

Some characteristics of 3,7-dinitro-, 3,7-dinitroso- and dinitrate compounds derived from 1,3,5,7-tetraazabicyclo[3.3.1]nonane

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Abstract

The paper presents a set of some literature data and the authors' own experimental results of stability, sensitivity and explosion parameters of energetic Mannich *N*-bases, 3,7-dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane (DPT), 3,7-dinitroso-1,3,5,7-tetraazabicyclo[3.3.1]nonane (DNPT) and hexamethylenetetramine dinitrate (HEXADI). Both their chemical and thermal reactivities are discussed. The results of small-scale cook-off test, determination of initiation ability, detonation velocity, impact sensitivity and performance show that the lowest process safety risks are connected with HEXADI.

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Keywords: 3,7-Dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane; 3,7-Dinitroso-1,3,5,7-tetraazabicyclo[3.3.1]nonane; Hexamethylenetetramine dinitrate; Detonation; Impact sensitivity; Kinetics; Performance; Reactivity; Stability

1. Introduction

The research, development and production of energetic materials have revealed a number of compounds with non-negligible energy potential, which are sometimes referred to as tertiary explosives (about the explosives, see Ref. [1]). These compounds are prepared or manufactured in relatively large volumes, most often as various intermediates. Their properties and parameters are interesting and important from the standpoint of technology and/or safety; however, they have not been sufficiently presented in currently accessible information sources so far.

These compounds include 3,7-dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane (DPT), its dinitroso analogue, i.e. 3,7-dinitroso-1,3,5,7-tetraazabicyclo[3.3.1]nonane (DNPT), and also hexamethylenetetramine dinitrate (HEXADI). All these compounds are Mannich *N*-bases, and as such they are reactive. This reactivity makes them technologically attractive, but also risky during their production, isolation, handling and further treatment.

DPT can be used for efficient synthesis of octogen (HMX). Its goal-directed isolation is carried out rather exceptionally [2], but it is synthesised in significant quantities “in vitro” during all existing processes of production of HMX in media of lower acidity [2,3].

DNPT has been produced and applied predominantly as the active component of blowing agents in rubber industry [4,5] (blowing agents Chempor manufactured by Chemko Co., Vulcacer BN 94 manufactured by Vulnax Int., Cellular D produced by Eiwa Kasey Kogyo, DNPT 100 produced by A&C Co., New Jersey, etc.). The mass scale of this production has also been recently reflected in relatively good documentation of process safety characteristics, which mostly have not yet been accessible to public though. It must be stated that this mass-production belongs already to history due to toxicological problems connecting with DNPT application.

HEXADI is an interesting raw material in production of DPT, hexogen (RDX) and HMX as a source of the methylene base and the simultaneously bound “anhydrous” nitric acid in an advantageous crystalline and relatively stable form [3]. HEXADI also belongs among compounds that have been little documented.

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Therefore, the present paper is particularly focused on the basic stability characteristics of the compounds studied (i.e. on their resistance to water, thermal reactivity and explosive decomposition) and it does not ignore some of the other physicochemical data of the compounds studied.

2. Experimental

2.1. Substances and data

For the investigation of basic physicochemical, sensitivity, and stability parameters, the samples of DPT and HEXADI were prepared in the quality grade “pure” (DPT was persistently recrystallised from dimethyl sulphoxide, and HEXADI from ethanol, to the maximal thermal stability was attained) in connection with Thesis [6]. In cooperation with Slovak Comp. Chemza Ltd., Strážske, we also prepared at pilot-plant conditions a sufficient amount of the material for investigation of basic detonation characteristics—initiation ability and detonation velocity in paper casing. The preparation of technical DPT at the conditions mentioned used the modified Haley way of synthesis [2,16], i.e. neutralisation of all reaction mixture after nitrolysis of hexamethylenetetramine with aqueous ammonia. DNPT was prepared by nitrosoly-

sis of hexamethylenetetramine in acetic acid medium [29] with subsequent stabilisation by washing with 2% ammonia solution; this product was of relatively high quality (see Fig. 3), and in its stability it did not differ from the sample recrystallised from dimethyl sulphoxide (the sample was a chromatographic individuum—specification of its purity, see Ref. [20]). Many of the physicochemical and explosion data of the compounds studied were found in literature (see the references in Tables 1–3).

