Communication

Convenient Preparation, Thermal Properties and X-Ray Structure Determination of 2,3-Dihydro-5,6,7,8-tetranitro-1,4-benzodioxine (TNBD): a Promising High Energy Density Material (HEDM)

Jonas Šarlauskas *

Posted Date: 12 April 2024

doi: 10.20944/preprints202404.0833.v1

Keywords: 1,4-benzodioxane; nitration; nitro derivatives; tetranitro; synthesis; X-ray crystallography; structure; thermal analysis; high energy high density material (HEDM)

Communication

Convenient Preparation, Thermal Properties and X-ray Structure Determination of 2,3-Dihydro-5,6,7,8-tetranitro-1,4-benzodioxine (TNBD): A Promising High Energy Density Material (HEDM)

Jonas Šarlauskas

Department of Xenobiotics Biochemistry, Institute of Biochemistry of Vilnius University, Sauletekio 7, LT-10257 Vilnius, Lithuania; jonas.sarlauskas@bchi.vu.lt

Abstract: 2,3-dihydro-5,6,7,8-tetranitro-1,4-benzodioxine (TNBD), molecular formula =C8H4N4O10 is a completely nitrated in aromatic ring 1,4-benzodioxane derivative. The convenient method of TNBD synthesis was developed (yield=81 %). The detailed structure of this compound has been investigated by X-ray crystallography. The results of differential thermal analysis (DTA) obtained with twice re-crystallized material showed onset at 247 and isoterm at 288 ⁰C, with further total degradation at 300 ⁰C. The experimental density 1,85 g/cm^3 of TNBD was determined by X-ray crystallography. The spectral properties of TNBD (NMR, FT-IR, Raman) were explored. The detonation properties of TNBD calculated by EXPLO 5 code was slightly superior in comparison to standard high energy material - tetryl (detonation velocity of TNBD - 7727 m/s; detonation pressure - 278 kbar; tetryl – 7570 m/s and 226.4 kbar at 1.614 g/cm^3, or 260 kbar at higher density - 1.71 g/cm^3. The obtained preliminary results might suggest TNBD can be a potential thermostable high energy and density material (HEDM).

Keywords: 1,4-benzodioxane; nitration; nitro derivatives; tetranitro; synthesis; X-ray crystallography; structure; thermal analysis; high energy high density material (HEDM)

1. Introduction

Aromatic polynitroderivatives are among the most popular high energy materials (HEMs) [1–5]. From the practical standpoint, HEM must hold not only high energetic properties but also satisfy other strict requirements [4–8]. The most significant are chemical stability, shock-insensitivity, high density and thermostability [5,9–12].

The most well-known "old" energetic materials are mostly benzene derived polynitrocompounds. Later, *N*-heterocyclic high energy materials (HEMs) began to be considered as perspective candidates for replacing conventional high explosives, such as TNT, RDX, HMX, and PETN [9,10,13–15].

Althought mixed *O*,*N*-heterocycles, such as 1,2,5-, 1,2,4- and 1,3,4-oxadiazoles [16–20], as well as oxadiazole *N*-oxides (furoxans) [21–26] , are now amongst the most popular newly designed energetic compounds [27], derivatives of "pure" *O*-heterocycles as energetic materials have hardly been mentioned in scientific literature (except for unstable cyclic peroxides) [28]. 1,4-Benzodioxane (also known as 1,2-ethylenedioxybenzene, benzo-1,4-dioxane (old chemical names) or 2,3-dihydro-1,4-benzodioxin (new systematic name)) is one of many benzene annulated oxygen *O*-heterocycles [29].

It should be noted that there are three known structural isomers of benzodioxane (BD): unstable 1,2- benzodioxane [30–32], 1,3-benzodioxane [33] and most stable1,4-benzodioxane [34]:

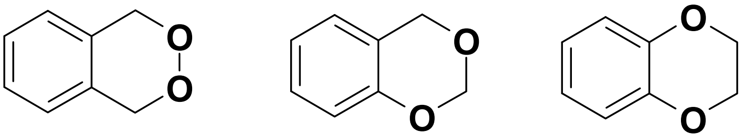

Figure 1. Three structural isomers of benzodioxane (1,2- , 1,3- and 1,4 BD).

It is worth noting that the latest isomer, 1,4-benzodioxane (2,3-dihydro-1,4-benzodioxine), originally synthesized by German chemist Vorländer [35] possessed the highest chemical and thermal stability [36].

Current practical applications of 1,4-benzodioxane include its use in medicinal chemistry and pharmacy, where it serves as an excellent core for structurally diverse pharmacologically active agents [37–39].

From 1960 onwards, 1,4-benzodioxane derivatives were extensively synthesised and investigated as biologically active compounds for their wide-spectrum pharmacological activity (e.g., anti-inflamatory, anti-histaminic, local anaesthetic, among others) at our University under the direction of Prof. Hab. Dr. Daukšas V. K. (1935-2013) [40–42].

Later, in the same laboratory, nitro and amino derivatives of 1,4-benzodioxane were used as a core structural fragment for the synthesis of novel annelated *O*, *N*-heterocyclic derivatives [43–47].

Surprisingly, nitro derivatives of 1,4-benzodioxane have not received much attention for their perspective use *as energetic materials*. One of the primary reasons is probably the relatively high cost of 1,4-benzodioxane as a starting material (31.40 Eu per 10 g, according to Merck Company).

In this work, we expanded our previous investigation [48] of 1,4-benzodioxane polynitro derivatives and chose one of them, tetranitro-1,4-benzodioxane (TNBD), for a a more detailed study of crystal structure, thermal stability, and other properties, with the goal of perspective using it as thermally stable high-energy high-density material.

The current research focuses on TNBD compound, an annulated O-heterocycle 1,4-benzodioxan derivative that has been completely nitrated in the aromatic benzene ring.

A more convenient, optimized synthesis of TNBD substance and its structural characterization via X-ray crystal diffraction analysis are reported below.

2. Results and Discussion

2.1. Materials and Methods

All chemicals and solvents for the synthesis of the benzodioxane derivatives were from Sigma Aldrich (St. Louis, MO, USA). NMR spectra were recorded on Varian Unity Inova 300 spectrometer (300MHz) with tetramethylsilane (TMS) as internal standard. Chemical shifts were reported in ppm (δ). Infrared spectra recorded for KBr discs on Perkin-Elmer Spectrum GX FT-IR. Raman spectra registered on FT-Raman spectrometer Horiba HR800 for the 633-nm-excited spectra. Melting points determined on capillary melting point apparatus Melt-Temp. Thermogravimetric analysis performed on LINSEIS STA PT 1600, Thermogravimetric Analyzer. Quantum mechanical calculation was carried out using PC Spartan '10 (Wavefunction Inc., version 1.1.0). Single crystal X-ray diffraction evaluated using instrument "Bruker-Nonius KappaCCD" (Computing data collection 'KappaCCD') and computing data reduction "Denzo and Scalepak (Otwinowski & Minor, 1997)" were applied. All diagrams and calculations performed using maXus (Bruker Nonius, Delft & MacScience, Japan).

2.2. Optimized Synthesis of TNBD by Nitration of 6,7-Dinitro-1,4-benzodioxane (6,7-dinitro-2,3-dihydro-1,4-benzodioxine):

6,7-Dinitro-2,3-dihydro-1,4-benzodioxine (prepared according to the procedure [49]) (25 g, 0.11 M) was added in small portions to the stirred 100% HNO_3 (100 ml, 1.05 M), cooled up to 10 °C. The reaction mixture was allowed to warm by gradually increasing the temperature from 10 to 70 °C through external heating in a water bath. After cooling to 40–50 °C, 50 ml of 98% H_2SO_4 was added by drops, and stirring was continued for 30 min. at 70 °C. The reaction was finalized by adding 60 ml of fuming sulfuric acid, containing 30% SO_3, and stirring for 2 hours at 80 °C. After cooling to room temperature, the reaction mixture was poured into 0.5 kg of broken ice.

