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*Research paper*

## Effective Synthesis, Thermal Properties and X-ray Structure Determination of 6,7,8,9-Tetranitro-3,4-dihydro-2H-1,5-benzodioxepine (TNDX), a Potential Thermally Stable High Energy Material

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**Abstract:** This work is dedicated to the investigation of the preparation, single crystal structure determination and physicochemical properties of fused *O*-heterocyclic 1,5-benzodioxepine completely nitrated in the aromatic ring. Efficient synthetic procedures are described for the precursor 3,4-dihydro-2H-1,5-benzodioxepine and its main polynitro derivatives: 7,8-dinitro-, 6,7,8-trinitro-, and 6,7,8,9-tetranitro-3,4-dihydro-2H-1,5-benzodioxepine (TNDX). The detailed structure of TNDX has been investigated by X-ray crystallography. This compound crystallizes from 2-butanone in the monoclinic space group P21/c. An experimental density of 1.805 g/cm<sup>3</sup> was determined by X-ray crystal analysis and it was found to be in good agreement with the value obtained by computer calculations (1.799 g/cm<sup>3</sup>). Spectral analysis was performed using FT-IR, RAMAN, and NMR spectroscopy. The calculated oxygen balance (OB/CO<sub>2</sub> = -53.31%) was very similar to the OB of known high-energy materials, including TATB (C<sub>6</sub>H<sub>6</sub>N<sub>6</sub>O<sub>6</sub>) and *N*-ethyltetryl (C<sub>8</sub>H<sub>7</sub>N<sub>5</sub>O<sub>8</sub>). Preliminary investigation suggests that TNDX (C<sub>9</sub>H<sub>6</sub>N<sub>4</sub>O<sub>10</sub>) may serve as a potential high-energy material, exhibiting generally favorable physicochemical properties. Thermogravimetric analysis revealed a decomposition temperature of 286 °C, exceeding that of the benchmark energetic compound RDX and approaching the thermal stability of the heat-resistant

energetic material DATB (1,3-diamino-2,4,6-trinitrobenzene). Taken together, these results highlight that underexplored oxygen-containing fused cyclic aromatic polynitro compounds could be promising candidates for thermally stable energetic materials with the desirable physicochemical properties.

**Keywords:** 6,7,8,9-tetranitro-3,4-dihydro-2*H*-1,5-benzodioxepine, TNDX, synthesis, X-ray crystallography, thermal analysis, energetic materials

### Supplementary Information (SI)

SI contains Figure S1, with selected X-ray-based projections of the TNDX molecule generated by rotation using Mercury software (Cambridge Crystallographic Data Centre), and selected structural parameters of the TNDX crystal are presented in Tables S1-S3.

### Synonyms and abbreviations

- DNDX 7,8-Dinitro-3,4-dihydro-2*H*-1,5-benzodioxepine, molecular formula:  $C_9H_5N_2O_6$
- HEM High-energy material
- TNBD 2,3-Dihydro-5,6,7,8-tetranitro-1,4-benzodioxine, molecular formula:  $C_8H_4N_4O_{10}$
- TNDX 6,7,8,9-Tetranitro-3,4-dihydro-2*H*-1,5-benzodioxepine, molecular formula:  $C_9H_6N_4O_{10}$

## 1 Introduction

Aromatic polynitro derivatives containing two, three or four nitro groups represent an important class of high-energy materials (HEMs) [1-3]. From a practical perspective, modern HEMs must possess not only superior energetic performance but also satisfy stringent fundamental requirements. Among these, the most critical are low sensitivity to shock, high density, and good thermal stability [4-8].

Recent publications highlight a renewed interest in benzene nitrocompounds containing ether groups, *e.g.* 2,4-dinitroanisole (DNAN) as a component for insensitive munitions formulations (for example IMX-101) [9]. DNAN was primarily chosen due to its low sensitivity, demonstrating significantly higher shock resistance compared with TNT [10-13]. It has been demonstrated in previous publications [14-16] that fully nitrated aromatic tetranitro compounds containing fused *N*-heterocyclic rings exhibit several advantageous properties,

such as relatively high density, improved chemical stability, and enhanced thermal stability. Recently developed energetic materials are largely based on derivatives of nitrogen heterocycles, including imidazoles, 1,2,3-triazoles, 1,2,4-triazoles, tetrazoles, pyrazoles, pyrazines and 2,3,4,5-tetrazines, as well as their fused heterocyclic frameworks [17, 18]. In contrast, polynitro derivatives of *O*-heterocycles, including cyclic benzene ethers (formerly known as “1,2-alkylenedioxybenzenes”), have received comparatively limited attention [19].

