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Synthesis and Crystal Structure of 6*b*-Nitrohexahydro-2*H*-1,3,5-trioxacyclopenta[*cd*]-pentalene-2,4,6-triyl trinitrate

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Abstract: An energetic plasticizer 6*b*-nitrohexahydro-2*H*-1,3,5-trioxacyclopenta[*cd*]-pentalene-2,4,6-triyl trinitrate (**2**) was synthesized from glyoxal and nitromethane via the condensation and nitration reactions with a total yield of 40.90%, and its structure was characterized by elemental analysis, IR, NMR. The single crystal of compound **2** was obtained firstly. It was found that its crystal belongs to the monoclinic system, and its space group is $P2_1/n$ with $a=7.792(9)\text{\AA}$, $b=8.534(9)\text{\AA}$, $c=19.41(2)\text{\AA}$, $\beta=117.624(4)^\circ$, $M_r=370.16$, $V=1305(2)\text{\AA}^3$, $Z=4$, $D_c=1.884\text{ g}\cdot\text{cm}^{-3}$, $\lambda=0.71073\text{\AA}$, $F(000)=752$, $\mu=0.189\text{ mm}^{-1}$, $S=1.097$, the final $R_1=0.0488$, and $wR_2=0.1289$.

Key words: 6*b*-nitrohexahydro-2*H*-1,3,5-trioxacyclopenta[*cd*]-pentalene-2,4,6-triyl trinitrate, synthesis, crystal structure

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1 Introduction

Nitric acid esters have long been recognized as one class of useful and promising functional group in the design and synthesis of energetic plasticizer, such as 1,2,3-propanetriol trinitrate (nitroglycerin), nitrocellulose, and pentaerythritol tetranitrate (PETN), which are used in propellants, explosives, and pyrotechnics^[1-6]. An energetic plasticizer 6*b*-nitrohexahydro-2*H*-1,3,5-trioxacyclopenta[*cd*]-pentalene-2,4,6-triyl trinitrate (**2**)^[7], which could be compared to PETN on sensitivity, thermal stability and performance, was synthesized by condensation and nitration reactions. The pellets were used to prepare unconfined charges for measuring the detonation velocity, which was found to highly be $(7.8\pm 0.3)\text{ km}\cdot\text{s}^{-1[7]}$. In this work, we developed a preferable nitration method with the mixture of nitric and sulfuric acid as the nitration reagent, to improve the yield of nitration reaction and obtain a higher yield of 68.16%. And the crystal structure of title compound was reported for the first time, and its structure was composed by three nearly coplanar tetrahydrofuran rings, three nitric acid esters, and a nitro group.

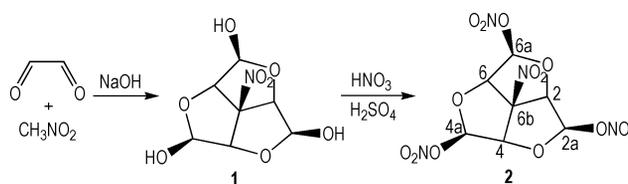
2 Experimental

2.1 Reagents and measurements

All chemical reagents from commercial sources were of analytically pure grade except for the industrial conc. sulfuric acid (95%–98%) and nitric acid (98%). Melting point was measured on a X-6 Melting-Point Apparatus with Microscope. Elemental analysis was performed by a Vario EL III elementary analysis instrument. IR spectra were recorded on a Nexus 870 FT-IR instrument using KBr pellet in the 4000–400 cm^{-1} . NMR

spectrum was obtained on a Bruker AV 500-MHz spectrometer with tetramethylsilane (TMS) as the internal standard and acetone- d_6 as the solvent.

