

Synthesis and Energetic Properties of 1,3,7,9-Tetranitrobenzo[c]Cinnoline-5-Oxide (TNBCO)

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Abstract: New and efficient method for synthesis of 1,3,7,9-tetranitrobenzo[c]cinnoline-5-oxide (TNBCO) via direct nitration of benzo[c]cinnoline-5-oxide was described. TNBCO and precursor were fully characterized by using spectroscopic (IR, NMR) and thermal analysis methods (DTA/TG). Activation energy of decomposition process was calculated

by using Kissinger's equation. Standard enthalpy of formation was calculated by using experimentally determined heat of combustion. Detonation parameters were calculated with CHEETAH code and are comparable or higher than those known for E-2,2',4,4',6,6'-hexanitrostilbene (HNS) and 2,4,6-trinitrotoluene (TNT).

Keywords: low sensitivity explosive • detonation parameters • synthesis • NMR spectroscopy • nitration

1 Introduction

The designing of new thermally stable energetic materials is usually carried out by selecting thermally and chemically stable core followed by direct or indirect introduction of explosives into it. The commonly known examples are: N, N'-diphenylpyridine-2,6-diamine, dibenzo-1,3a,4,6a-tetraazapentalene, and 2,2'-bibenzimidazole for synthesis of PYX [1], TATB [2] TACOT [3] and TNBBI [4] respectively. The interesting molecule which joins stability of biphenyl and azoxybenzene is benzo[c]cinnoline N-oxide (BCO) with melting point of 142 °C [5].

Benzo[c]cinnoline N-oxide was first synthesized by Ernst Täuber in 1891 [5] but first mononitroderivatives of BCO were described after 1945 [6–9]. Dinitrobenzo[c]cinnoline was firstly synthesized in 1954 [10] but in 1966 it was noticed that polynitro benzo[c]cinnolines can exhibit energetic properties [11]. Detailed research on nitration of BCO was carried out by Bell and Read; they synthesized two tri- and one tetranitro- BCO derivatives [12]. The authors determined the melting and decomposition temperatures for the mentioned compounds by using a DSC method (but have not published DSC curves) and sensitivity to impact with Rotter Impact test. On the basis of high thermal stability (decomp. 367 °C) the authors stated that 1,3,7,9-tetranitro-BCO (TNBCO) derivative is very promising energetic compound. Unfortunately, the experimental or calculated detonation parameters for TNBCO have not been published to this date.

In this work we present the results of systematic studies of BCO nitration, full spectroscopic characterization of selected prospective compounds, results of sensitivity tests and thermochemical calculation of detonation parameters for TNBCO.

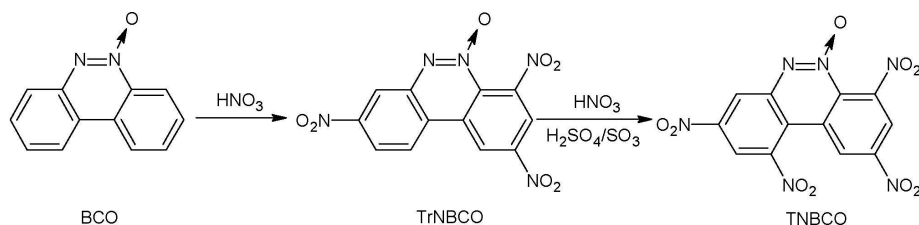
2 Experimental Section

Caution! Nitro derivatives of BCO have low sensitivity for mechanical stimuli but the materials are formally explosive. Laboratories and personnel should be properly grounded, and safety equipment such as heavy Kevlar/steel gloves, reinforced Kevlar coats, ballistic face shields, ear plugs, and blast screens are necessary.

All chemicals were analytical grade and obtained from commercial sources (Avantor, Sigma-Aldrich). NMR experiments were conducted in a Bruker Avance III HD 500 MHz spectrometer (field 11.7 T). ¹H and ¹³C spectra were referenced to tetramethylsilane (TMS) protons and carbons respectively. ¹⁵N NMR spectrum was referenced to liquid ammonia. The spectra of all pure samples were measured at room temperature, with sweeps 15 ppm (¹H), 300 ppm (¹³C), number of scans depends on tested nuclei (32–4096). Spectra were acquired and processed using standard Bruker software (TopSpin 3.1.). The Fourier transform infrared spectroscopy (FTIR) analysis was carried out using Thermo Scientific NICOLET 6700 spectrometer. DTA measurements were made to determine the decomposition temperatures of products in open Al₂O₃ crucibles (50 µL in volume) in a argon flow atmosphere (50 mL/min) at a constant heating rate (10 K/min) between 25 and 500 °C for a sample mass

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Scheme 1. Reaction route for synthesis of 1,3,7,9-tetranitrobenzo[c]cinnoline-5-oxide (TNBCO).

ca. 10 mg. Analyses were carried out with a LabSYS apparatus (Setaram).

