



Research paper / Praca doświadczalna

Preparation and investigation of the properties of hexanitrohexaazatricyclododecanidione (HHTDD) *Otrzymywanie i badanie właściwości heksanitroheksaazatricyklododekanidionu (HHTDD)*

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Abstract: Literature descriptions of methods for obtaining hexanitrohexaazatricyclododecanedione are discussed. The most advantageous method for preparing the compound on a laboratory scale was selected for experimental research. A full structural and qualitative analysis of the final product was carried out. The heat of combustion was determined calorimetrically and the standard enthalpy of HHTDD formation was calculated based on this value. The sensitivity of the material to mechanical stimuli (impact and friction) was determined.

Streszczenie: Przedyskutowano literaturowe opisy metod otrzymywania heksanitroheksaazatricyklododekanidionu. Do badań eksperymentalnych wytypowano metodę najkorzystniejszą z punktu widzenia otrzymywania związku w skali laboratoryjnej. Wykonano pełną analizę strukturalną i jakościową produktu finalnego. Kalorymetrycznie wyznaczono ciepło spalania i na tej podstawie obliczono standardową entalpię tworzenia HHTDD. Określono wrażliwość materiału na bodźce mechaniczne (uderzenie i tarcie).

Keywords: hexanitrohexaazatricyclododecanodione, high energy materials, high nitrogen explosives

Słowa kluczowe: heksanitroheksaazatricyklododekanidion, materiały wysokoenergetyczne, wysokoazotowe materiały wybuchowe

1. Introduction

High velocity of detonation explosives have been the focus of military and civilian research centres for many years [1]. Intensive theoretical and experimental studies are conducted in the field of heterocyclic cage compounds in which the nitro groups are bonded to a carbon or nitrogen atom. A separate interesting group of compounds is the one lacking nitro groups, in which oxygen is present in the form of N-oxide groups. Explosives, in which the difluoroamino group is the highly energetic entity, are also well known [2]. The result of intensive research was the design of a number of compounds with high predicted detonation parameters such as tetranotetrazine tetra-N-oxide (TTTO) [3], furoxanetetrazine di-N-oxide (FXTO), octanitrocuban (ONC) [4], 1,3,4,6-tetranitroglycoluryl (TENGU) [5], hexanitrohexaazaisowurtzitan (HNIW) [6] etc. To date, the synthesis

of many of these modelled materials has not been possible (e.g. TTTO). Some of these turned out to be chemically unstable (TENGU) and the production of ONC was too expensive to be utilised in practice. Among the modern explosives, HNIW seems to be the most promising. It combines high detonation parameters with good thermal stability and chemical resistance. A serious disadvantage of HNIW is the relatively complicated synthetic procedure.

Regardless of the intensive studies carried out on simplifying HNIW synthesis, research concerning the potential substitutes for this material is underway. One of the explosives which could replace HNIW in some future applications is 2,6-dioxo-1,2,4,5,7,8-hexanitrohexaazatricyclododecanedione (HHTDD). This compound was first described in 1991 by Vedachalam *et al.* [7]. It exhibits thermal stability up to 210 °C, a calculated detonation velocity of 9800 m·s⁻¹ at a density of 2.07 g·cm⁻³ [8] and an oxygen balance of 0%. Despite the interesting properties of HHTDD, so far no experimental data on the explosive properties of the compound or its sensitivity to mechanical stimuli, have been published.

The aim of this study was the selection of the optimal HHTDD synthesis method and to confirm the structure of the product. Subsequent examination of the compound's sensitivity to mechanical stimuli and determination of the velocity of detonation was planned.

2. HHTDD Synthesis Methods

According to literature, hexanitrohexaazadodecanodione is obtained by a three-step process. Condensation of formamide with glyoxaldehyde gives 1,4-diformyl-2,3,5,6-tetrahydropiperazine (DFTHP). In the second stage of the reaction of DFTHP with urea, 2,6-dioxodecahydro-1*H*,5*H*-diimidazo[4,5,4',5']pyrazine hydrate dihydrochloride (HTDD) is formed. In the last step, HTDD is nitrated to HHTDD.