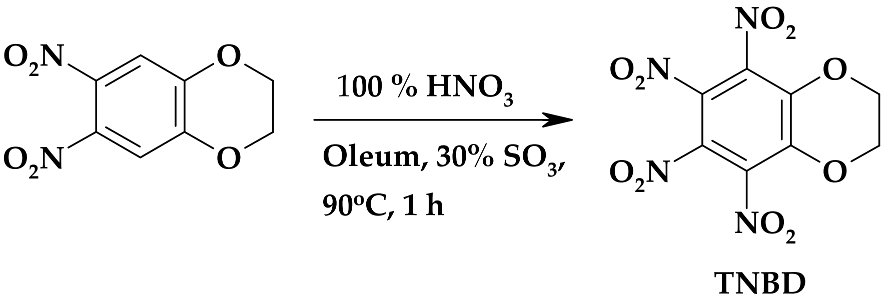

Figure 1. Synthesis scheme of TNBD.

The supernatant was filtered, washed several times with cold distilled water, and dried at room temperature. Yield: 28g, 81%. The analytical sample of TNBD was obtained after two re-crystallizations with acetone. M. p. 286-288 °C (lit. m.p. 286 °C [50]). It must be noted that this optimized synthesis gave a better yield than our two previously tested variants: starting from 6-nitro-2,3-dihydro-1,4-benzodioxine (63%), or from 5,7-dinitro-2,3-dihydro-1,4-benzodioxine (71%), and using analogous reaction conditions.

2.1. Structure and Properties Investigation

2.1.1. Physicochemical Properties

Molecular weight – 316.14, molecular formula = $C_8H_4N_4O_{10}$, molecular composition (C 30.39% H 1.28% N 17.72% O 50.61%). Oxygen balance OB_{CO2}= - 40.48 %.

TNBD is a white powder in a dispersed state, colorless prisms in crystalline state, crystals almost insoluble in water and conc. sulfuric acid. TNBD is well soluble and crystallizes from methylacetate, acetone, and 2-butanone, but is significantly less soluble in benzene and toluene and almost insoluble in other solvents such as hexane, dichloroethane or CCl_4. Many solvents were tested for the TNBD solubility but only 2-butanone (methylethyl ketone) was found to be the best for growing of high quality crystals, suitable for X-ray diffraction analysis. It is worth noting, that TNBD is substantially more hydrolyticaly stable than analogous structured compounds such as 1,2,3,4-TetrNB (tetranitrobenzene) and HNB (hexanitrobenzene) (further details are discussed below).

2.1.2. Chemical/Hydrolytic Stability

It is generally known that more nitro groups affording benzenes with higher energy suffering from lesser chemical stability [51]. Similarly, higher levels of nitration also induce reduced hydrolytic stability. 1,2,3,4-Tetranitrobenzene is an impact sensitive explosive that easely decomposes in the presence of moisture to 2,4-dinitro-1,3-dihydroxy benzene. Hexanitrobenzene (HNB), another well-known and extremely potent nitroarene explosive [3,5,52], easily hydrolyzes to trinitrophloroglucine when exposed to air humidity [53,54]. It is worth noting that among various poly-substituted benzene nitroderivatives, TNBD possess much superior chemical and thermal stability than 1,2,3,4-tetranitrobenzene and hexanitrobenzene (Figure 3):

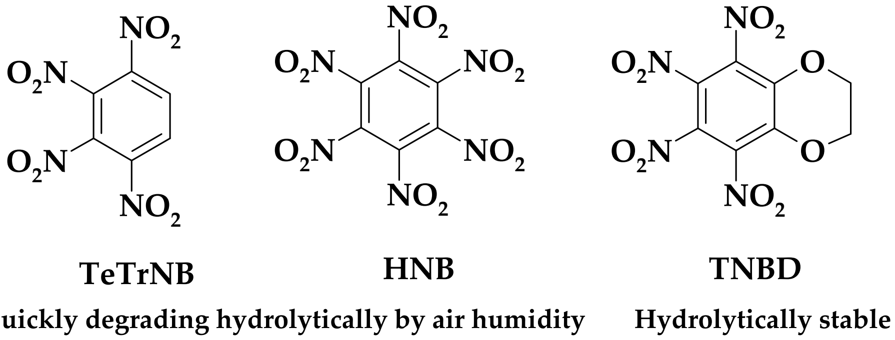

Figure 3. Benzene tetra- and hexanitrocompounds and TNBD stability comparison.

Under normal conditions, TNBD has a good hydrolytic stability. Surprisingly, we found no any degradation products after 20 years of storing TNBD samples in our laboratory at normal temperature. An additional dioxan ring in the structure of the TNBD molecule appears to have a strong stabilizing effect. Hydrolytic lability, light sensitivity, and other undesirable properties of hexanitrobenzene (HNB) limited its practical application [55]. Contrary to these HNB properties, synthesized in this work TNBD compound exhibited good chemical stability under normal conditions.

2.1.3. Spectral Properties

NMR spectra: ^{13}**C** spectrum (ẟ, [ppm, d$_6$-DMSO, freq. – 75 MHz): 143,91; 132,43; 129,02; 66,31; ^{1}**H** spectrum (d$_6$-DMSO, freq.- 300MHz): 4,73 (s, 4H).

FT-IR spectrum (cm^{-1}): 2967, 2889, 1597, 1573, 1566,1558, 1492, 1442, 1382, 1342,1335, 1309, 1249, 1230, 1078, 995, 951, 902, 860, 838, 797, 778, 726, 710, 654, 628, 438.

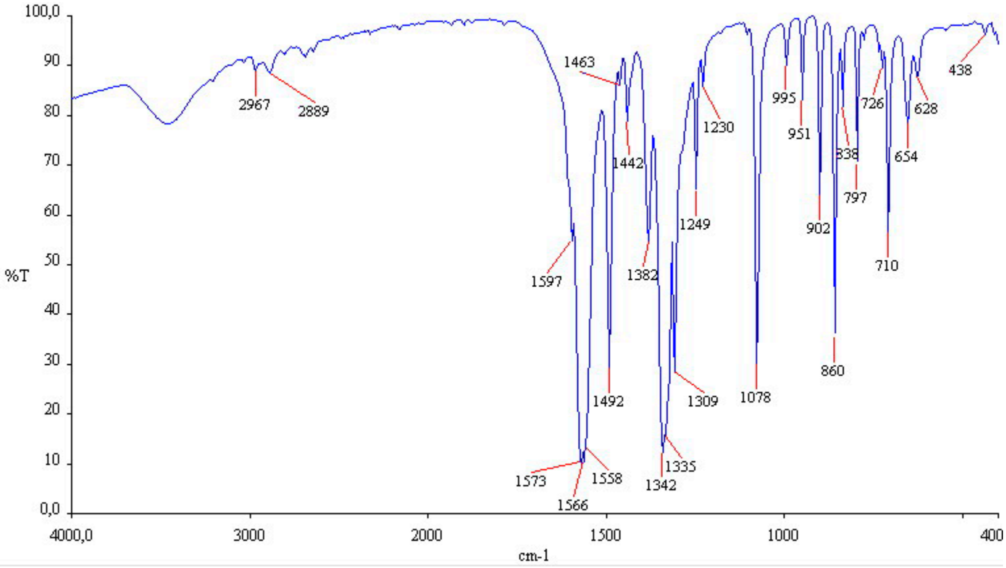

Figure 4. FT-IR spectrum of TNBD registered in KBr disc.

Raman shift spectra measurements were conducted using instrument FT-Raman spectrometer “Horiba HR800” for the 633-nm-excited spectra. The laser beam was focused to a spot of ca. 1-mm^2 area (laser power – 300 mW).

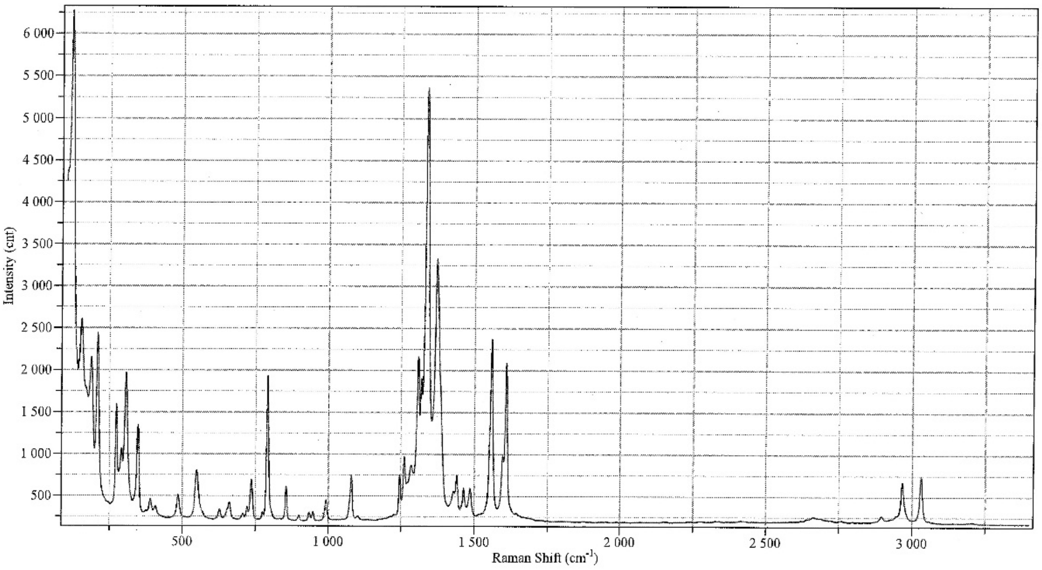

Figure 5. FT-Raman spectrum (100 scans) of TNBD (5,6,7,8-tetranitro-2,3-dihydro-1,4-benzodioxine) powder.