2.1 Synthesis

The reaction route for synthesis of TrNBCO and TNBCO is shown on Scheme 1. In first step benzo[c]cinnoline-5-oxide was synthesized via reductive coupling of 2,2'-dinitrobiphenyl [6]. Next BCO was nitrated with fuming nitric acid in original one step procedure to 2,4,8-trinitrobenzo[c]cinnoline-6-oxide (TrNBCO). The crude TrNBCO was purified by crystallization and after that nitrated with HNO_3 /oleum system to 1,3,7,9-tetranitrobenzo[c]cinnoline-5-oxide (TNBCO). Many attempts to synthesize TNBCO in one step failed because TNBCO was formed with very small yield (ca. 1 %) and had to be isolated only by using column chromatography. Details of the syntheses are described below.

2.1.1 Synthesis of Benzo[c]cinnoline-5-Oxide (BCO)

3.0 g of 2,2'-dinitrobiphenyl was dissolved in 55 cm³ of anhydrous ethanol and heated up to 70 °C. Then mixture of 6.0 g of sodium sulphite nonahydrate and 1.5 g of NaOH in 10 cm³ of water was slowly added by addition funnel at 70 °C. After four hours of heating, ethanol was distilled and 100 cm³ of water was added. Dark brown precipitate was filtered under reduced pressure, dried and crystallized from aqueous ethanol. 1.7 g of benzo[c]cinnoline-5-oxide was obtained. Yield 71 %. mp. 139.8 °C [6]. Crude product is suitable for further experiments, nevertheless for nitration BCO crystallized from ethanol was used.

2.1.2 Synthesis of 2,4,8-Trinitrobenzo[c]cinnoline-6-Oxide (TrNBCO)

1.0 g of BCO was dissolved in 10 ml of fuming nitric acid ($d = 1.52 \text{ g/cm}^3$) and heated up to 70–75 °C and maintained for 2 h at this temperature. Next, mixture was poured into 150 g of crushed ice. Yellow precipitate was filtered under reduced pressure, crystallized from acetone and dried. 0.6 g of TrNBCO was obtained. Yield 36 % (calculated on BCO). Mp. 257.9 °C. IR (cm⁻¹): 3149 ($\text{C}_{\text{Ar}}\text{--H}$), 2942 (N–H), 3074 ($\text{C}_{\text{Ar}}\text{--H}$), 1603 ($\text{C}_{\text{Ar}}=\text{C}_{\text{Ar}}$), 1539 (N=O (–NO₂)), 1440 (C–N), 1358 (N=O (–NO₂)), 1144 (N–H), 1050 ($\text{C}_{\text{Ar}}\text{--H}$), 864 ($\text{C}_{\text{Ar}}\text{--NO}_2$), 3169 (N–H), 1505 (N=O), 854 (m) ($\text{C}_{\text{Ar}}\text{--NO}_2$); 730 (s) ($\text{C}_{\text{Ar}}\text{--H}$). Elemental anal-

ysis calcd (%) for $\text{C}_{12}\text{H}_5\text{N}_5\text{O}_7$: C43.52; H1.22; N21.14; found: C43.50; H1.20; N21.15.