Our previous research focused on 2,3-dihydro-5,6,7,8-tetranitro-1,4-benzodioxine (TNBD), an annulated six-membered *O*-heterocycle, 1,4-benzodioxan derivative, in which the aromatic benzene ring is completely nitrated [20]. In the present work, we expand our previous investigation [20] of polynitro derivatives of fused oxygen heterocycles and chose one of them, 6,7,8,9-tetranitro-3,4-dihydro-2*H*-1,5-benzodioxepine (TNDX), for a more detailed study in order to estimate its potential use as a heat resistant high-energy material.

3,4-Dihydro-2*H*-1,5-benzodioxepine (synonym: 3,4-dihydro-2*H*-benzo[*b*][1,4]dioxepane) is a bicyclic aromatic heterocycle composed of a benzene ring fused with a seven-membered saturated *O*-heterocycle 1,4-dioxepane, containing two oxygen atoms at positions 1 and 4 [21].

Many bicyclic derivatives of 1,4-dioxepane have recently emerged as promising building blocks for drug discovery, offering high three-dimensionality, conformational flexibility, and potential as bioisosteres for saturated oxygen heterocycles such as morpholine or benzodioxane [21].

Various bioactive synthetic derivatives of this *O*-heterocycle have been developed in recent years, including compounds with antimicrobial [22], anticancer [23], anti-inflammatory [24-26], local anesthetics and antiarrhythmic [27, 28], and anti-diabetic activities [29]. A notable group of pharmacologically active naturally occurring compounds containing the 3,4-dihydro-2*H*-1,5-benzodioxepine moiety are strobilurins D, G, I and K, which have demonstrated antiparasitic and antimalarial activity [30, 31]. Interestingly, a variety of 1,5-benzodioxepine derivatives have been employed in the fragrance industry, with 7-methyl-2*H*-1,5-benzodioxepin-3(4*H*)-one serving as an example known for its characteristic marine aroma [32-34].

To the best of our knowledge, the development of energetic materials incorporating a fused heterocyclic 3,4-dihydro-2*H*-1,5-benzodioxepine structure remains unexplored. In prior research [20], we investigated the tetranitro compound TNBD, consisting of an aromatic ring fused with a six-membered *O*-heterocycle (1,4-dioxane), which displayed high density and excellent thermal

stability. In the present work, we extended our efforts to design energetic molecules by introducing an oxygen heterocycle into a fully nitrated aromatic moiety. This study is focused on the seven-membered fused oxygen heterocycle 3,4-dihydro-2*H*-1,5-benzodioxepine, fully nitrated at the benzene ring. Our efforts focused on developing an efficient synthesis, determining the single-crystal X-ray structure, and characterizing the key physicochemical properties of 6,7,8,9-tetranitro-3,4-dihydro-2*H*-1,5-benzodioxepine (TNDX).

## 2 Experimental

### 2.1 General

All chemical reagents and solvents were obtained from Sigma-Aldrich, Fluka and Merck, and were used as received. Samples of starting compounds: 3,4-dihydro-2*H*-1,5-benzodioxepine [35], 7,8-dinitro-3,4-dihydro-2*H*-1,5-benzodioxepine (DNDX) (m.p. 113 °C, light yellow cryst. from 2-propanol) and 6,7,8-trinitro-3,4-dihydro-2*H*-1,5-benzodioxepine (m.p. 133 °C, yellow cryst. from 2-propanol) were synthesized and characterized in our laboratory according to the modified conventional procedures reported previously [36, 37].