2.1.4. Thermal Properties

Analysis of thermal properties of TNBD was performed on LINSEIS STA PT 1600, Thermogravimetric analyzer (at 5 ^{0}C/min.):

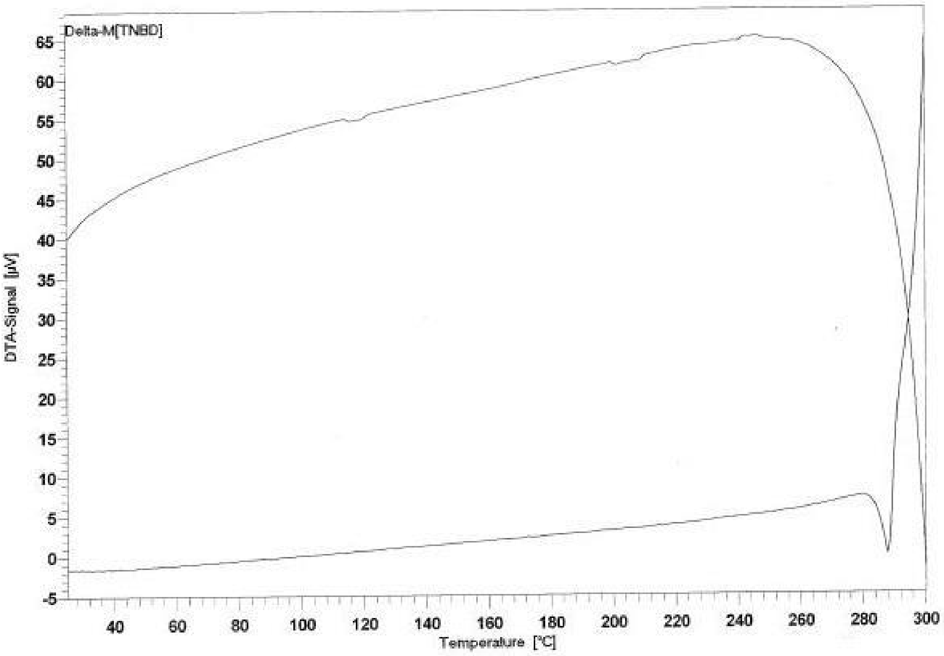

Figure 6. Thermogravimetric analysis (DTA) of TNBD sample (23 mg, at 5 ^{o}C/min).

The differential thermal analysis (DTA) of twice re-crystallized material revealed onset at 247 and isotherm at 288 ^{0}C. The investigated material degraded completely after reaching 300 ^{o}C, demonstrating thermostability of TNBD being close to that of HNS (hexanitrostilbene), also known as thermostable HEM [56].

Thermal stability of TNBD was found to be significantly higher than that of its analogues, 1,2,3,4-tetranitrobenzene (m.p. 120-121 ^{0}C) and hexanitrobenzene (HNB) (m.p. 245-262 ^{0}C, with decomposition) [53].

2.1.5. Crystal Properties and Structure Factors Leading to High Density

It was undertaken to establish TNBD three dimensional structure and density. The crystals of TNBD for its X-ray diffraction was obtained by slow evaporation at room temperature of solution in 2-butanone. The geometries of TNBD are tabulated below. All diagrams and calculations were performed using maXus (Bruker Nonius, Delft & MacScience, Japan).

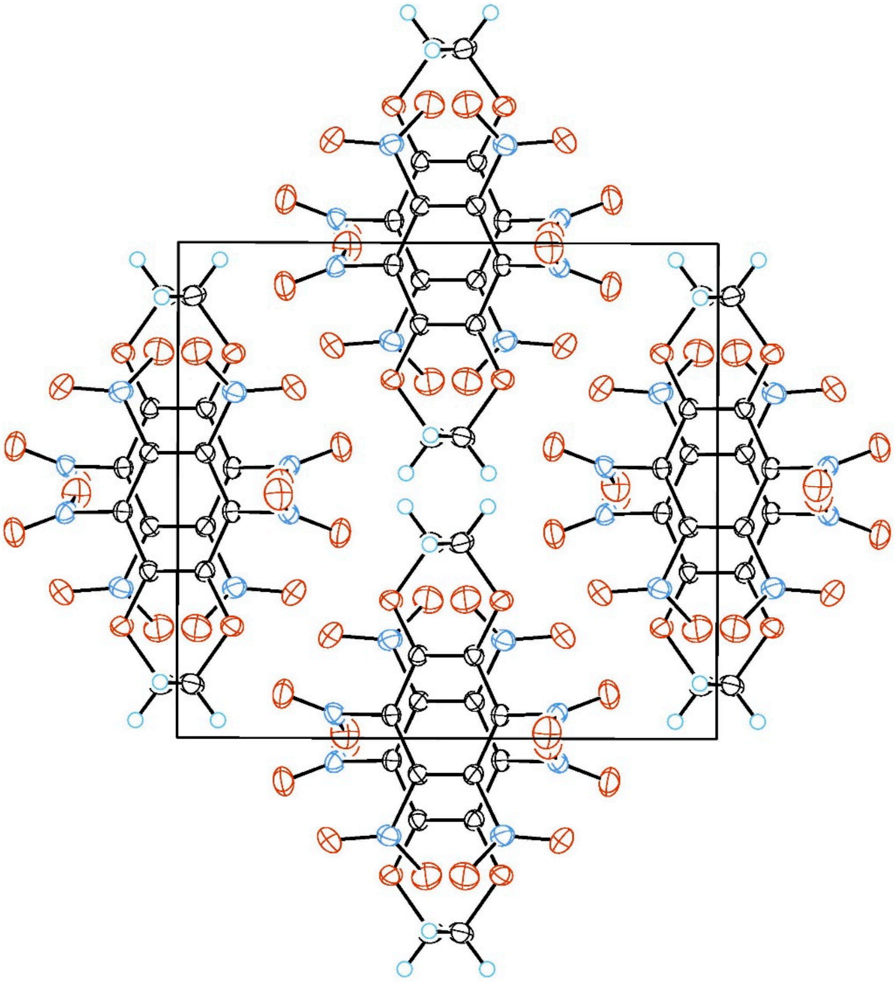

Figure 7a. TNBD - crystal cell package (OrtepPack).