2.1.3 Synthesis of 1,3,7,9-Tetranitrobenzo[c]cinnoline-5-Oxide (TNBCO)

1.0 g of 2,4,8-trinitrobenzo[c]cinnoline-6-oxide was suspended in 8 cm³ of 15 % oleum. Next mixture containing 2 cm³ of fuming nitric acid and 2 cm³ of 15 % oleum was added dropwise at ambient temperature. Then mixture was heated up to 125 °C and maintained for 2 h at this temperature and poured into 200 g crushed ice. Yellow precipitate was filtered under reduced pressure and crystallized from acetone. 0.5 g of crude 2,4,8-tetranitrobenzo[c]cinnoline-6-oxide was obtained. Filtrate, after crystallization from acetone, was evaporated to dryness, dissolved in boiling ethyl acetate and crash precipitated by addition hexane (1:1 by volume). 0.4 g of TNBCO was obtained, yield 35 %. mp. 266.4 °C. IR (cm⁻¹): 3149 ($\text{C}_{\text{Ar}}\text{--H}$), 2942 (N–H), 3074 ($\text{C}_{\text{Ar}}\text{--H}$), 1603 ($\text{C}_{\text{Ar}}=\text{C}_{\text{Ar}}$), 1539 (N=O (–NO₂)), 1440 (C–N), 1358 (N=O (–NO₂)), 1144 (N–H), 1050 ($\text{C}_{\text{Ar}}\text{--H}$), 864 ($\text{C}_{\text{Ar}}\text{--NO}_2$), 3169 (N–H), 1505 (N=O). Elemental analysis calcd (%) for $\text{C}_{12}\text{H}_4\text{N}_6\text{O}_9$: C38.31; H1.07; N22.34, found: C38.29; H1.05; N22.31

2.2 NMR Spectroscopy

NMR spectroscopy (¹H; ¹³C; ¹⁵N) was applied to confirm the structure of the main product. A ¹H NMR spectrum of TNBCO (Figure 1) shows four sharp doublets with chemical shifts of 8.82; 9.43; 9.45 and 9.63 ppm respectively. The first signals represent protons in positions 2; 4; 8 and 10 of TNBCO system. ⁴J_{HH} coupling constant for signals in positions 2; 4 and 8; 10 is equal 2.1 and 2.4 Hz respectively. The values and ranges of chemical shifts and coupling constants are typical for C–H protons in nitro-substituted aromatic rings. Due to the unsymmetrical character of TNBCO molecule the ¹³C NMR spectrum (Figure 2) shows 12 separate signals with chemical shifts (carbons N° in brackets): 114.85 (5); 120.90 (4); 121.86 (2); 122.00 (10); 123.90 (6); 124.26 (8); 138.44 (11); 139.95 (12); 144.90 (7); 145.97 (9); 147.02 (3) and 148.55 (1) ppm. Nitrogen spectrum (¹⁵N{¹H}) (Figure 3) shows six signals with chemical shifts 317.42 (N=); 322.01 (=N–O); 361.40 (C9–NO₂); 362.85 (C3–NO₂); 365.08 (C1–NO₂) and 369.42 (C7–NO₂) ppm.

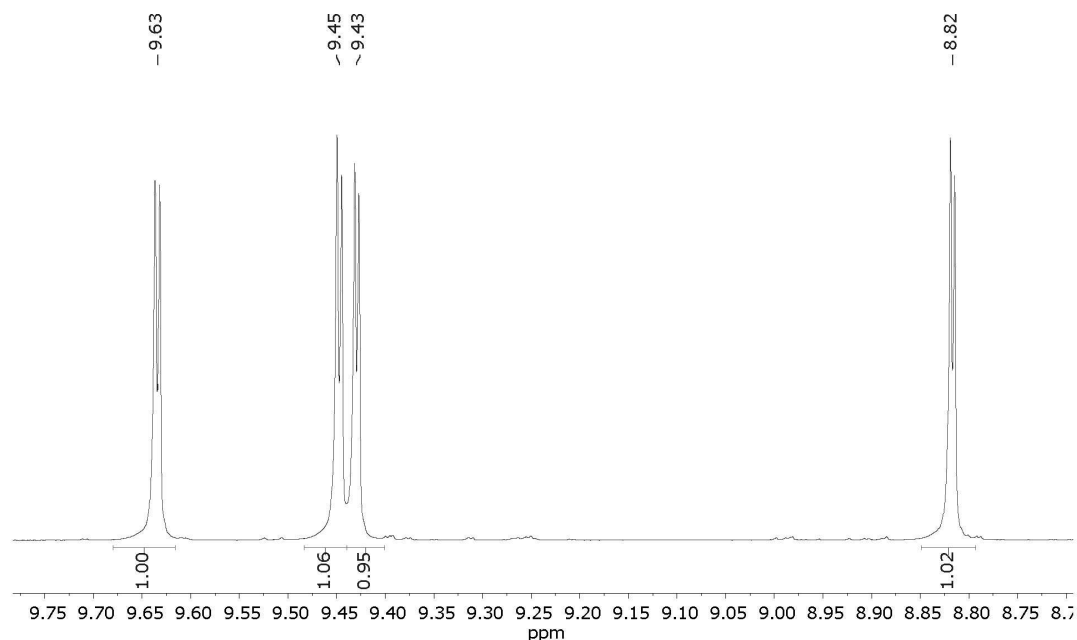


Figure 1. ^1H -NMR spectrum of 1,3,7,9-tetranitrobenzo[c]cinnoline-5-oxide.