2.2 Synthesis of the title compound



Scheme 1

2.2.1 Synthesis of 6*b*-Nitrohexahydro-2*H*-1,3,5-trioxacyclopenta[*cd*]-pentalene-2,4,6-triyl trinitrate (**1**)

Nitromethane (2.5 mL, 47 mmol) was added to aqueous glyoxal (40%, 8 mL, 70 mmol), and then aqueous solution of sodium hydroxide (10%, 2 mL) was added dropwise at 15–20 °C. The mixture was kept at room temperature for 2 h and the precipitated product was filtered off, washed with water. After crystallization from water and drying, the 6*b*-nitrohexahydro-2*H*-1,3,5-trioxacyclopenta[*cd*]-pentalene-2,4,6-triyl trinitrate (**1**) was obtained with yield of 60%. m. p.: 152–153 °C, ¹H NMR (DMSO- d_6 , 500 MHz), δ : 4.94 (s, 3H, H2a, H4a, H6a), 5.37 (d, $J=3.5\text{ Hz}$, 3H, H2, H4, H6), 6.96 (d, $J=3.75$, 3H, OH); ¹³C NMR (DMSO- d_6 , 125 MHz) 91.16 (C2a, C4a, C6a), 102.45 (C2, C4, C6), 106.85 (C6b); IR (KBr, ν/cm^{-1}): 3318 (—OH), 2978 (—CH), 1556, 1356 (—NO₂); Anal. Calcd for C₇H₉NO₈: C 35.75, H 3.86, N 5.96; Found: C 34.90, H 3.73, N 5.50.

2.2.2 Synthesis 6*b*-nitrohexahydro-2*H*-1,3,5-trioxacyclopenta[*cd*]-pentalene-2,4,6-triyl trinitrate (**2**)

Nitric acid (2 mL, 45 mmol) was added to conc. sulfuric acid (4.8 mL, 90 mmol), and then compound **1** (2.34 g, 10 mmol) was added slowly at 0–5 °C, with vigorously stir-

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ring. The mixture was kept at this temperature for 45 min and poured over crushed ice. A solid precipitate was filtered off and washed with water until to neutral. After the crystallization from methanol, pure compound **2** was obtained with the yield of 68.16%, m. p. 119–120 °C. ^1H NMR (acetone- d_6 , 500 MHz), δ : 5.64 (s, 3H, H2a, H4a, H6a), 6.61 (s, 3H, H2, H4, H6); ^{13}C NMR (acetone- d_6 , 125 MHz), δ : 91.08 (C2a, C4a, C6a), 104.90 (C6b), 106.9 (C2, C4, C6), ^{14}N NMR (acetone- d_6 , 36.13 MHz), δ : 284.11 ($\nu_{1/2}$ = 1450 Hz), 325.15 ($\nu_{1/2}$ = 750 Hz), ^{15}N NMR (acetone- d_6 , 50.67 MHz), δ : 327.76, 368.4; IR (KBr, ν/cm^{-1}): 2978 (—CH), 1571, 1306 (—NO $_2$); Anal. Calcd for C $_7$ H $_6$ N $_4$ O $_{14}$: C 22.71, H 1.63, N 15.14; Found: C 23.00, H 1.61, N 14.95.

2.3 X-ray crystal structure determination

The title compound **2** was dispersed into ethanol/*n*-butyl alcohol (V/V = 1/1) with a stirrer, and the impurities were eliminated by filtration. The saturated solution of compound **2** was put in a conical flask for two weeks at room temperature statically, and evaporated slowly to obtain single crystal of compound **2**.

A colorless single crystal of compound **2** with dimensions of 0.37 mm × 0.31 mm × 0.25 mm was selected for X-ray single diffraction analysis, and the data collection was performed on a Bruker SMART Apex II CCD X-ray diffractometer equipped with a graphite-monochromatized Mo K $_{\alpha}$ radiation ($\lambda = 0.71073$ Å) using the φ - ω scan mode ($2.12^\circ < \theta < 25.10^\circ$) at 296(2) K. A total of 6234 reflections were collected, of which 2326 were independent ($R_{\text{int}} = 0.0426$) and 1986 with $I > 2\sigma(I)$ were considered to observed and used for the refinement.