The main parameters of unit cell are listed as following:

a = 10.9946(4), A alpha = 90.0 deg.
b = 10.1532(4), A beta = 94.415(2) deg.
c = 10.1814(3), A gamma = 90.0 deg.
Cell volume 1133.18(7) Å^3

Remarkably, only a half of this compound molecule is located in a separate crystal cell unit. A full molecule structure is shown below in **Figure 7b**:

TNBD - 5,6,7,8-tetranitro-2,3-dihydro-1,4-benzodioxine

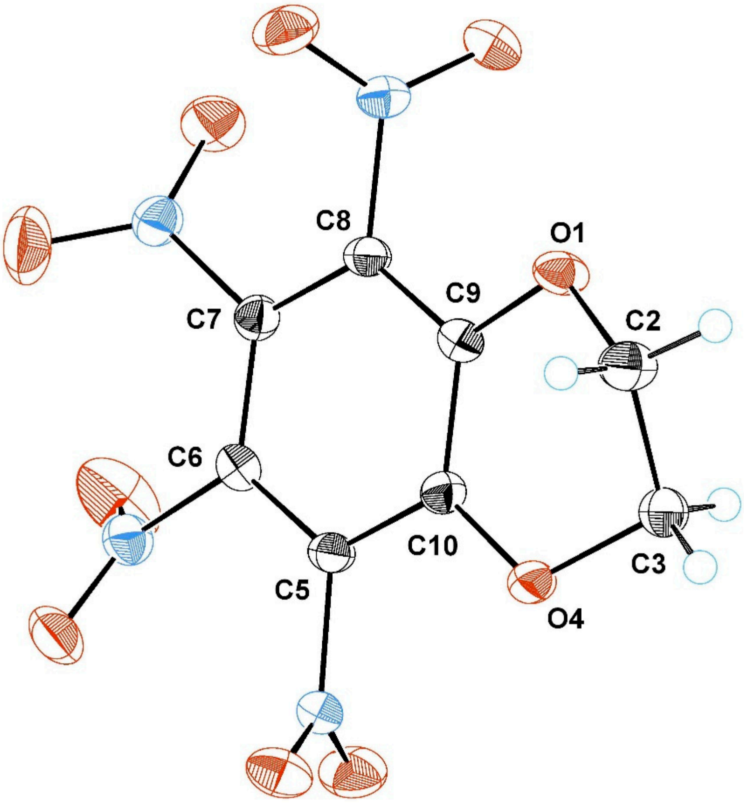

Figure 7b. ORTEP representation of TNBD. The thermal ellipsoids are presented with 50% probability (*CCDC 2320894*) (crystal was grown from 2-butanone).

Table 1. The main crystallographic data for TNBD:.

Empirical formula	$C_8 H_4 N_4 O_{10}$
Formula weight	316.138
Temperature	173(2) K (-100 ^{0}C)
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C 2/c
Unit cell dimensions	a = 10.9946(4), A alpha = 90.0 deg.
	b = 10.1532(4),A beta = 94.415(2) deg.
	c = 10.1814(3), A gamma = 90.0 deg.
Volume	1133.18(7) Å^3
Z	4
Density (calculated)	1.853 g/cm^3
Density (measured, pycnom.)	1.84 g/cm^3
Absorption coefficient	0.176 mm^{-1}
F(000)	640
Crystal size	0.31 x 0.22 x 0.21 mm
Two theta max. for data	58.0 deg.
Reflections collected	2368
Independent reflections	1464 [R(int) = 0.020]
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1292 / 0 / 108
Final R indices [I>3sigma(I)]	R_1 = 0.032, wR_2 = 0.077
R indices (all data)	R_1 = 0.041, wR_2 = 0.116

Largest diff. peak and hole	0.41 and -0.37 e.Å^{-3}

(Full geometry tables for the compound TNBD are presented below in Apendix A)

(Apendix A: Geometry tables for the compound TNBD:
A.1 INTRAMOLECULAR BOND LENGTHS
A.2 INTRAMOLECULAR BOND ANGLES
A.3 INTRAMOLECULAR TORSION ANGLES (H omitted)
A.4 INTERMOLECULAR NON-BONDED DISTANCES
A.5 DIHEDRAL ANGLES FORMED BY LSQ PLANES)

It is worth noting, that nitrogroups in positions 7 and 8 of TNBD are twisted out of the benzene ring plane by different angles, **46.143** and **68.706** degrees (because symmetry, the similar angles are observed for another two NO_2 groups in positions 5 and 6 correspondingly.

For comparison, in HNB (hexanitrobenzene), nitrogrups are rotated at **53^o** [52,53] .

In the crystal structure of TNBD, the molecules are in special positions; each molecule lies on a symmetry axis of order 2. Therefore, atoms O1 and O4, C2 and C3, C9 and C10, etc. are symmetrically equivalent. Figure 8 shows a projection of the molecule along the axis of symmetry. This figure clearly indicates that the dioxane ring in TNBD is characterized by a *twist* conformation. The exit of the C2 atom from the planar phenyl ring of the molecule is equal to 0.384(2) Å (correspondingly, the exit of the C3 atom is –0.384(2) Å). The dihedral angle between the phenyl ring of the molecule and the "triangle" O1–C2–C3 is 41.8(1)° (due to symmetry, the same angle is observed between the phenyl ring and the "triangle" C2–C3–C4).

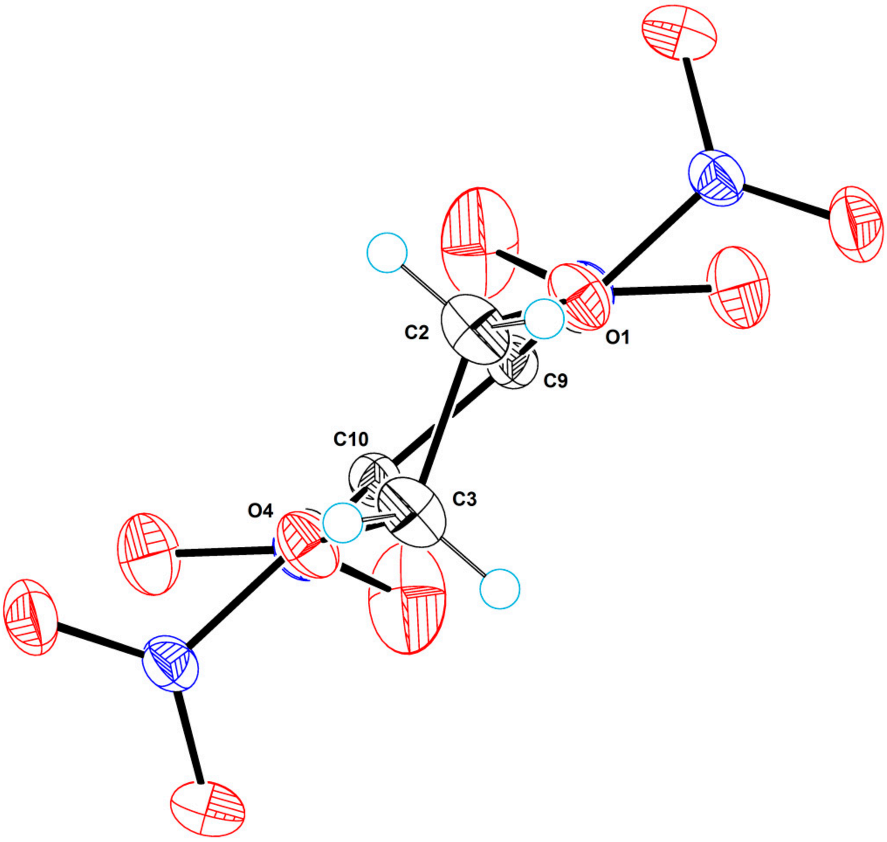

Figure 8. A projection of the molecular structure of TNBD along the twofold axis.

The packing of TNBD molecules in the crystal lattice is quite dense. The packing index, calculated using Kitaigorodsky's approach [57,58], is equal to 0.745. The crystal structure is characterized by strong intermolecular sigma-hole interactions (see Figure 9). The distance between

doi:10.20944/preprints202404.0833.v1

the O52 and O61 atoms of neighboring molecules is 2.910(2) Å (the same distance occurs between the atoms O82 and O71 due to symmetry). Also noteworthy is the strong interaction between atoms O1 and O62 (as well as atoms O4 and O72), which is characterized by a distance of 2.910(2) Å. In addition, the carbon atom C2 (like C3) has increased electronegativity because it is bonded to oxygen. This promotes the formation of intermolecular hydrogen bonds of CH···O type (see in Figure 9). The parameters of this H-bond are the following: C2···O82 = 3.321(3) Å, H2B···O82 = 2.75(2) Å, C2-H2B···O82 = 122(3)°; i.d., this bond is quite weak. Nevertheless, it participates in stabilizing the crystal structure. By means of these intermolecular interactions and hydrogen bonds, the molecular chains along the long parameter of the lattice are formed in the crystal structure. The consequence of these features of the crystal structure of TNBD is a significant packing index value and, in accordance with this, a quite high density of the substance.