The condensation of formamide with glyoxal, resulting in the formation of DFTHP, requires a basic catalyst and inorganic bases such as sodium bicarbonate, sodium carbonate, sodium hydroxide, and organic bases such as trialkyl substituted amines, e.g. trimethylamine, triethylamine [9] *etc.*

The reaction of DFTHP with urea takes place in a concentrated aqueous hydrogen chloride solution, the product of which is 2,6-dioxodecahydro-1*H*,5*H*-diimidazo[4,5,4',5']pyrazine hydrate dihydrochloride (HTDD). HTDD is transformed into monohydrochloride or nitrate, by precipitation with methanol from an aqueous solution or by the addition of sodium nitrate, respectively [7].

2,6-Dioxodecahydro-1*H*,5*H*-diimidazo[4,5,4',5']pyrazine hydrate monohydrochloride is converted into HHTDD by gradual nitration with isolation of the tetra or pentanitrite derivative of HTDD. The one-step preparation of HHTDD from HTDD requires the use of dinitrogen pentoxide (N₂O₅). The use of only fuming nitric acid as well as its mixtures with acetic anhydride, sulfuric(VI) acid (H₂SO₄), and oleum allows solely a pentanitric derivative to be obtained.

A three-stage pathway was selected for experimental research, including the isolation of indirect products. In the first step, DFTHP was obtained and in the second – the dodecanedione hydrochloride, which in the third step was nitrated to HHTDD.

3. Experimental Section

3.1. Materials and test methods

The following reagents were used in the studies: formamide (POCH), glyoxal (Merck), triethylamine (Lachner), hydrochloric acid (POCH), urea (POCH), phosphorus pentoxide (POCH), nitric acid (Merck) and acetone (POCH). Nuclear magnetic resonance (NMR) spectra of a sample dissolved in deuterated dimethyl sulfoxide (D₆-DMSO) were recorded at 30 °C using a Bruker DRX 500 apparatus.

The heat of combustion was measured using an automatic calorimeter with an isothermal water jacket (KL-10, Precyzja Bydgoszcz), in a standard calorimetric bomb filled with oxygen at an initial pressure of 2.0 MPa.

The heat capacity of the calorimetric system, determined under identical conditions to those used in the subsequent measurements, was $(13188 \pm 40) \text{ J} \cdot \text{deg}^{-1}$.

Sensitivity to friction was determined using a standard Julius Peters apparatus, in accordance with the PN-EN-13631-3 standard, performing 10 tests at each loading of the friction peg. In the impact sensitivity tests, in accordance with the PN-EN-13631-4 standard, a Kast fall hammer and 5 kg weight were used with 10 tests being performed for each height.

3.2. The synthesis of hexanitrohexaazadodecanedione

3.2.1. The synthesis of 1,4-diformyl-2,3,5,6-tetrahydropiperazine (DFTHP)

The DFTHP synthesis scheme is shown in Fig. 1.

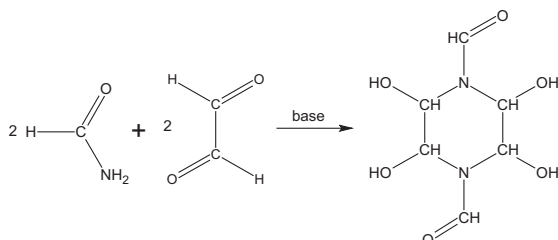


Figure 1. Synthesis scheme for 1,4-diformyl-2,3,5,6-tetrahydropiperazine

299.0 g of a 40% aqueous solution of glyoxal and 93.0 g of formamide were added to a 500 cm³ spherical reaction vessel equipped with an anchor stirrer and thermocouple. 23.0 g of triethylamine were added dropwise to the resulting solution over 10 min. The reaction was carried out at ambient temperature for 2 h. The prepared mixture, in the form of a thick yellow suspension, was transferred to a sintered funnel and filtered under reduced pressure. The obtained fine-crystalline precipitate was first washed with a large amount of water, and then with methanol to remove water insoluble impurities and to accelerate the drying process. The white, fine-crystalline THDFP precipitate obtained was dried and weighed. 169.0 g of DFTHP was obtained, which was 66% of the theoretical yield.