The structure was solved by direct methods and refined by full-matrix least squares techniques on F^2 using SHELXS-97 and SHELXL-97 programs [8–10]. All non-hydrogen atoms were refined anisotropically. The atomic scattering factors and anomalous dispersion corrections were taken from X-ray crystallography [8]. The final refinement gave $R = 0.488$, $wR = 0.1289$ ($w = 1/[\sigma^2(F_o^2) + (0.0708P)^2 + 0.4691P]$, where $P = (F_o^2 + 2F_c^2)/3$), $S = 1.097$, $(\Delta/\sigma)_{\text{max}} = 0.001$, $(\Delta\bar{n})_{\text{max}} = 0.478$ and $(\Delta\bar{n})_{\text{min}} = -0.266$ e/Å 3 . Crystal data and structural refinement parameters for compound **2** were listed in Table 1.

3 Results and discussion

3.1 Synthesis of title compound

Using nitromethane and glyoxal as the starting materials, compound **2** was synthesized by the process of condensation and nitration reactions, and the total yield could reach 40.90%. Stanistaw [7] synthesized compound **2** using nitric acid as the nitration reagent with 55% yield. In order to increase the yield of nitration reaction, the different nitration agents were used and the results were given in Table 2. The product wasn't found with a mixture of potassium nitrate in conc. sulfuric acid as the nitration reagent. The mixture of nitric acid and conc. sulfuric acid were strong nitration agent and gave the target product in a yield of 68.16%. The elemental analysis, IR, ^1H NMR, ^{13}C NMR, ^{14}N NMR and ^{15}N NMR for the product are in good agreement with the title compound.

Table 1 Crystal data of compound **2**

formula	C $_7$ H $_6$ N $_4$ O $_{14}$
formula mass	370.16
crystal system	Monoclinic
space group	$P2(1)/n$
$a/\text{Å}$	7.792(9)
$b/\text{Å}$	8.534(9)
$c/\text{Å}$	19.41(2)
$\beta/(\circ)$	117.624(4)
crystal size/mm 3	0.37 × 0.31 × 0.25
volume/Å 3	1305(2)
Z	4
$D_c/\text{g} \cdot \text{cm}^{-3}$	1.884
$F(000)$	752
T/K	296(2)
$\lambda/\text{Å}$	0.71073
$2\theta/(\circ)$	50.20
reflections collected/unique	6234/2326
parameters	227
GOF on F^2	1.097
final R_1 , $wR_2(I > 2\sigma(I))$	0.0488, 0.1289
final R_1 , wR_2 (all data)	0.0567, 0.1348
largest diff peak and hole/e $ \cdot \text{Å}^{-3}$	0.478 and -0.266

Table 2 Influence of the nitration reagent on the yield of compound **2**

nitration reagent	KNO $_3$ /H $_2$ SO $_4$	HNO $_3$ /Ac $_2$ O	N $_2$ O $_5$ /CH $_3$ CN	HNO $_3$ /H $_2$ SO $_4$
yield/%	—	45.98	51.98	68.16

3.2 Crystal structure

The molecular structure and packing diagram of compound **2** are depicted in Fig. 1 and Fig. 2. The bond lengths and angles of the compound is presented in Table 3 and Table 4, which shows in the molecule are within normal ranges [11]. The structure of compound **2** is rotational symmetry, which looks like a red-wine glass with a nitro on the bottom and three nitric acid esters in flank. There are three tetrahydrofuran rings in the molecular. Moreover, the four carbon atoms of the tetrahydrofuran ring are nearly in a plane (the dihedral angles of C(1)—C(6)—C(7)—C(2) is -10.2°). The dihedral angles between plane defined by C(1)—O(12)—C(2) and plane C(2)—C(7)—C(6), between plane by C(1)—C(6)—C(7) and plane C(2)—C(7)—C(6) are 36.16° and 26.16° , respectively.