### 2.2 Testing methods

The melting points of the compounds synthesized were determined using open capillaries. Their purities were monitored by thin-layer chromatography (TLC) on silica gel 60 F254 aluminium plates (Merck). UV-VIS spectra were recorded with a Perkin-Elmer Lambda 25 UV-VIS spectrophotometer, and IR spectra were obtained in KBr using a Perkin-Elmer spectrophotometer (FT-IR Spectrum BX II). NMR spectra were recorded on a Varian Unity Inova (400 MHz for <sup>1</sup>H NMR).

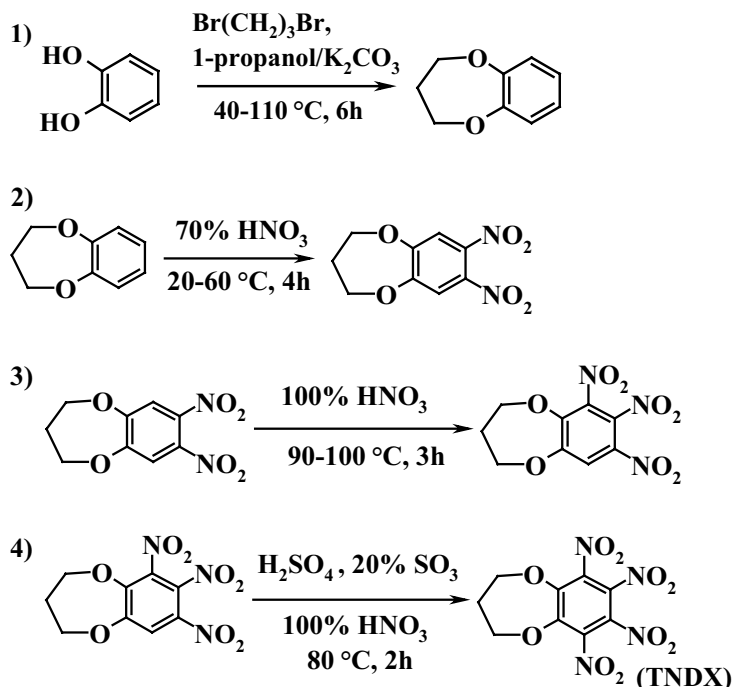
X-ray diffraction analysis was performed on a Bruker-Nonius diffractometer equipped with a KappaCCD detector. A fine-focus sealed tube served as the radiation source, and a graphite monochromator was used. Hydrogen atoms in the crystal structure were located and refined.

Thermal analysis was carried out using a Perkin-Elmer DSC 8000 differential scanning calorimeter.

*CAUTION! Dinitro-, trinitro-, and tetranitro- derivatives of 3,4-dihydro-2*H*-1,5-benzodioxepine were shown in preliminary tests, including hammer and anvil experiments, to be non-hazardous and insensitive to various stimuli. Nevertheless, standard safety precautions should be taken when preparing these nitro derivatives on a multigram scale.*

### 3 Synthesis

A general scheme illustrating the preparation of 3,4-dihydro-2*H*-1,5-benzodioxepine and its nitro derivatives is shown in Figure 1.



**Figure 1.** General scheme of 3,4-dihydro-2*H*-1,5-benzodioxepine synthesis and its stepwise nitration

#### 3.1 Synthesis of 3,4-dihydro-2*H*-1,5-benzodioxepine

To a solution of catechol (45.3 g, 0.41 M) in 1-propanol (350 mL) was added powdered  $K_2CO_3$  (150 g, 1.1 M) and 1,3-dibromopropane (92 g, 0.46 M). The resulting mixture was stirred at room temperature under argon atmosphere during 2 h, and then the temperature was gradually raised to 85-90 °C and heating continued for an additional 4 h. The reaction mixture was allowed to cool to room temperature, and water (2000 mL) was added. The mixture was extracted with ethyl acetate (3×400 mL), and the combined organic extracts was washed with 10% NaOH/H<sub>2</sub>O solution (3×300 mL), dried over  $MgSO_4$ , filtered, and concentrated under reduced pressure to give the desired compound, 54.5 g (87%) of 3,4-dihydro-2*H*-benzo[1,5]dioxepine as a brown liquid that solidified at

14 °C upon cooling. The product obtained can be used directly in the subsequent steps. For purification, the compound can be distilled under reduced pressure (94 °C/8 mm), affording a light yellow liquid ( $d_{20} = 1.103 \text{ g/cm}^3$ ) with an aromatic odor.  $^1\text{H NMR}$  (400 MHz,  $(\text{CD}_3)_2\text{CO}$ ):  $\delta = 2.194 \text{ ppm}$  (quint, 2H), 4.217 ppm (t, 4H), 6.903-6.952 ppm (m, 2H), 6.966-6.998 ppm (m, 2H).