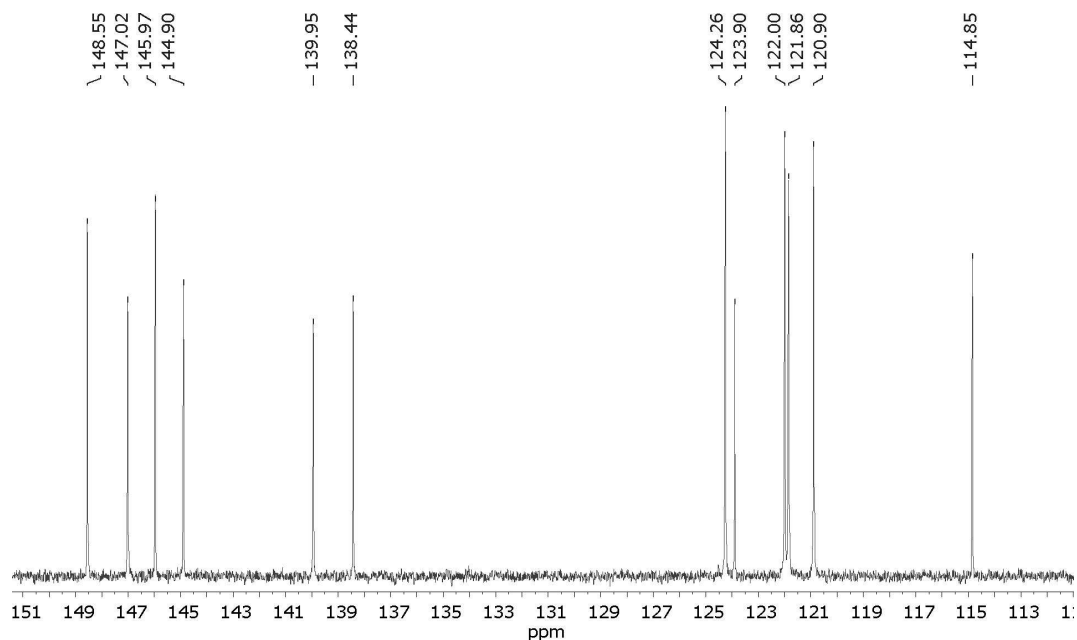


Figure 2. ^{13}C -NMR spectrum of 1,3,7,9-tetranitrobenzo[c]cinnoline-5-oxide.

2.3 Thermal Analysis

Differential thermal analysis examination results (Figure 4) of TNBCO exhibit two peaks (first endothermic at 266.4 °C, second exothermic 347.3 °C). Endothermic peak can be assigned to melting of TNBCO, because no weight loss was observed on TG curve. The decomposition peak shape is typical for secondary explosives but full-width at half-max-

imum (FWHM) is relatively high and looks like this known for RDX. The overall mass loss during DTA-TG test is 61%. Thermal stability of 1,3,7,9-tetranitrobenzo[c]cinnoline-5-oxide is lower than commonly accepted reference compounds for heat resistant explosives like TATB (350 °C). The usage of TNBCO is limited by its melting point and for tested compound is 266 °C and is similar to 3-nitro-1,2,4-triazol-5-one (NTO, 270 °C [13]).