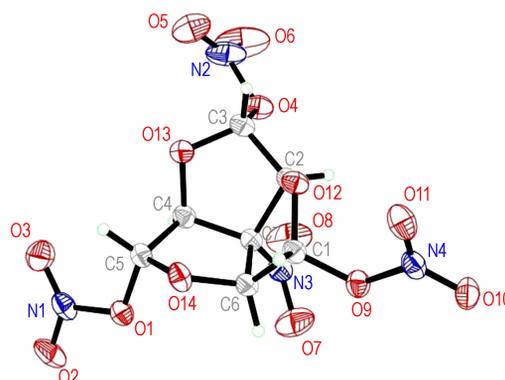


Fig. 1 Crystal structure of compound **2**

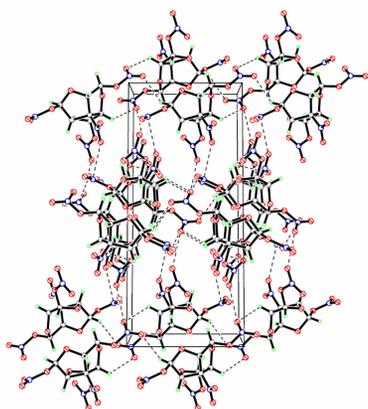


Fig. 2 Molecular packing diagram of the unit cell of compound 2

The final three dimensional networks (Fig. 2) are formed by classical intramolecular hydrogen bonds C(6)—H(6)...O(7), intermolecular hydrogen bonds C(2)—H(2)...O(11) ($-x+1, -y+2, -z+2$) and C(5)—H(5)...O(10) ($-x+1, -y+2, -z+2$), and the detailed information could be seen in Table 5. Moreover, it is also found that several weak intermolecular contacts are between O and N, O and O in the crystal. All of the hydrogen bonds and intermolecular contacts, which not only further stabilize the solid structure, but also lead to a sufficiently dense structure ($D_c = 1.884 \text{ g} \cdot \text{cm}^{-3}$).

Table 3 Selected bond lengths of compound 2

bond	lengths/Å	bond	lengths/Å
N(1)—O(2)	1.191(3)	N(3)—C(7)	1.496(3)
C(1)—C(6)	1.515(3)	N(1)—O(3)	1.194(3)
O(1)—C(5)	1.442(3)	C(1)—H(1)	0.9800
N(1)—O(1)	1.416(3)	O(12)—C(1)	1.386(3)
C(2)—C(7)	1.537(3)	N(3)—O(8)	1.177(3)
O(12)—C(2)	1.424(3)	C(2)—H(2)	0.9800
N(3)—O(7)	1.185(3)		

Table 4 Selected bond angles and torsion angles of compound 2

bond	angle/(°)
O(2)—N(1)—O(3)	131.5(3)
O(12)—C(1)—C(6)	106.35(18)
C(3)—C(2)—H(2)	113.4
O(2)—N(1)—O(1)	111.5(2)
O(9)—C(1)—C(6)	103.96(18)
C(7)—C(2)—H(2)	113.4
O(3)—N(1)—O(1)	117.0(2)
O(12)—C(1)—H(1)	111.5
N(3)—C(7)—C(6)	114.3(2)
O(8)—N(3)—O(7)	122.5(2)
O(9)—C(1)—H(1)	111.5
N(3)—C(7)—C(4)	114.20(18)
O(8)—N(3)—C(7)	117.3(2)
C(6)—C(1)—H(1)	111.5
C(6)—C(7)—C(4)	105.24(17)
O(7)—N(3)—C(7)	120.1(2)
O(12)—C(2)—C(3)	106.47(18)