### 3.2 Synthesis of DNDX and 6,7,8-trinitro-3,4-dihydro-2H-1,5-benzodioxepine

The dinitro- and trinitro-derivatives of 3,4-dihydro-2H-1,5-benzodioxepine were prepared according to previously published procedures [36, 37], as shown above in Figure 1 (see Section 3).

### 3.3 Synthesis of TNDX by nitration of DNDX

DNDX (24 g, 0.1 M) was added in small portions to stirred 100%  $\text{HNO}_3$  (100 mL), cooled to 10 °C using an external water/ice bath. Subsequently, fuming sulphuric acid (100 mL), containing 20%  $\text{SO}_3$ , was added dropwise, and the mixture was stirred for 60 min at 60 °C, followed by an additional 2 h at 80 °C. The reaction product tends to foam, floating on the surface of the nitrating mixture. After cooling to room temperature, the reaction mixture was poured onto crushed ice (0.5 kg). The resulting supernatant was filtered off, washed several times with dist. water and dried at room temperature. Yield: 25 g (76%). An analytical sample of TNDX was obtained after two re-crystallizations from 2-butanone, m.p. 184-185 °C.

### 3.4 Synthesis of TNDX by nitration of 6,7,8-trinitro-3,4-dihydro-2H-1,5-benzodioxepine

To a suspension of 6,7,8-trinitro-3,4-dihydro-2H-1,5-benzodioxepine (28.5 g, 0.1 M) in stirred 100%  $\text{HNO}_3$  (80 mL), cooled to 10 °C using an external water/ice bath, was added dropwise fuming sulphuric acid (100 mL), containing 20%  $\text{SO}_3$ . The mixture was then stirred for an additional 2 h at 80 °C. The reaction product tends to foam, floating on the surface of the nitrating mixture. The reaction mixture was cooled to room temperature, and the resulting supernatant containing the crude tetranitro derivative was filtered off through a sintered glass filter (pore size 16-40  $\mu\text{m}$ ), washed several times with ice-water, and dried at room temperature. Yield: 27.45 g (83%). The crude product (TNDX) contained minor amounts (2-4%) of unreacted trinitro derivative. After two recrystallizations from 2-butanone, pure TNDX was obtained, m.p. 185-186 °C.