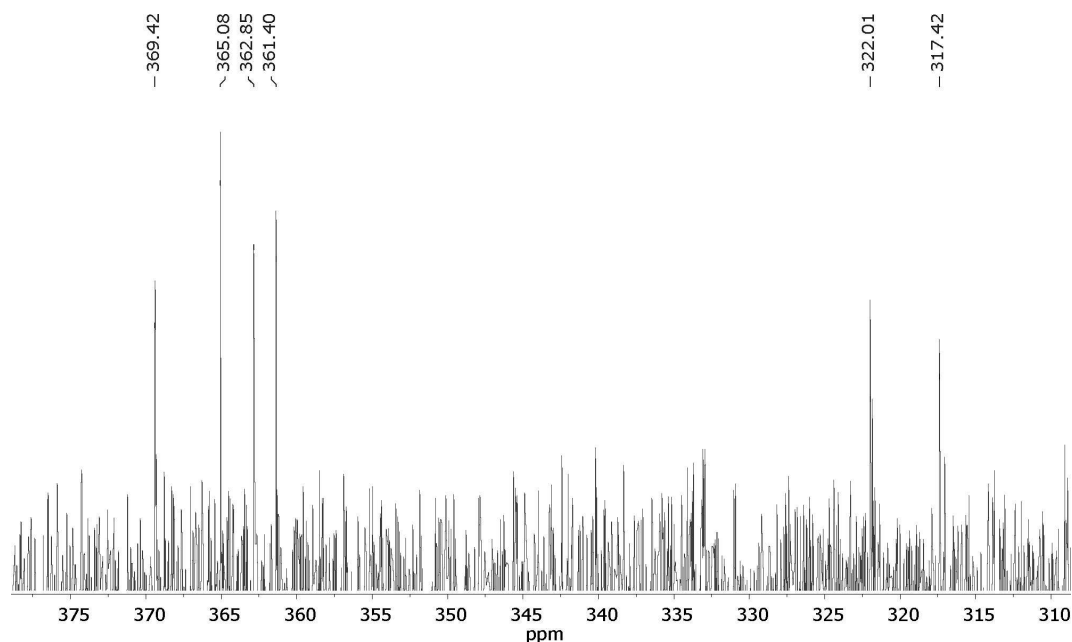


Figure 3. ^{15}N -NMR spectrum of 1,3,7,9-tetranitrobenzo[c]cinnoline-5-oxide.

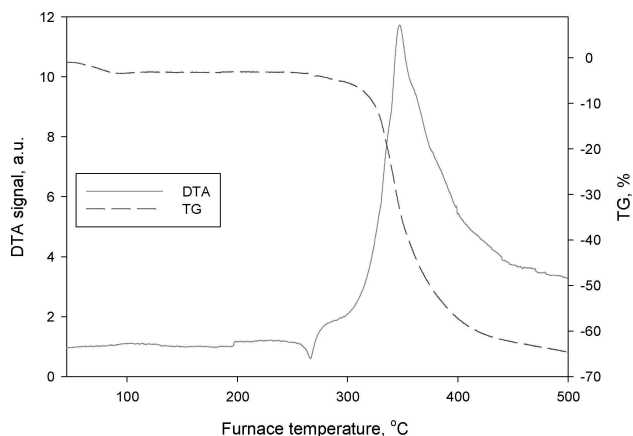


Figure 4. DTA-TG curves for TNBCO (Ar, 10 K/min).

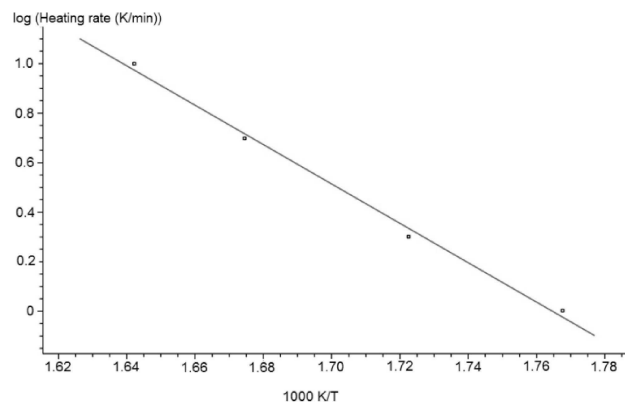


Figure 5. Kissinger's plot used for calculation of apparent activation energy for TNBCO.

Kissinger's method was applied for determination of apparent activation energy for decomposition of TNBCO. Four DTA curves were registered for heating rates 1; 2; 5 and 10 K/min. Kissinger's plot for obtained results is shown in Figure 5. Using the main exothermic peak temperatures, the apparent activation energy E_a and pre-exponential factor A were estimated to be $142 \pm 7 \text{ kJ/mol}$ and $6.2 \cdot 10^9 \text{ s}^{-1}$ respectively, with correlation coefficient $r^2 = 0.99$ [14]. Calculated activation energy for TNBCO is smaller than typical energetic materials e.g. HNIW 183 kJ/mol [15], TATB 200 kJ/mol, RDX 212 kJ/mol [16] PYX 261 kJ/mol [17]. This observation can be used for explanation of relatively high FWHM of decomposition peak observed on DTA curve. The activation energy of a reaction determines the rate at which

it will proceed. The higher the activation energy, the slower the decomposition of energetic material will be; for TNBCO we observed a relatively broad peak of exothermic decomposition. A similar phenomenon is observed for RDX decomposition during DTA or DSC examination.