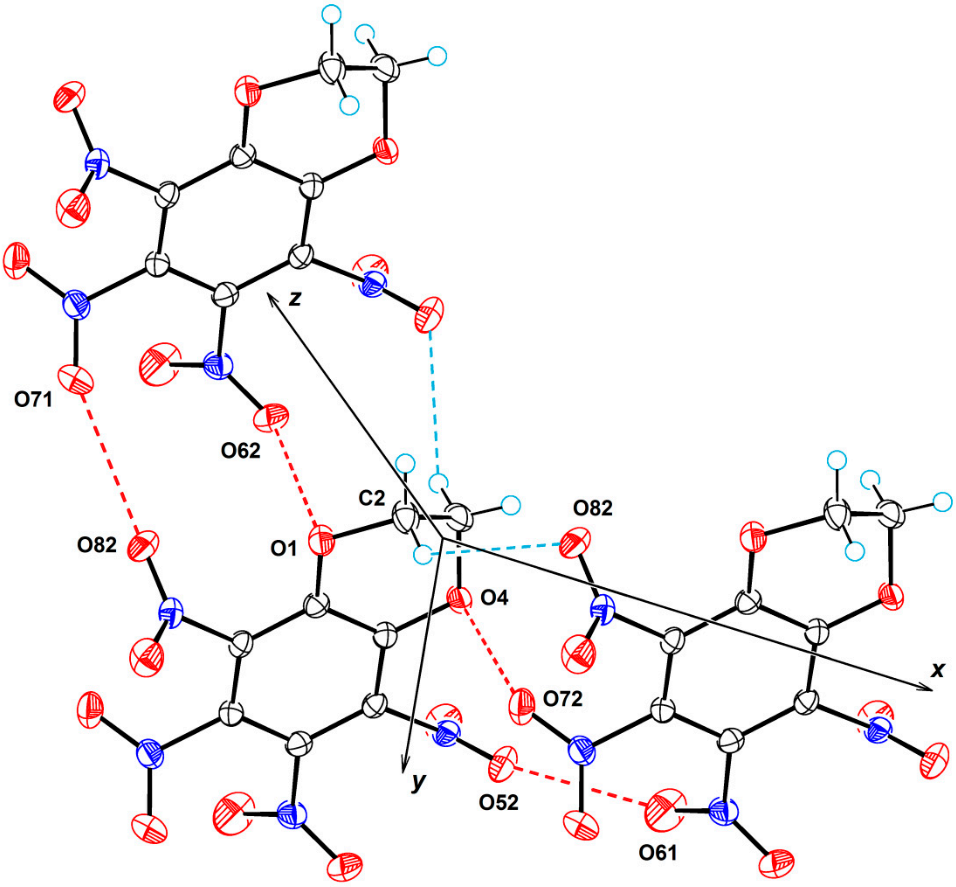

Figure 9. The formation of a molecular chain in the crystal structure of TNBD shows sigma-hole interactions and H-bonds. .

2.1.6. Electrostatic Potential Map (MEP) for TNBD Molecule

The initial refinement of TNBD geometry was performed by semi-empirical (PM6) method, and further optimization and calculation were performed by DT-B3LYP functional method in conjunction with 6-311G(d,p) basis set. The compounds' structure were globally optimized with symmetry restriction, and their local minima were characterized by the harmonic frequency analysis.

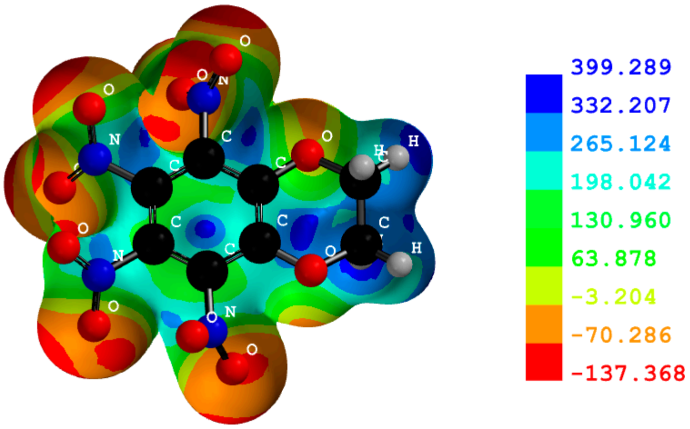

Figure 10. The surface of the electrostatic potential (MEP) of TNBD, calculated by DFT-B3LYP/6-311G(d, p) method. The colours red and blue depict the compound's negatively and positively charged regions (MEP isovalue = 0.002). .

2.1.6. Main Calculated Detonation Performance Parameters of TNBD in Comparison with Known Energetic Materials Possessing Close Structural Patterns

The main calculated detonation parameters of TNBD (at density 1,85 g/cm^3).

The calculated enthalpy of TNBD formation was estimated as (-382 kJ/M) (HF). The detonation heat -5112.9 kJ/M. The main parameters calculated for TNBD by EXPLO 5 [59–61] are represented below:

Table 2. The main calculated detonation parameters of TNBD (at density 1.85 g/cm^3), compared to known energetic materials:.

Detonation parameters	TNBD	DNAN, 2,4-dinitro-anisole	TNAN, 2,4,6-Trinitro-anisole	TNT	Tetryl
Oxygen balance, %	-40.48	-96.90	-62.50	-73.97	-47.40
Detonation temperature (K)	3874	2743	2366	3744	3370
Detonation pressure (kbar)	277.84	159	205	202	260
Detonation velocity (m/s)	7726.9 at d=1.85 g/cm^3	5706 at d=1.341 g/cm^3	6800 at d=1.57 g/cm^3	6950 at d=1.64g/cm^3	7570 at d= 1.71 g/cm3
Volume of detonation products (L/kg)	555.8	626	760	730	800

These data demonstrate that the calculated detonation velocity (D) of TNBD is somewhat greater than that of the well-known energetic tetranitrocompound tetryl [1] (7727 vs. 7570 m/s), and similarly for detonation pressure (P) (278 vs. 260 kbar (exp. [3]), whereas the energetic properties of TNBD in terms aforementioned parameters significantly outperformed DNAN, TNAN, and TNT.

Conclusions

This study leads to the following conclusions:

TNBD (5,6,7,8-tetranitro-1,4-benzodioxane or 5,6,7,8-tetranitro-2,3-dihydro-1,4-benzodioxine, molecular formula - $C_8H_4N_4O_{10}$) has been synthesized in 81% yield by nitration of 6,7-dinitro-1,4-benzodioxane.

Interestingly, TNBD has been found to have good hydrolytic stability and can be stored under normal conditions for 20 years without displaying any signs of degradation.

TNBD shares structural similarities with well-known energetic materials 2,4-dinitroanisole (DNAN) and 2,4,6-trinitroanisole (TNAN), and might be seen as their cyclic, more oxygen-rich and more powerful analogue. Furthermore, due to its higher density, it may be a better choice for high-density and high-energy materials (HDEM).

The spectral characteristics, crystal structure, and experimental density of TNBD (1,85g/cm^3) were investigated.

There are only a few hydrogen atoms in the structure of TNBD, but there are also significant sigma-hole interactions that contribute to is increased density. Another factor is the formation of intermolecular hydrogen bonds of CH···O type.

All of these factors are contributing to the increasing packing density of TNBD molecules.

The results of thermal analysis (DTA) obtained from re-crystallized material showed onset at 247 and isoterm at 288 °C; however, total degradation (100% weight) of the compound is reached only at 300 °C, indicating that the thermostability of TNBD is very close to that of HNS (hexanitrostilbene), also known as thermostable HEM [19].

The main detonation parameters were computed using M. Sućesca - EXPLO 5 programme code.

The detonation velocity and detonation pressure of TNBD were found to be significantly higher than those of the standard aromatic energetic tetranitrocompound tetryl (*N*-methyl-*N*,2,4,6-tetranitroaniline), as well as those of other known energetic materials with similar structural patterns such as TNT (2,4,6-trinitrotoluene), DNAN (2,4-dinitroanisole) and TNAN (2,4,6-trinitroanisole).

To summarize all this data, TNBD appears to be a promising energetic compound that deserve further in-depth research in future.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The author is grateful to Dr. Žilvinas Anusevičius (Vilnius University, Institute of Biochemistry) for the computer calculations of enthalpy of formation of TNBD, Dr. Audrius Misiūnas (Institute of Biochemistry) for vibrational spectra and Mrs. Marytė Krenevičienė (Vilnius University) for the NMR spectra registration. The author also is grateful to Dr. Sergey Belyakov (Latvian Institute of Organic Synthesis, Riga, Latvia) for performing the X-ray analysis and valuable discussion about packing structure details, Dr. Edmundas Spudulis (VGTU, Institute of Thermal insulation, Vilnius) for the substantial help with thermal analysis and Prof. Narimantas Čėnas for his continuing interest in my work. The author is especially indebted to Dr. Muhamed Sućeska (Brodarski Institute, Croatia) for his kind help with calculation of detonation parameters for TNBD with the program code EXPLO 5 and Mrs. Lina Marčiulionytė (Lecturer at Vilnius University) for proofreading the manuscript.