## 4 Properties of TNDX

### 4.1 Physico-chemical properties of TNDX

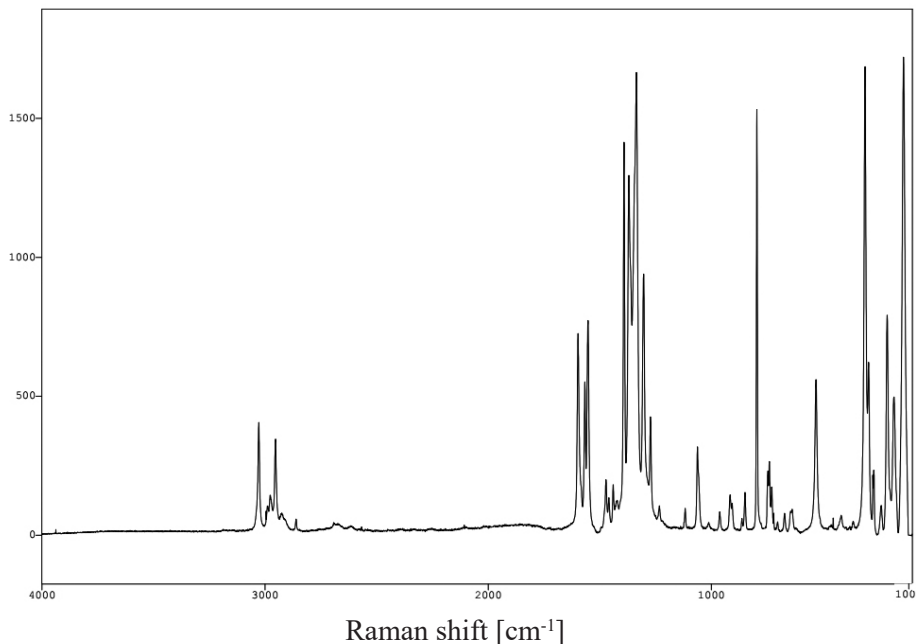
Molecular formula of TNDX:  $C_9H_6N_4O_{10}$ ; molecular weight: 330.165 g/mol; molecular volume: 235 Å<sup>3</sup>, logP = 1.731; number of atoms in molecule: 23. In the dispersed state, TNDX is a white powder, while in the crystalline state it forms colourless or light-yellow prisms. TNDX crystals m.p. 185-186 °C. Molecular composition (calc.): 32.74% C, 1.83% H, 16.97% N and 48.46% O. The theoretical density, calculated by ACD Labs ChemScetch software, is 1.799 g/cm<sup>3</sup>, while a value of 1.805 g/cm<sup>3</sup> was determined from X-ray data, at -100 °C. For comparison, the density of the novel heat resistant HEM 5,5'-bis(2,4,6-trinitrophenyl)-2,2'-bi(1,3,4-oxadiazole) (TKX-55) is 1.837 g/cm<sup>3</sup> (pycnometric measurement at 298 K) [53].

The calculated oxygen balance of TNDX ( $OB_{CO_2} = -53.31\%$ ) was estimated to be comparable to that of known HEMs, such as *N*-ethyltetryl ( $C_8H_7N_5O_8$ ) (-61.09%) [38], TKX-55 (-57.13%) and TATB (-55.80%) [39-44]. As reported in our previous work [20] on the homologous compound TNBD (5,6,7,8-tetranitro-2,3-dihydro-1,4-benzodioxine), the oxygen balance was significantly higher ( $OB_{CO_2} = -40.48\%$ ). Like many polynitroaromatics, TNDX exhibits notable photosensitivity, with its crystals turning yellow upon prolonged exposure to bright daylight, particularly under direct sunlight.

TNDX is readily soluble in common organic solvents, including alcohols, acetone, 2-butanone, DMF, and DMSO, but is insoluble in water. It is stable toward mineral acids, exhibiting moderate solubility in concentrated HNO<sub>3</sub> and very low solubility in H<sub>2</sub>SO<sub>4</sub>. Despite its marked resistance to acidic media, TNDX is comparatively sensitive to basic agents, alkali, ammonia or aliphatic amines, which can interact with the activated nitro groups at the 6 or 8 positions of the benzene ring. TNDX samples stored in the author's laboratory for 25 years showed no detectable changes in quality and purity.

### 4.2 Spectral properties of TNDX

The spectral characteristics of TNDX are shown below. Figure 2 shows a facsimile of the full-range (4000-100 cm<sup>-1</sup>) Raman spectrum: 138, 181, 212, 272, 295, 311, 531, 729, 740, 746, 796, 849, 907, 916, 1062, 1273, 1303, 1336, 1370, 1391, 1553, 1567, 1597, 2953, 2977 and 2996 cm<sup>-1</sup>.