2.4 Sensitivity to Mechanical Stimuli

The impact and friction sensitivity were examined by Kast Hammer Fall apparatus and Julius Peters apparatus. For each impact energy and friction force six trials were done. The impact energy for mechanical stimuli is 8 J. TNBCO is insensitive to friction ($> 360 \text{ N}$) and no positive reactions were observed. The sensitivity of TNBCO to classical me-

Table 1. Comparison of combustion and detonation characteristics of TNBCO and other explosives.

Properties	TNBCO	HNS	TNC	TNT
Density [g·cm ⁻³]	1.75	1.74[20]	1.74[21]	1.60[20]
Melting/decomposition temp. [°C]	264/347	318 dec.	285/310	81/260
Impact sensitivity [J]	8	5	6	15
Friction sensitivity [N]	> 360	240	> 360	> 360
Heat of combustion [kJ mol ⁻¹]	5570	6449	5459	3402
Enthalpy of formation [kJ mol ⁻¹]	276.2	78.2[22]	18.9[21]	-74.5
Detonation pressure [GPa]	23.4	23.2	19.6	17.9
Detonation velocity [km s ⁻¹]	7223	7227	6778	6710
Detonation temperature [K]	4071	4048	3526	3686
Detonation energy [J g ⁻¹]	4779	4804	4228	4519

chanical stimuli is comparable to other explosives containing azoxy group (diaminoazoxyfurazan (DAAF)) 7 J). Sensitivity to mechanical stimuli is enough to handle and press TNBCO without phlegmatization.

2.5 Bomb Calorimetry and Thermochemical Calculations

The heat of combustion of TNBCO was determined experimentally by using a standard water calorimeter (Precyzja bit., Bydgoszcz, Poland) equipped with a standard stainless calorimetric bomb. Weighted and pressed samples of TNBCO were placed in a quartz crucible and insert into the calorimetric bomb, which was then filled with pure oxygen at an initial pressure of 2.5 MPa. Three tests were performed. The average heat of combustion was 5570 kJ/mol with a maximum deviation of less than 30 kJ/mol. The standard enthalpy of formation of TNBCO was calculated using Hess's law for combustion products CO₂, H₂O and N₂. The value +276.2 kJ/mol was determined. The density of TNBCO in a form of pressed cylindrical charges (mass 0.8 g, mold diameter 10.0 mm) was 1.75 g/cm³. The detonation parameters were calculated by thermochemical code CHEETAH [18] using the BKWC set of parameters for the BKW EOS [19]. Combustion and detonation characteristics of TNBCO are listed in Table 1 and compared with those of other explosives with similar structure, i.e., 2,2',4,4',6,6'-hexanitrostilbene (HNC) and 1,3,6,8-tetranitrocarbazole (TNC). The detonation parameters calculated for TNT are also added in Table 1.

The detonation parameters (velocity, pressure, temperature and energy) calculated for TNBCO are close to those calculated for HNS but they are higher than TNC or TNT parameters. The theoretical detonation characteristics of TNBCO require experimental confirmation.

3 Conclusion

1,3,7,9-tetranitrobenzo[c]cinnoline-5-oxide is a new high-energetic material with detonation parameters similar to HNS but with higher decomposition temperature. The ele-

mental composition of TNBCO is very close to tetranitrocarbazole but detonation parameters are significantly higher due to the higher density and much higher positive standard enthalpy of formation. The sensitivity of TNBCO to classical mechanical stimuli is smaller than for TNC and HNS. High heat of combustion of 1,3,7,9-tetranitrobenzo[c]cinnoline-5-oxide makes it a promising candidate as new ingredient of propellants with low vulnerability. Calculated activation energy for TNBCO is relatively small and indicate that kinetic of exothermic decomposition is relatively low. The observations are in good agreement with DTA and mechanical stimuli tests results.

Acknowledgements

This work was supported by the Ministry of Science and High Education through the Institute of Chemistry, Military University of Technology under Grant GB MON 13-994. The authors would like to thank prof. Stanisław Cudziło for financial support and inspiring discussions, and Dr. J. Szulc for proofreading.

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Manuscript received: June 5, 2019

Revised manuscript received: July 12, 2019

Version of record online: August 14, 2019