Appendix A. X-ray Difraction Analysis Data. Geometry Tables for the Compound TNBD

Table 3. Geometry tables for the compound TNBD:.

INTRAMOLECULAR BOND LENGTHS			
Minimum bond length= 0.80Å : Maximum bond length= 1.60Å			
O(1) - C(9)	1.338(2)	O(1) - C(2)	1.453(2)
O(82) - N(8)	1.212(2)	O(72) - N(7)	1.212(2)
O(81) - N(8)	1.225(2)	N(7) - O(71)	1.215(2)
N(7) - C(7)	1.473(2)	N(8) - C(8)	1.472(2)
C(7) - C(7)	1.383(3)	C(7) - C(8)	1.388(2)
C(9) - C(9)	1.405(3)	C(9) - C(8)	1.391(2)
C(2) - C(2)	1.503(3)	C(2) - H(2A)	0.92(3)
C(2) - H(2B)			0.91(2)
INTRAMOLECULAR BOND ANGLES			

Minimum bond length= 0.80Å : Maximum bond length= 1.60Å			
C(9) - O(1) - C(2)	113.81(11)	O(72) - N(7) - O(71)	126.22(14)
O(72) - N(7) - C(7)	116.99(12)	O(71) - N(7) - C(7)	116.79(12)
O(82) - N(8) - O(81)	126.22(13)	O(82) - N(8) - C(8)	117.17(12)
O(81) - N(8) - C(8)	116.61(13)	N(7) - C(7) - C(7)	121.79(8)
N(7) - C(7) - C(8)	118.94(13)	C(7) - C(7) - C(8)	119.18(8)
O(1) - C(9) - C(9)	122.69(7)	O(1) - C(9) - C(8)	118.69(12)
C(9) - C(9) - C(8)	118.60(8)	N(8) - C(8) - C(7)	120.19(12)
N(8) - C(8) - C(9)	117.51(12)	C(7) - C(8) - C(9)	122.21(14)
O(1) - C(2) - C(2)	110.23(11)	O(1) - C(2) - H(2A)	108.(2)
O(1) - C(2) - H(2B)	105.6(15)	C(2) - C(2) - H(2A)	106.(2)
C(2) - C(2) - H(2B)	111.9(14)	H(2A) - C(2) - H(2B)	115.(2)
INTRAMOLECULAR TORSION ANGLES (H omitted)			
Minimum bond length= 0.80Å : Maximum bond length= 1.60Å			
C(2) - O(1) - C(9) - C(9)	167.41(11)	C(2) - O(1) - C(9) - C(8)	165.99(13)
C(9) - O(1) - C(2) - C(2)	-136.50(10)	O(72) - N(7) - C(7) - C(7)	43.76(9)
O(72) - N(7) - C(7) - C(8)	47.05(10)	O(71) - N(7) - C(7) - C(7)	-135.42(12)
O(71) - N(7) - C(7) - C(8)	-132.12(14)	O(82) - N(8) - C(8) - C(7)	-113.15(13)
O(82) - N(8) - C(8) - C(9)	70.38(11)	O(81) - N(8) - C(8) - C(7)	67.25(11)
O(81) - N(8) - C(8) - C(9)	-109.22(12)	C(7) - C(7) - N(7) - O(72)	-136.24(14)
N(7) - C(7) - C(7) - N(7)	0.00(8)	C(7) - C(7) - N(7) - O(71)	44.58(11)
N(7) - C(7) - C(7) - C(8)	-176.70(13)	C(8) - C(7) - N(7) - O(72)	47.05(10)
C(8) - C(7) - N(7) - O(71)	-132.12(14)	N(7) - C(7) - C(8) - N(8)	0.40(9)
N(7) - C(7) - C(8) - C(9)	176.7(2)	C(8) - C(7) - C(7) - N(7)	176.70(12)
C(7) - C(7) - C(8) - N(8)	-176.39(15)	C(7) - C(7) - C(8) - C(9)	-0.09(10)
C(8) - C(7) - C(7) - C(8)	0.00(8)	O(1) - C(9) - C(9) - O(1)	0.00(7)
O(1) - C(9) - C(9) - C(8)	178.59(13)	C(9) - C(9) - O(1) - C(2)	-12.59(9)
O(1) - C(9) - C(8) - N(8)	-1.20(8)	O(1) - C(9) - C(8) - C(7)	-177.6(2)
C(8) - C(9) - O(1) - C(2)	165.99(13)	C(8) - C(9) - C(9) - O(1)	-178.59(12)
C(9) - C(9) - C(8) - N(8)	177.44(14)	C(9) - C(9) - C(8) - C(7)	1.05(10)
C(8) - C(9) - C(9) - C(8)	0.00(8)	C(7) - C(8) - N(8) - O(82)	-113.15(13)
C(7) - C(8) - N(8) - O(81)	67.25(11)	N(8) - C(8) - C(7) - N(7)	0.40(9)
N(8) - C(8) - C(7) - C(7)	3.61(8)	N(8) - C(8) - C(9) - O(1)	-1.20(8)
C(9) - C(8) - N(8) - O(82)	70.38(11)	C(9) - C(8) - N(8) - O(81)	-109.22(12)
N(8) - C(8) - C(9) - C(9)	-2.56(7)	C(7) - C(8) - C(9) - O(1)	-177.6(2)
C(9) - C(8) - C(7) - N(7)	176.7(2)	C(9) - C(8) - C(7) - C(7)	179.90(13)
C(7) - C(8) - C(9) - C(9)	-178.95(13)	O(1) - C(2) - C(2) - O(1)	-0.02(7)
C(2) - C(2) - O(1) - C(9)	43.50(10)		

INTERMOLECULAR NON-BONDED DISTANCES											
Minimum distance= 1.95Å : Maximum distance= 3.50Å											
Atom(1)		Atom(2)	distance	ns	np	Ta	Tb	Tc	x(2)	y(2)	z(2)
O(1)	-	O(82)	3.0534(15)	3	1	0	0	1	0.19772	0.08779	0.59972
O(1)	-	O(71)	3.235(2)	2	1	0	1	1	-0.03531	0.22086	0.61436
O(1)	-	N(8)	3.448(2)	3	1	0	0	1	0.29370	0.04775	0.56425
O(82)	-	H(2A)	3.03(3)	3	1	0	0	1	0.42330	0.46537	0.67214
O(82)	-	H(2B)	3.25(2)	3	1	0	0	1	0.53069	0.38884	0.62140
O(72)	-	O(81)	3.388(2)	3	1	0	1	1	0.31223	1.00975	0.45335
O(72)	-	C(7)	3.457(2)	5	1	0	0	0	-0.05135	0.57427	0.20630
O(81)	-	C(7)	3.262(2)	2	1	0	1	1	-0.05135	0.42573	0.70630
O(81)	-	C(8)	3.220(2)	6	1	0	1	0	0.10141	0.54512	0.83681

O(81)	-	C(2)	3.461(2)	3	1	0	0	1	0.47263	0.39265 0.68007

ns is the symmetry operator number - (* denotes inversion indicator)
np is the lattice point number

DIHEDRAL ANGLES FORMED BY LSQ PLANES

PLANE - PLANE		ANGLE	E.S.D
PLANE	1 (C5 C6 C7 C8 C9 C10)	PLANE 2 (O71 N7 O72)	PLANE 3 (O81 N8 O82)
1	2	46.143	0.081
1	3	68.706	0.103