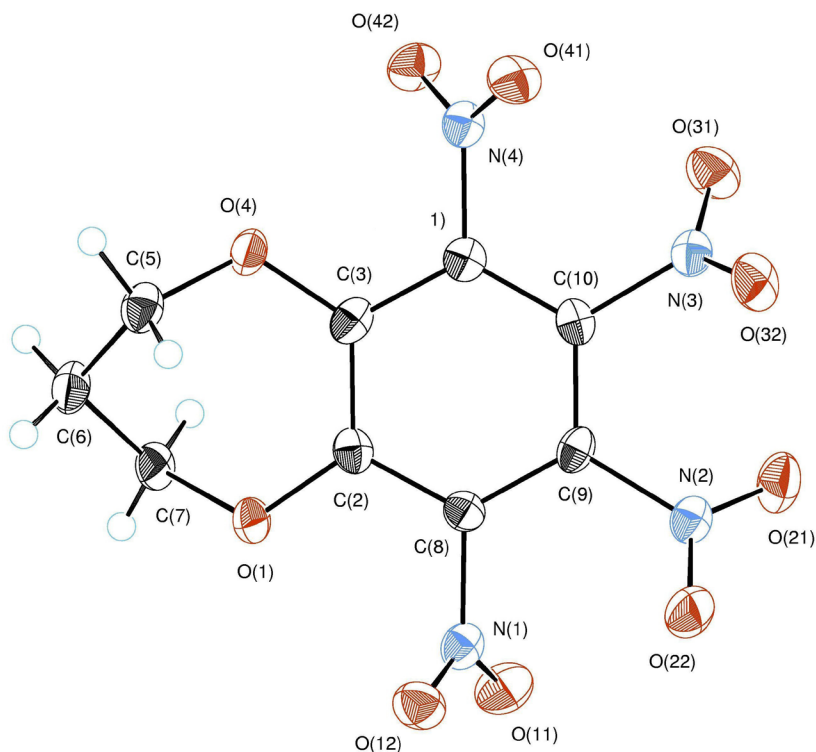
**Figure 2.** Raman spectrum of TNDX

FT-IR spectrum (KBr tablet,  $\nu/\text{cm}^{-1}$ ): 2987w, 2920w, 1569s, 1556s, 1544s, (br, as.  $\text{NO}_2$ ), 1482m, 1456m, 1332s, (s. br. sim.  $\text{NO}_2$ ), 1307s, 1269m, 1057s, 1010m, 962m, 914m, 850s, 794s, 703s, 670m and 644m.

$^1\text{H}$  NMR (400 MHz),  $(\text{CD}_3)_2\text{CO}$  spectrum,  $^{13}\text{C}$  NMR (100 MHz)  $(\text{CD}_3)_2\text{CO}$  spectrum,  $\delta$ : 29.96, 74.03, 115.84, 137.87, 149.30 ppm.

### 4.3 Crystal structure characterization by X-ray diffraction

To date, only a limited number of 3,4-dihydro-2*H*-1,5-benzodioxepine derivatives with reported X-ray crystallographic data have been described [45-48]. The study of TNDX was conducted to determine its three-dimensional structure and density. Crystals, suitable for X-ray diffraction, were obtained by slow evaporation of a solution of TNDX in 2-butanone. Crystals for analysis were carefully selected under a microscope at 40 $\times$  magnification. The molecular structure of TNDX in the crystalline state (Figure 4) was determined using a Bruker-Nonius diffractometer equipped with a KappaCCD detector. Hydrogen atoms in the crystal structure were located and refined. Selected structural parameters are presented in Tables S1-S3 (SI).



**Figure 3.** ORTEP representation of the molecular structure of TNDX with thermal ellipsoids drawn at the 50% probability level (CCDC 2321383)

#### 4.4 Single crystal cell parameters

The main parameters and image of the single crystal cell are presented below:

