—C(6)—N(1)	127.0(2)
O(6)—N(9)—N(5)	116.2(2)	O(1)—C(6)—N(5)	126.3(2)
O(5)—N(9)—N(5)	116.8(2)	N(1)—C(6)—N(5)	106.77(19)
O(7)—N(10)—O(8)	126.2(2)	O(2)—C(7)—N(2)	128.2(2)
O(7)—N(10)—N(6)	116.2(2)	O(2)—C(7)—N(6)	125.6(2)
O(8)—N(10)—N(6)	117.6(2)	N(2)—C(7)—N(6)	106.24(19)
O(10)—N(11)—O(9)	127.4(2)	N(7)—C(8)—N(6)	112.60(19)
O(10)—N(11)—N(7)	118.4(2)	N(7)—C(8)—C(3)	101.76(19)
O(9)—N(11)—N(7)	114.2(2)	N(6)—C(8)—C(3)	104.00(19)
O(12)—N(12)—O(11)	125.6(2)	N(7)—C(8)—H(8)	112.6
O(12)—N(12)—N(8)	117.7(2)	N(6)—C(8)—H(8)	112.6
O(11)—N(12)—N(8)	116.6(2)	C(3)—C(8)—H(8)	112.6
N(1)—C(1)—N(4)	114.06(19)	O(3)—C(9)—N(3)	127.7(3)
N(1)—C(1)—C(5)	103.35(18)	O(3)—C(9)—N(7)	127.5(2)
N(4)—C(1)—C(5)	103.98(17)	N(3)—C(9)—N(7)	104.8(2)
N(1)—C(1)—H(1)	111.6	O(4)—C(10)—N(4)	127.8(2)
N(4)—C(1)—H(1)	111.6	O(4)—C(10)—N(8)	126.8(2)
C(5)—C(1)—H(1)	111.6	N(4)—C(10)—N(8)	105.43(18)

rings was 122.833°. The N—NO$_2$ bond lengths in TNDGU are 0.1387 nm, 0.1399 nm, 0.1413 nm, and 0.1445 nm, respectively, which are all shorter than the isolated C—N single bond (0.1471 nm) and longer than the isolated C—N double bond (0.1237 nm). This result is consistent with N—NO$_2$ bond lengths in nitramines in 5- and six-membered rings.

3.3 Thermal Analysis of TNDGU

Differential scanning calorimetry (DSC) was used for the thermal analysis of TNDGU at several heating rates (5, 10, 15, 20 and 25 K min^{-1}). In the DSC curve (Figure 3), there was only a narrow and sharp exothermic peak, suggesting that it could decompose directly from solid to gas without melting process. It was also found that by increasing the

Table 3. Non-isothermal kinetic parameters of TNDGU.

β [K min^{-1}]	T_p [K]	Kissinger's method		Ozawa's method	T_{P0} [K]	T_b [K]
		E_k [kJ mol^{-1}]	$\ln(A[S^{-1}])$	E_0 [kJ mol^{-1}]		
5	549.95					
10	557.92					
15	564.44	174.53	37.16	174.84	538.096	552.65
20	568.40					
25	573.12					

Figure 3. DSC curves of TNDGU at various heating rates, from left to right, (a), (b),(c), (d), and (e) is 5, 10, 15, 20, and 25 °C min^{-1}, respectively.

heating rate, the decomposition temperature peak shifted to higher temperature. Additionally, the DSC curve showed that the sole exothermic process occurred in the range of 260–305 °C with a peak temperature of 284.8 °C at heating rate of 10 K min^{-1}. The high decomposition temperature indicated that it had higher thermal stability than the commonly used explosives 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX, $T_{dec}=275$ °C), 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX, $T_{dec}=219$ °C) and 1,1-diamino-2,2-dinitroethylene (Fox-7, $T_{dec}=238$ °C). Therefore, TNDGU should be an energetic material with high thermal stability.

Based on the multiplenon-isothermal DSC curves (Figure 3) with five different heating rates of 5, 10, 15, 20, and 20 K min^{-1}, Kissinger method and Ozawa method were used to obtain the kinetic parameters (the apparent activation energy (E) and pre-exponential constant (A)) of the exothermic process for TNDGU.

The Kissinger Equation (1) and Ozawa Equation (2) are the following:

$$\ln \frac{\beta}{T_p^2} = \ln \frac{AR}{E} - \frac{E_k}{RT_p} \tag{1}$$

$$\lg\beta + \frac{0.4567E_0}{RT_p} = C \tag{2}$$

where β is the linear heating rate (K min^{-1}), T_p is the peak temperature of DSC curve (K), A is the pre-exponential constant; R is the gas constant (8.314 J·mol^{-1}K^{-1}) and C is a constant.