3.2.2. The synthesis of 2,6-dioxodecahydro-1*H*,5*H*-diimidazo [4,5,4',5']pyrazine hydrochloride (HTDD)

The scheme for the HTDD synthesis is shown in Fig. 2.

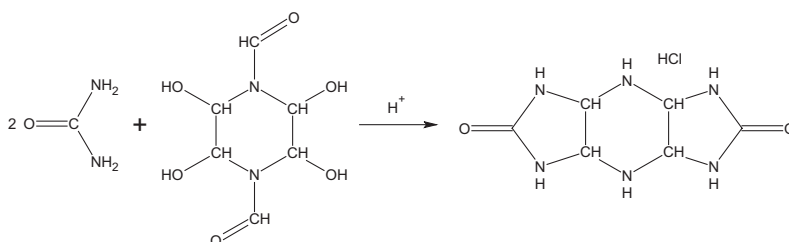


Figure 2. The scheme for the synthesis of 2,6-dioxodecahydro-1*H*,5*H*-diimidazo[4,5,4',5']pyrazine

200 cm³ of a 35% aqueous hydrogen chloride solution was placed in a 500 cm³ reaction vessel followed by the addition of 42.0 g of dry urea. At ambient, 48.0 g of THDFP was added over 20 min. The system was then conditioned for 90 h at 20 °C. The precipitated product was filtered under reduced pressure and washed with methanol. 56.4 g of dihydrochloride hydrate (DCHTDD) were obtained, representing

80.2% of the theoretical yield.

DCHTDD was dissolved in water ($22 \text{ cm}^3 \cdot \text{g}^{-1}$) and then recrystallised from cold methanol ($50 \text{ cm}^3 \cdot \text{g}^{-1}$). 20.6 g of HTDD hydrochloride was obtained, which constitutes 38% of the theoretical yield. Its decomposition temperature was measured as 183-185 °C.

3.2.3. HHTDD synthesis

The scheme for the synthesis of hexanitrohexaazatricyclododecanedione is shown below:

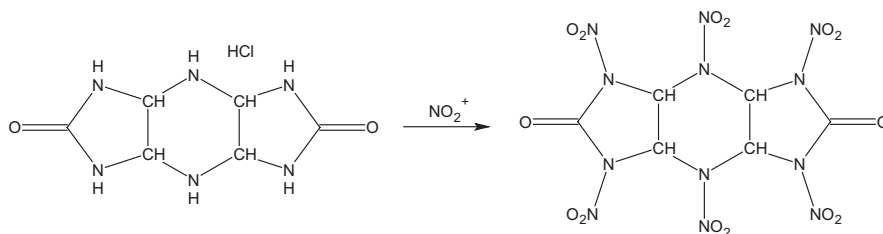


Figure 3. The synthesis scheme for HHTDD

To a 500 cm³ beaker equipped with a mechanical stirrer and a thermometer, was added 150 cm³ of 100% nitric acid and – at a temperature not exceeding 30 °C – 78.0 g P₂O₅. The mixture was conditioned for 40 min at 30 °C and then cooled to –15 °C before addition of 6.0 g of HTDD over 30 min, maintaining a temperature of (–10)–15 °C. When the substrate addition was complete, the mixture was allowed to warm to 25 °C over 1.5 h. The system was kept at this temperature for 30 min and then for 1 h at 35 °C and 2 h at 45 °C. The mixture was subsequently cooled and poured with continuous stirring into 1500 g of ice-water. The precipitate was filtered off, washed with cold water, followed by washing with dichloromethane and drying at 50 °C. 6.0 g of HHTDD were obtained, which constitutes 50% of the theoretical yield. The product was purified by recrystallisation with water from acetone. The filtered product was dried for 35 h at 100 °C to remove residual solvent. Losses during purification were approx. 5%.