$$a = 8.8838(4) \text{ \AA},$$

$$b = 15.7434(9) \text{ \AA},$$

$$c = 9.4742(6) \text{ \AA},$$

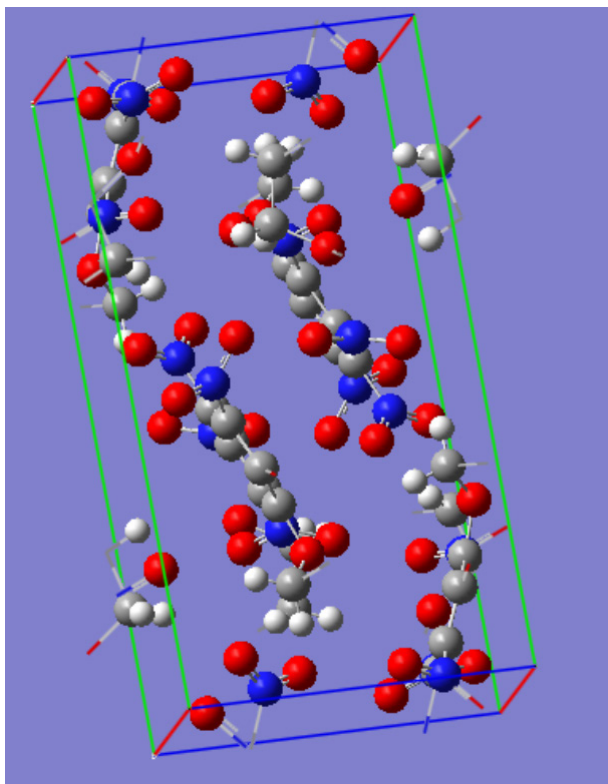
$$\alpha = 90.00^\circ,$$

$$\beta = 113.549(3)^\circ,$$

$$\gamma = 90.00^\circ,$$

$$V = 1214.72(12) \text{ \AA}^3.$$

The crystal cell image (Figure 4) reveals that the TNDX molecules are arranged in a wave-like pattern within the crystal lattice.



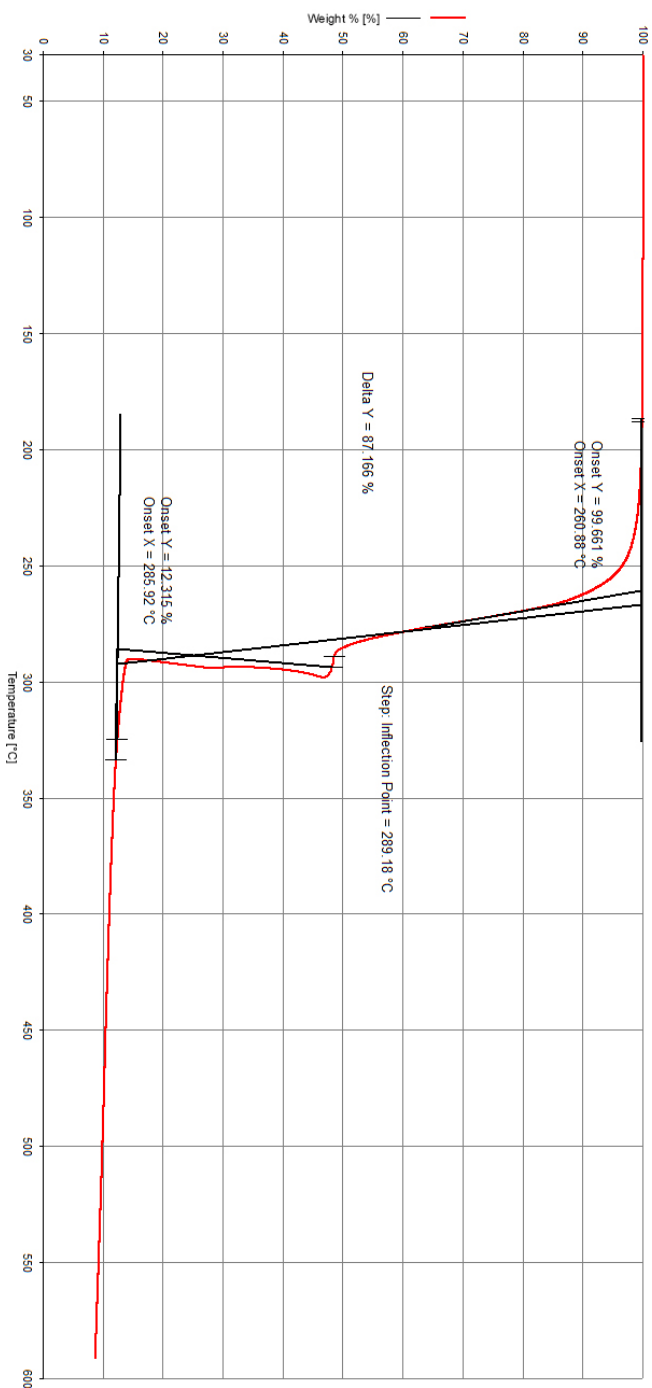
**Figure 4.** Single cell in the crystal structure of TNDX

#### 4.5 Thermal analysis

The thermal behaviour of TNDX was investigated using thermogravimetry (TG). As shown in Figure 5, the decomposition of TNDX commenced at 260 °C and was complete at 286 °C, with a total mass loss of 87.17%, at a constant heating rate of 10 °C/min. By comparison, the previously studied six-membered homolog, TNBD, decomposed between 239 and 330 °C [20], indicating that TNDX has higher thermal stability than its homolog TNBD.