Based on the original data, the apparent activation energy E_k (E_0) and pre-exponential factor A are determined and listed in Table 3. The Arrhenius equation of the exothermic decomposition process could be expressed in E_k and $\ln A_k$ as the following:

$$\ln K = 37.16 - 174.84 \times 10^3/(RT).$$

Other kinetic parameters for the exothermic decomposition process were obtained from the relevant equation [33, 34]. The value of the peak temperature (T_{p0}), which corresponded to $\beta \to 0$ and obtained from the following Equation (3), was 538.1 K, where b, c and d were coefficients.

$$T_{pi} = T_{p0} + b\beta_i + c\beta_i^2 + d\beta_i^3 \quad (i = 1 - 4) \tag{3}$$

The corresponding critical temperature of thermal explosion (T_b) was 552.7 K according to Equation (4), where R is the gas constant, E_k is the value of E_k obtained by Kissinger's method.

$$T_b = (E_k - \sqrt{E_k^2 - 4E_kRT_{p0}})/(2R) \tag{4}$$

The entropy of activation ($\Delta S^{\neq}$), enthalpy of activation ($\Delta H^{\neq}$), and free energy of activation ($\Delta G^{\neq}$) of the decomposition of TNDGU, which were obtained from Equation (5), Equation (6) and Equation (7), were 193.134 J K^{-1} mol^{-1}, 170.056 kJ·mol^{-1}, and 66.131 kJ mol^{-1}, respectively, where K_B is the Boltzman constant and h is the Plank constant.

$$A_k = \frac{K_B T}{h} \exp(\Delta S^{\neq}/R) \tag{5}$$

$$\Delta H^{\neq} = E_k - RT_{p0} \tag{6}$$

$$\Delta G^{\neq} = \Delta H^{\neq} - T\Delta S^{\neq} \tag{7}$$

3.4 Sensitivity Test

The impact test was conducted by using a falling hammer apparatus. With a step of 0.04 cm, 35 ± 1 mg of test speci-

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mens were used and a 5 kg of drop weight was allowed to fall freely from different heights. The results were reported in terms of height for 50 % probability of explosion (H_{50}) of the sample. The results showed that the H_{50} was 17.04 cm with a standard deviation of 0.24. The sensitivity of TNDGU to friction was determined by explosion probability method. The sample was tested under the following conditions: Tilt angle was $90 \pm 1°$; positive pressure was 3.92 ± 0.07 MPa; and test specimen mass was 20 ± 1 mg. The result showed that the explosion probability was 96 %. The sensitivity of TNDGU to electric discharge was measured under the following conditions: Reservoir capacitance was 2000 ± 50 pF; charging voltage was 23000 ± 100 V; distributed inductance ≤ 1.8 µH; distributed capacitance ≤ 100 pF; electrode gap was 0.18 ± 0.01 mm; and test specimen mass was 20 ± 0.1 mg. Results showed that no explosion occurred.

The impact and friction sensitivity data of TNDGU were compared to other explosives tested by the similar method (Table 4).

3.5 Theoretical Prediction of Performance of TNDGU

The stable geometry of TNDGU structure was fully optimized at B3LYP/6-31G** theoretical level [35] by using Gaussian 98 program [36] and frequency calculations, which indicated that this geometry had the potential energy surface. Since the density and enthalpy of formation were two key roles in designing and estimating a novel explosive, the density of TNDGU was predicted by using Equation (8) [37], where v is the balance parameter and σ_{tot}^2 is the total variance.

$$\rho_{crystal} = 0.9183(M/V_m) + 0.0028(v\ \sigma_{tot}^2) + 0.0443 \quad (8)$$

Its enthalpy of formation could be obtained by relevant equation [38] and the detonation properties could be predicted according to enthalpy of formation and density by using VLW equation [39,40]. The result showed that the density of TNDGU is 1.93 g cm^{-3} and its enthalpy of formation is -279.7 kJ mol^{-1}. Detonation performances were calculated, the calculated detonation velocity was 8305 m s^{-1} and the calculated detonation pressure is 29.86 GPa. Table 5 shows the theoretical performance properties of TNDGU are comparable to that of other high-energetic materials.

Data in Table 5 indicate that the calculated density for TNDGU is higher than that of RDX, HMX and TATB. The calculated VOD of TNDGU are comparable to that of RDX and DINGU, but higher than that of 1,3,5-triamino-2,4,6-trinitrobenzene (TATB). This calculation results show that the compound has excellent detonation properties, and might be a potential candidate of high energetic density compound (HEDC).

4 Conclusions

Tetranitrodiglycoluril (TNDGU) was synthesized from glycoluril dimer with a high yield for the first time, and its structure had been fully characterized. The theoretically calculated density and VOD are comparable to that of widely used energetic materials (such as RDX, HMX and DINGU), but higher than that of TATB. Compared to HMX, RDX and Fox-7, TNDGU also has a better thermal stability. The Arrhenius Equation could be obtained as the following: $\ln K = 37.16 - 174.84 \times 10^3/(RT)$. The obtained sensitivity data of TNDGU showed that it is insensitive to electric discharge.

Table 4. Sensitivity data of TNDGU in comparison with common energetic materials.

Compound	Impact sensitivity H_{50} [cm]	Friction sensitivity Probability [%]
TNDGU	17.04	96
RDX	15.8	76
HMX	22.91	100
PETN	14.6 [a]	100

a) A 2.5 kg hammer was used.

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Table 5. Theoretical performances of TNDGU in comparison with other high-energetic materials.

Parameter	TNDGU	DINGU	TNGU	HMX	RDX	TATB
Density [g cm^{-3}]	1.93	1.98	1.98	1.90	1.816	1.79
Enthalpy of formation [kJ mol^{-1}]	-279.7	-74	–	$+76$	$+63$	-139
Oxygen balance [%]	-39.34	-27.57	4.97	-21.61	-21.61	-55.77
Velocity of detonation [m s^{-1}]	8305	8000	9150	9110	8440	7860
Detonation pressure [GPa]	29.86	34.1	–	38.39	33.92	28.46
Detonation temperature [K]	4057	4565	–	4500	4500	2600

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