3.3. Product analysis

3.2.1. Analysis of the intermediate products

1,4-Diformyl-2,3,5,6-tetrahydropiperazine has been known since 1967 and has been extensively characterised [9]. In the synthesis of explosives, it is used as a direct substrate for the preparation of 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo-[5.5.0.0^{5,9}.0^{3,11}]-dodecane (TEX). To confirm that DFTHP was obtained as the product, differential scanning calorimetry (DSC) was performed. At 170 °C, the onset of the endothermic peak decomposition was observed, which reached a maximum at 200 °C. At approximately 220 °C a wide exothermic peak was observed, which can be attributed to the changes in the decomposition products. The course of the DSC curve and the characteristic temperatures are consistent with the reference data [9]. The resulting 2,6-dioxodecahydro-1*H*,5*H*-diimidazo[4,5,4',5']pyrazine hydrochloride was subjected to DSC testing. An endothermic peak starting at 180 °C, which can be attributed to the endothermic decomposition of the sample, was observed. The melting point of the compound reported by Vedachalam *et al.* [7] was 182 °C. The theoretical percentage composition of individual elements was calculated based on the structural formula of HTDD. The results of the experiments and the calculations are shown in Table 1.

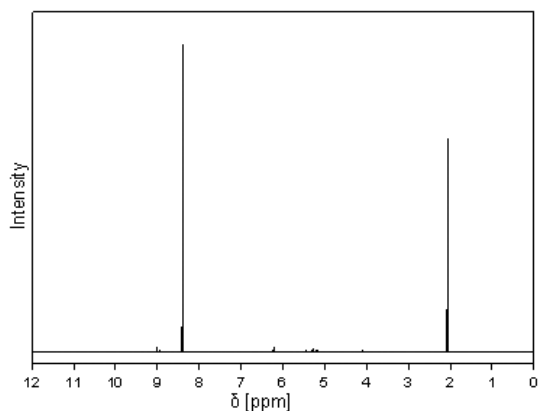
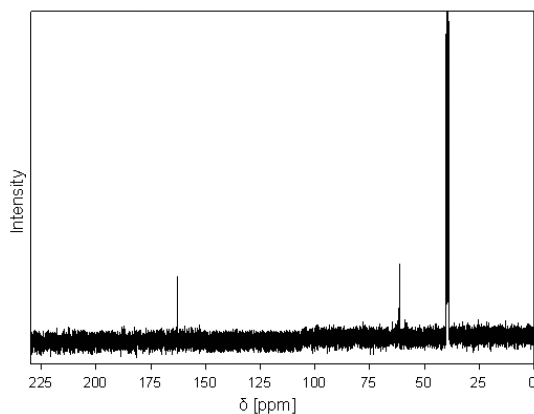
Table 1. Theoretical, experimental and reference composition of HTDD

Result	Mass content [%]		
	C	H	N
Theoretical:	30.71	4.73	35.82
- Study no. 1	30.63	4.75	35.78
- Study no. 2	30.70	4.71	35.80
- Average from tests 1 and 2	30.67	4.73	35.79
Reference [7]	30.54	4.81	35.80

Results of the elemental analysis confirm that the obtained compound has a quantitative and qualitative composition (within ± 0.2 error limits) identical to the composition of the HTDD molecule.

3.2.2. HHTDD analysis

To determine the structure of the HTDD nitration product, a ^1H and a ^{13}C NMR spectrum of the product purified by recrystallisation with water from acetone, was recorded. The obtained spectra are presented in Fig. 4 and 5.

**Figure 4.** ^1H NMR spectrum of the HHTDD sample**Figure 5.** ^{13}C NMR spectrum of the HHTDD sample

Fourier Transform Infrared (FTIR) spectroscopy was used for further analysis of HHTDD. The results are shown in Table 2.