#### 4.6 Conformational analysis of 3,4-dihydro-2*H*-1,5-benzodioxepine derivatives

Conformational analysis of seven-membered cycles reported in the literature [49, 50] clearly demonstrates that the unsubstituted 3,4-dihydro-2*H*-1,5-benzodioxepine exists predominantly in the chair form (80%) in  $\text{CHFC}_2$



**Figure 5.** TG plot demonstrating weight loss during TNDX decomposition (heating rate 10 °C/min and N<sub>2</sub> flow 20 mL/min)

solution, with a twisted boat form representing a minor population (20%). The free energy barrier for the chair-to-chair inversion was determined to be 6.5 kcal/mol. However, substituents can have a significant impact on the preferred conformation of alicyclic rings [51-54]. Stick models were constructed using the Cambridge CCDC Mercury program (version 2.3) based on the X-ray crystallographic data. Four representative projections are presented in Figure S1 (see SI). The projections presented in Figure S1 clearly illustrate the nonplanar molecular geometry of TNDX and its adoption of a chair conformation in the crystal structure.

## 5 Conclusions

The following conclusions can be drawn from this study:

- ◆ TNDX was synthesized for the first time *via* nitration of 7,8-dinitro-3,4-dihydro-2*H*-1,5-benzodioxepine (DNDX), affording 76% yield. A higher yield of 83% was achieved through an alternative approach involving nitration of 6,7,8-trinitro-3,4-dihydro-2*H*-1,5-benzodioxepine.
- ◆ The spectral characteristics, crystal structure, and experimental density of TNDX (1.805 g/cm<sup>3</sup>) and its oxygen balance with respect to CO<sub>2</sub> (OB<sub>CO<sub>2</sub></sub> = -53.31%) were investigated. The determined density was significantly lower than those previously reported for its closest six-membered homolog TNBD, molecular formula: C<sub>8</sub>H<sub>4</sub>N<sub>4</sub>O<sub>10</sub>), which has a density of 1.85 g/cm<sup>3</sup>.
- ◆ Thermogravimetric analysis (TG) of the re-crystallized material showed that decomposition of TNDX begins at 260 °C and is complete by 286 °C, which exceeds that of the benchmark energetic compound RDX and is approaching the thermal stability of the heat-resistant energetic material DATB (1,3-diamino-2,4,6-trinitrobenzene), and is comparable to that of HMX (octogen). While comparing TNDX with the novel heat-resistant explosive TKX-55 (5,5'-bis(2,4,6-trinitrophenyl)-2,2'-bi(1,3,4-oxadiazole), recently discovered in the Klapötke lab, we can reveal that TKX-55 shows substantially better thermal properties and a higher decomposition temperature: 335 vs 286 °C than TNDX. For TKX-55: OB<sub>CO<sub>2</sub></sub> = -57.12%, while for TNDX this value is slightly better: -53.31%. There are also slight differences in their crystal densities: 1.837 g/cm<sup>3</sup> for TKX-55 (pycnometric measurement at 298 K) and 1.805 g/cm<sup>3</sup> for TNDX (determined from X-ray data at 173 K).
- ◆ The thermal stability and decomposition temperature of TNDX were found

to be slightly higher than those of the closest six-membered homolog TNBD (which started to decompose at 239 °C), so one may conclude, that TNDX's thermostability is substantially better than its homolog). This difference may be attributed to the impact of the seven-membered 1,4-dioxepane TNDX compared to the 1,4-dioxane ring in the TNBD molecule.

- ◆ This work demonstrates that nitration of 3,4-dihydro-2*H*-1,5-benzodioxepine can produce TNDX, a fully nitrated derivative that may serve as a promising energetic material.
- ◆ Overall, the preliminary findings suggest that TNDX is a promising candidate for further in-depth investigation as a novel HEM.

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### Authorship contribution statement

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