References

1. Klapötke, T.M. *Chemistry of high-energy materials*. 6th ed. Walter de Gruyter, Berlin/Boston. 2022, pp. 1–937. ISBN 978-3110739497.
2. Meyer, R.; Köhler, J.; Homburg, A. *Explosives*, 6th ed. Wiley-WCH Verlag Gmbh & Co. 2007, pp. 1-433. ISBN: 978-3-527-61703-6.
3. Agrawal, J.P.; Hodgson, R. *Organic Chemistry of Explosives*. Wiley Interscience, N.Y. 2007, pp.1-416. ISBN: 978-0-470-02967-1. Urbanski, T. *Chemistry and Technology of Explosives*. Warszawa. 1964, Vol. 1, pp. 1-635.
4. Orlova,Ye.Yu., *Chemistry and Technology of High Explosives.* Leningrad, Khimiya, 1973, pp. 1-686. (Ru)
5. Zeman, S. Influence of the energy content and its outputs on sensitivity of polynitroarenes. *J. Energ. Mater.* **2019**, *37*, 445-458. https://doi.org/10.1080/07370652.2019.1634159.
6. Matyáš, R.; Pachman, J. *Primary explosives*. Germany: Springer-Verlag, Berlin, Heidelberg. 2013, pp. 1-338. ISBN: 978-3-642-28436-6. https://doi.org/10.1007/978-3-642-28435-6
7. Östmark, H.; Bemm, U.; Bergman, H.; Langlet, A. *N*-Guanylurea-Dinitramide: A New Energetic Material with Low Sensitivity for Propellants and Explosives Applications. *Termochim. Acta*. **2002**, *384*, 253-259. https://doi.org/10.1016/S0040-6031(01)00800-0
8. Coburn, M.D.; Harris, B.W.; Lee, K.-Y.; Stinecipher, M.M.; Heyden, H.H. Explosives synthesis at Los Alamos, *Ind. Eng. Chem. Prod. Res. Dev*. **1986,** *25*, p. 68-72. https://doi.org/10.1021/i300021a015
9. Tselinskii, I.V. Applications of energetic materials in engineering, technology and national economy. *Soros Educat. J.* **1997,** *11*, 46-52.
10. Zeman, S. Sensitivities of high energy compounds. In *Structure and Bonding*, Klapoetke T. (Ed.), *High Energy Density Compounds*, Springer. 2007, Vol. 125, pp. 195-271. https://doi.org/10.1007/430_2006_052
11. Akhavan, J. *The Chemistry of Explosives*, 4th ed.; RSC, London, UK, 2022, pp.1-359. ISBN: 978-1-83916-446-0.
12. Agrawal, J.P. Past, Present and Future of Thermally Stable Explosives. *Cent. Eur. J. Energ. Mater.* **2012**, *9*, 273-290. ISSN: 1733-7178
13. Bellamy, A.; Ward, S.J.; Golding, P. A New Synthetic Route to 1,3,5-Triamino-2,4,6-Trinitrobenzene (TATB), *Propellants, Explos. Pyrotech.* **2002**, *27*, p. 49-58. https://doi.org/10.1002/1521-4087(200204)27:2<49::AID-PREP49>3.0.CO;2-4
14. Pagoria, P.F.; Lee, G.S.; Mitchell, A.R.; Schmidt, R.D. A review of energetic materials synthesis. *Thermochim. Acta*, **2002**, *84*, 187-204. https://doi.org/10.1016/S0040-6031(01)00805-X
15. Cao, W.L.; Li, Z.M.; Yang, J.Q.; Zhang, J.G. Recent advances on the nitrogen-rich 1, 2, 4-oxadiazole-azoles-based energetic materials. *Def. Technol.* **2022**, *18*, 344-367. https://doi.org/10.1016/j.dt.2021.12.002
16. Wang, Z.; Zhang, H.; Jabeen, F.; Gopinathan-Pillai, G.; Arami, J.A.; Killian, B.J.; Stiegler, K.D.; Yudewitz D.S.; Thiemann, P.L.; Turk, J.D.; Zhou, W. Synthesis and Properties of Energetic 1, 2, 4-Oxadiazoles. *Eur. J. Org. Chem.* **2015**, *34*, 7468-7474. https://doi.org/10.1002/ejoc.201501056
17. Wang, Z.; Zhang, H.; Killian, B.J.; Jabeen, F.; Pillai, G.G.; Berman, H.M.; Mathelier, M.; Sibble, A.J.; Yeung, J.; Zhou, W.; Steel, P.J. Synthesis, Characterization and Energetic Properties of 1, 3, 4-Oxadiazoles. *Eur. J. Org. Chem.* **2015**, *23*, 5183-5188. https://doi.org/10.1002/ejoc.201500583
18. Xiong, H.; Yang, H.; Lei, C.; Yang, P.; Hu, W.; Cheng, G. Combinations of furoxan and 1, 2, 4-oxadiazole for the generation of high performance energetic materials. *Dalton Trans.* **2019**, *48*, 14705-14711. https://doi.org/10.1039/C9DT02684C
19. Fershtat, L.L.; Makhova, N.N. 1, 2, 5-Oxadiazole-Based High-Energy-Density Materials: Synthesis and Performance. *ChemPlusChem*. **2020**, *85*, 13-42. https://doi.org/10.1002/cplu.201900542
20. Zhou, J.; Huang, M.; Zhang, J.; Zhai, L.; Cao, Y.; Wang, X.; Qiu, L.; Wang, B.; Meng, Z. Thermal chemistry and decomposition behaviors of energetic materials with trimerizing furoxan skeleton. *Propellants, Explos. Pyrotech.* **2024**, e202300267. https://doi.org/10.1002/prep.202300267
21. Qian, L.; Yang, H.; Xiong, H.; Gu, H.; Tang, J.; Xue, Y.; Cheng, G. Low sensitive energetic material based on the combination of furoxan and 1, 3, 4-oxadiazole structures. *Energ. Mater. Front.* **2020**, *1*, 74-82. https://doi.org/10.1016/j.enmf.2020.09.004
22. Li, Y.; Zhang, Z.; Ge, Z.; Wang, B.; Lai, W.; Luo, Y.. Study of furoxan derivatives for energetic applications. *Chin. J. Chem.* **2013**, *31*, 520-524. https://doi.org/10.1002/cjoc.201201169