Table 2. Results of the FTIR analysis of the crystallised HHTDD sample

Vibration wavenumber [cm ⁻¹]	Intensity	Signal Interpretation
3380	weak	ν_{stretch} C=O, overtone
3018	weak	ν_{stretch} III [≠] C-H
1804	high	ν_{stretch} C=O
1595	high	ν_{asym} N-O (NO ₂)
1411	weak	ν_{stretch} C-N (NO ₂)
1302	medium	ν_{sym} N-O (NO ₂)
1194	medium	ν_{stretch} C-NH ₂
1098	high	ν_{stretch} N-N
835	high	ν_{bending} C-H
708	high	ν_{bending} C-C

The heat of combustion of HHTDD, measured under an oxygen atmosphere, was determined as 4390 kJ·mol⁻¹. Assuming that this combustion occurs according to the Equation 1:



and that the enthalpies of carbon dioxide and water formation are equal to -393.51 and -285.83 kJ·mol⁻¹, respectively [10], the standard enthalpy of HHTDD formation was calculated as $\Delta_f H^0 = 1455$ kJ·mol⁻¹.

The sensitivity to mechanical stimuli was tested using the Julius Peters friction apparatus and the Kast fall hammer. The HHTDD sensitivity to friction is 120 N. In the impact sensitivity tests, the lower sensitivity limit (LSL) was determined, *i.e.* the greatest height of the hammer drop, below which the probability of initiating an explosive reaction is equal to zero. It was found that for the tested HHTDD sample this parameter is < 2.5 J. A phlegmatised material with 5% of Viton A was used for testing the detonation velocity. Eight charges with a diameter of 16.1 mm and 1 charge of phlegmatised hexogen with a hole for the igniter were made. In the process of pressing the charges (following removal from the matrix), localised darkening of the material was observed. During preparation of the velocity measurement system, the number and the total area of points with the changed colour, increased. This may indicate HHTDD decomposition. The average density of loads was 1.75 g·cm⁻³. Two measuring bases 35.05 and 34.94 mm were utilised. No results were obtained due to the interruption of the explosion process after the first short-circuit sensor. No further trials were conducted.

4. Discussion of results and conclusions

Hexanitrohexaazaisowurtzitane may be obtained by a one-step nitration of hydrochloride 2,6-dioxodecahydro-1*H*,5*H*-diimidazo[4,5,4',5']pyrazine using a solution of P₂O₅ in 100% HNO₃. The direct precursor of the nitronium cation in this system is dinitrogen pentoxide produced as a result of nitric acid dehydration. HHTDD was obtained with a yield of 50%, while Vedachalam *et al.* [7] reports a yield of 74%. However, Vedachalam *et al.* [7] described only on the yield of the crude product without including any information on the purification losses. Utilisation of the original purification method consisting of precipitation of HHTDD from a solution in acetone, allowed for a high purity product to be obtained, with minor losses and reduced use of reagents.

The product structure was verified by nuclear magnetic resonance (NMR). As expected, 1 signal with a chemical shift of 8.4 ppm, which corresponds to the protons bonded to carbon atoms in the piperazine ring, was observed in the proton spectrum. In the carbon NMR spectrum, 2 resonance signals with shifts at 63 and 141 ppm were observed, which can be attributed to the four piperazine ring carbon atoms and two carbonyl carbons, respectively.

The recorded FTIR spectrum confirmed the presence of all functional groups attributed to the HHTDD molecule. The high value of the heat of combustion and the enthalpy of formation places HHTDD among powerful explosives such as HNIW and HMX.

During the pressing of HHTDD, local darkening of the resulting pellet was observed, which may indicate a limited stability of the compound. HHTDD contains a nitrourea group in the molecule which is prone to hydrolysis. The most well known example of hydrolytic susceptibility of the aforementioned group is tetranitroglycoluril, where this property absolutely prevents the use of this compound.

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