bond	angle/(°)
N(3)—C(7)—C(2)	112.28(18)
N(1)—O(1)—C(5)	113.74(18)
O(12)—C(2)—C(7)	105.09(16)
C(6)—C(7)—C(2)	105.40(17)
C(1)—O(12)—C(2)	109.29(16)
C(3)—C(2)—C(7)	104.29(19)
C(4)—C(7)—C(2)	104.47(19)
O(12)—C(1)—O(9)	111.67(18)
O(12)—C(2)—H(2)	113.4
O(2)—N(1)—O(1)—C(5)	-176.9(2)
C(7)—C(2)—C(3)—O(13)	25.0(2)
C(1)—C(6)—C(7)—N(3)	113.6(2)
O(3)—N(1)—O(1)—C(5)	3.9(3)
O(12)—C(2)—C(3)—O(4)	154.87(17)
C(1)—C(6)—C(7)—C(4)	-120.28(19)
C(2)—O(12)—C(1)—O(9)	78.3(2)
C(7)—C(2)—C(3)—O(4)	-94.3(2)
O(14)—C(6)—C(7)—C(2)	102.0(2)
C(2)—O(12)—C(1)—C(6)	-34.5(2)
O(12)—C(1)—C(6)—O(14)	-84.4(2)
C(1)—C(6)—C(7)—C(2)	-10.2(2)
N(4)—O(9)—C(1)—O(12)	72.5(2)
O(9)—C(1)—C(6)—O(14)	157.58(16)
O(13)—C(4)—C(7)—N(3)	-130.52(19)
N(4)—O(9)—C(1)—C(6)	-173.25(16)
O(12)—C(1)—C(6)—C(7)	26.7(2)
O(13)—C(4)—C(7)—C(2)	-7.5(2)
C(1)—O(12)—C(2)—C(3)	137.40(18)
O(9)—C(1)—C(6)—C(7)	-91.3(2)
O(12)—C(2)—C(7)—C(6)	-8.9(2)
C(1)—O(12)—C(2)—C(7)	27.1(2)
O(8)—N(3)—C(7)—C(6)	-172.2(3)
O(12)—C(2)—C(7)—C(4)	101.72(19)
O(12)—C(2)—C(3)—O(13)	-85.8(2)
O(7)—N(3)—C(7)—C(6)	4.1(3)

Table 5 Hydrogen bond lengths and bond angles

D—H...A	$d(\text{D—H})$ /Å	$d(\text{H...A})$ /Å	$d(\text{D...A})$ /Å	$\angle \text{DHA}$ /(°)
C(6)—H(6)...O7	0.9801	2.3370	2.743	103.882
C(2)—H(2)...O11#1	0.9795	2.529	3.117	118.460
C(5)—H(5)...O10#2	0.9798	2.539	3.070	113.924

Note: Symmetry codes, #1 $-x+1, -y+2, -z+2$; #2 $x, -y+1, z$.

4 Conclusions

The title compound was synthesized by using the mixture of nitric acid and conc. sulfuric acid instead of merely nitric acid. It can be indicated from X-ray single-crystal diffraction analysis that the structure of compound 2 is rotational symmetry with three tetrahydrofuran rings, three nitric acid esters and a nitro. Due to the weak intermolecular contacts, intramolecular and intermolecular hydrogen bonds, the density of compound 2 could reach up to $1.884 \text{ g} \cdot \text{cm}^{-3}$.

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6b-硝基-1,3,5-三氧环戊烷[cd]-并环戊二烯-2,4,6-三硝酸酯的合成与晶体结构

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摘要: 以乙二醛(40%)和硝基甲烷为原料,通过缩合、硝化两步反应生成了新型硝酸酯类含能增塑剂 6b-硝基-1,3,5-三氧环戊烷[cd]-并环戊二烯-2,4,6-三硝酸酯(**2**),总收率为 40.90%,并采用红外光谱、核磁共振光谱和元素分析对其进行了表征。首次培养并获得了化合物 **2** 的晶体结构,晶体结构分析表明,该化合物属于单斜晶系,晶体空间群为 $P2_1/n$; 晶胞参数为: $a=7.792(9)\text{Å}$, $b=8.534(9)\text{Å}$, $c=19.41(2)\text{Å}$, $\beta=117.624(4)^\circ$, $M_r=370.16$, $V=1305(2)\text{Å}^3$, $Z=4$, $D_c=1.884\text{g}\cdot\text{cm}^{-3}$, $\lambda=0.71073\text{Å}$, $F(000)=752$, $\mu=0.189\text{mm}^{-1}$, $S=1.097$, 最终偏差因子 $R_1=0.0488$, $wR_2=0.1289$ 。

关键词: 6b-硝基-1,3,5-三氧环戊烷[cd]-并环戊二烯-2,4,6-三硝酸酯; 合成; 晶体结构

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