23. Larin, A.A.; Bystrov, D.M.; Fershtat, L.L.; Konnov, A.A.; Makhova, N.N.; Monogarov, K.A.; Meerov, D.B.; Melnikov, I.N.; Pivkina, A.N.; Kiselev, V.G.; Muravyev, N.V. Nitro-, cyano-, and methylfuroxans, and their bis-derivatives: From green primary to melt-cast explosives. *Molecules*, **2020**, *25*, 5836. https://doi.org/10.3390/molecules25245836
24. Zhang, Q.; Zhang, X.; Pang, S.; He, C. Enhanced Energetic Performance *via* the Combination of Furoxan and Oxa-[5, 5] bicyclic Structures. *Int. J. Mol. Sci.* **2023**, *24*, 8846. https://doi.org/10.3390/ijms24108846
25. Chen, P.; Dou, H.; He, C.; Pang, S. Boosting the energetic performance of trinitromethyl-1, 2, 4-oxadiazole moiety by increasing nitrogen-oxygen in the bridge. *Int. J. Mol. Sci.*, **2022**, *23*, 10002. https://doi.org/10.3390/ijms231710002
26. Zlotin, S.G.; Churakov, A.M.; Egorov, M.P.; Fershtat, L.L.; Klenov, M.S.; Kuchurov, I.V.; Makhova, N.N.; Smirnov, G.A.; Tomilov, Y.V.; Tartakovsky, V.A. Advanced energetic materials: novel strategies and versatile applications. *Mendeleev Commun.* **2021**, *31*, pp.731-749. https://doi.org/10.1016/j.mencom.2021.11.001
27. Walker, R.W.; Morley, C. Basic chemistry of combustion, In: *Comprehensive Chemical Kinetics*, Ed.: Pilling, M.J., Elsevier, 1997, Vol. 35, pp.1-124. ISBN 9780444824851. https://doi.org/10.1016/S0069-8040(97)80016-7
28. Sainsbury, M. Compounds containing a Six-membered Ring having two Hetero-atoms from Group VIB of the Periodic Table: Dioxanes, Oxathianes and Dithianes. In *Rodd's Chemistry of Carbon Compounds*. Elsevier. 1964, pp. 375-426. https://doi.org/10.1016/B978-044453345-6.50780-X
29. Dao, L.H.; Hopkinson, A.C.; Lee-Ruff, E. Reactions of bishalomethylarenes with superoxide. *Can. J. Chem.* **1977**, *55*, 3791-3796. https://doi.org/10.1139/v77-534
30. Baran, A.; Aydin, G.; Savran, T.; Sahin, E.; Balci, M. Trisequential Photooxygenation Reaction: Application to the Synthesis of Carbasugars. *Org. Lett.* **2013**, *15*, 4350-4353. https://doi.org/10.1021/ol401823m
31. Roth, W.R.; Scholz, B.P. Zur Energiedelle von Diradikalen, II. Das 2,3-Dimethylen-1,4-cyclohexadiyl. *Chem. Ber.* **1982**, *115*, 1197–1208. https://doi.org/10.1002/cber.19821150335
32. Baker, W. CCXL.Cyclic esters of sulphuric acid. Part I. The reactions of methylene sulphate. *J. Chem. Soc.* **1931**, 1765–1771. https://doi.org/10.1039/jr9310001765
33. Pilkington, L.I.; Barker, D. Synthesis and biology of 1, 4-benzodioxane lignan natural products. *Nat. Prod. Rep.* **2015**, *32*, 1369-1388. https://doi.org/10.1039/C5NP00048C
34. Vorländer, D. Ethylenic salts of bibasic acids and phenols. *Justus Liebigs Ann. Chem.* **1894**, *280*, 167-206. https://doi.org/10.1002/jlac.18942800202
35. Matos, M.A.R.; Sousa, C.C.; Morais, V.M. Experimental and computational thermochemistry of 1, 4-benzodioxan and its 6-R derivatives. *J. Phys. Chem. (A).* **2008**, *112*, 7961-7968. https://doi.org/10.1016/j.jct.2008.06.003
36. Bolchi, C.; Bavo, F.; Appiani, R.; Roda, G.; Pallavicini, M. 1, 4-Benzodioxane, an evergreen, versatile scaffold in medicinal chemistry: A review of its recent applications in drug design. *Eur. J. Med. Chem.* **2020**, *200*, 112419. https://doi.org/10.1016/j.ejmech.2020.112419
37. Ahmed, B., Habibullah, H., & Khan, S. Chemistry and pharmacology of benzodioxanes (Microreview). *Org. Chem. an Indian J. (OCAIJ).* **2008**, *4*, 65-77.
38. Liu, Z.; Zhang, Y.; Dong, J.; Fang, Y.; Jiang, Y.; Yang, X.; Cheng, F. Synthesis and antitumor activity of novel hybrid compounds between 1, 4-benzodioxane and imidazolium salts. *Arch. Pharm.* **2022**, *355*, 2200109. https://doi.org/10.1002/ardp.202200109
39. Daukshas, V.K.; Udrenaite, E.B. Advances in chemistry in the benzo-1, 4-dioxane series. *Chem. Heterocycl. Compd.* **1975**, *11*, 1003-1017. https://doi.org/10.1007/BF00471284
40. Daukshas, V.K.; Purvanetskas, G.V.; Balyavichyus, L.Z.; Udrenaite, E.B.; Gineitite, V.L. Electrophilic substitution of acetamido- and acetoxybenzo-1,4-dioxanes. *Chem. Heterocycl. Compd.* **1977**, *13*, 373. https://doi.org/10.1007/BF00482777
41. Labanauskas, L.K.; Brukstus, A.B.; Gaidelis, P.G.; Buchinskaite, V.A.; Udrenaite, E.B.; Dauksas, V.K. Synthesis and anti-inflammatory activity of new derivatives of 6-benzoyl-1, 4-benzodioxane. *Pharm. Chem. J.* **2000**, *34*, 353-355.
42. Labanauskas, L.; Udrėnaitė, E.; Gaidelis, P.; Brukštus, A. Synthesis of 5-(2-, 3- and 4-methoxyphenyl)-4*H*-1, 2, 4-triazole-3-thiol derivatives exhibiting anti-inflammatory activity. *Il Farmaco*, **2004**, *59*, 255-259. https://doi.org/10.1016/j.farmac.2003.11.002
43. Labanauskas, L.; Brukstus, A.; Udrenaite, E.; Bucinskaite, V.; Susvilo, I.; Urbelis, G. Synthesis and anti-inflammatory activity of 1-acylaminoalkyl-3, 4-dialkoxybenzene derivatives. *Il Farmaco*, **2005**, *60*, 203-207. https://doi.org/10.1016/j.farmac.2004.12.003
44. Labanauskas, L.; Bucinskaite, V.; Brukstus, A.; Urbelis, G.; Sharlauskas, I. Synthesis of a Novel Heterocyclic System: 3-Chloro-7, 8-dihydro [1, 4] dioxino [2 ″, 3 ″: 4′, 5′] benzo [4, 5] imidazo [1, 2-c][1, 2, 3] thiadiazole. *Chem. Het. Comp.* **2005**, *41*, 802-803. ISSN 0009-3122

45. Šarlauskas, J.; Miliukienė, V.; Anusevičius, Ž.; Misevičienė, L.; Krikštopaitis, K.; Nemeikaitė-Čėnienė; A., Vitėnienė, I.; Čėnas, N. Redox properties and prooxidant cytotoxicity of benzofuroxans: a comparison with nitrobenzenes. *Chemija*. **2009**, *20*, 109-115.
46. Jonušis, M.; Šteinys, L.; Bukšnaitienė, R.; Čikotienė, I. Synthesis of Alkoxymethyl Groups Containing Isoxazoles and Chromones. *Synthesis*, **2017**, *49*, 1122-1130. https://doi.org/10.1055/s-0036-1588327 .
47. Šarlauskas, J. Polynitrobenzenes containing alkoxy and alkylenedioxy groups: potential HEMs and precursors of new energetic materials. *Cent. Eur. J. Energ. Mater.* **2010,** *7*, 313-324. ISSN 1733-7178
48. Takakis, I.M.; Hadjimihalakis, P.M. Influence of the heterocyclic side ring on orientation during nitrations of 1, 2-alkylenedioxy-annelated benzenes and their mononitro derivatives. *J. Het. Chem.* **1991**, *28*, 625-634. https://doi.org/10.1002/jhet.5570280316
49. Heertjes, P.M.; Dahmen, E.A.M.F.; Wierda, T.G. The nitroderivatives of 1:2 ethylenedioxybenzene (pyrocate-cholethylene ether) obtained by direct nitration. *Rec. trav. chim.* **1941**, *60*, 569-576.
50. Vogelsanger, B. Chemical stability, compatibility and shelf life of explosives. *Chimia*, **2004**, *58*, 401-408. https://doi.org/10.2533/000942904777677740.
51. Dashevskii, V.G.; Struchkov, Y.T.; Akopyan, Z.A. Conformation of overloaded aromatic nitrocompounds. *J. Struct. Chem*. **1967**, *7*, 555-561.
52. Akopyan, Z.A.; Struchkov, Y.T.; Dashevskii, V.G. Crystal and molecular structure of hexanitrobenzene. *J. Struct.Chem.* **1966**, *7*, 385-392.
53. Wang, R.; Liu, J.; He, X.; Xie, W.; Zhang, C. Decoding hexanitrobenzene (HNB) and 1, 3, 5-triamino-2, 4,6-trinitrobenzene (TATB) as two distinctive energetic nitrobenzene compounds by machine learning. *Phys. Chem. Chem. Phys.* **2022**, *24*, 9875-9884.
54. O'Sullivan, O.T.; Zdilla, M.J. Properties and promise of catenated nitrogen systems as high-energy-density
55. materials. *Chem. Rev.* **2020**,*120*, 5682-5744.
56. Lee, J.S.; Hsu, C. K.; Chang, C.L. A study on the thermal decomposition behaviors of PETN, RDX, HNS and HMX. *Thermochim. Acta.* **2002**, 173-176.
57. Kitaigorodsky, A.I. *Molecular Crystals and Molecules*. 1973. Academic Press, New York, pp.1-553. ISBN: 0124105505
58. Linghu, Y.; Zhang, C. Packing coeffcient determining the packing density difference of CHON-containing isomers. *Energ. Mater. Front.*, **2024** (In Press, Correct. Proof). https://doi.org/10.1016/j.enmf.2024.02.004 ; ISSN: 2666-6472
59. Sućeska, M. Calculation of Detonation Properties of CHNO Explosives. *Propellants, Explos., Pyrotech.* **1991**, *16*, 197-202.
60. Sućeska, M. *Test Methods for Explosives*. 1995. Springer-Verlag, New York, pp. 188-200.
61. Sućeska, M. Evaluation of Detonation Energy from EXPLO 5 Computer Results. *Propellants, Explos., Pyrotech.* **1999**, *24*, 280-285.