2.2. Non-isothermal differential thermal analysis

We used a DTA 550 Ex apparatus [7] specially developed in our department for thermal analysis of explosives (an ability to be resistant against sample explosion is an eligibility of the apparatus). The measurements were carried out at atmospheric pressure, the tested sample being in direct contact with the air atmosphere. The sample tested (0.05 g) was placed in a test tube made of Simax glass, 5 mm in diameter and 50 mm in length. The reference standard was 0.05 g aluminium oxide. We used linear rates of temperature increase 5 K min^{-1} . The results of these measurements were treated by means of the software delivered with the DTA apparatus [7]. Examples of the corresponding DTA records are presented in Figs. 1–4.

Table 1

A survey of the data of DPT

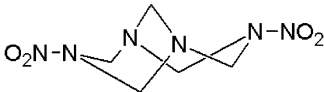
Chemical name	3,7-Dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane (IUPAC); 1,5-endomethylene-3,7-dinitro-1,3,5,7-tetraazacyclooctane; dinitropentamethylenetetramine; code designation DPT
Structural formula	
Appearance and form	White rhombic crystalline substance (crystallised from acetone) [13] two polymorph modifications [14]: (1) mp 222–223 °C; (2) mp 204–205 °C; “chair–chair” conformation in preference [15]
Theoretical maximal density (TMD, ρ_{TMD})	1680 kg m^{-3} [15]
Melting point	203–206 °C [16]; 204–205 °C [14]; 213–216 °C [17]
Heat of formation, ΔH_f	–18.14 kcal mol^{-1} [13] (i.e. –75.9 kJ mol^{-1})
Heat of combustion, ΔH_c	3793 kcal kg^{-1} [13] (i.e. 15869.9 kJ kg^{-1})
Heat of decomposition	146.50 \pm 25.10 kJ mol^{-1} [19] (i.e. 671.5 kJ kg^{-1}); 117.20 \pm 15.50 kJ mol^{-1} [20] (i.e. 537.2 kJ kg^{-1})
Onset of thermal decomposition by DTA	120–199 °C (393–472 K) [5]
Vacuum stability test (STABIL, in $\text{cm}^3 \text{ g}^{-1}$ for 20 h ^{–1})	0.00389 at 40 °C and 0.05477 at 70 °C for pure DPT; 0.11687 at 40 °C and 2.9668 at 70 °C for semi-plant DPT
Kinetic parameters of thermal decomposition	$E_a = 192.3 \text{ kJ mol}^{-1}$ and $\log A = 16.6 \text{ s}^{-1}$ in the solid state (extrapolated) [28]
Solubility	Good soluble: in low concentrated mineral acids (precipitation at pH 3.4) [16]; slightly soluble: in organic solvents (on example in acetone) [16]; practically insoluble: in cool water, in hot water decomposed
Oxygen balance	–80.67%
Impact sensitivity	50.0 J (detection by noise) [5]; DNPT is less sensitive than TNT [37] 10.2 J (as “the first reaction”) [31]
Performance (in Pb block, Trauzl test)	(10 g DPT + detonator No. 8): 245 cm^3 (for RDX it is 480 cm^3) [13]
Characteristics of detonation	D -value calculated: 7164 m s^{-1} for TMD; 5175 m s^{-1} for $\rho = 1000 \text{ kg m}^{-3}$; D -value experimental (this paper): 5033 m s^{-1} for $\rho = 869 \text{ kg m}^{-3}$; heat of explosion, Q_{max} : 4299 kJ kg^{-1} ; heat of explosion, Q_{real} : 3771 kJ kg^{-1} for TMD, 3151 kJ kg^{-1} for $\rho = 1000 \text{ kg m}^{-3}$; detonation pressure, P : 21.8 GPa for TMD, 7.7 GPa for $\rho = 1000 \text{ kg m}^{-3}$; volume of gaseous products of detonation: 771 $\text{dm}^3 \text{ kg}^{-1}$; Gurney energy (theor. calc. for TMD): 2412 m s^{-1}

Table 2
A survey of the data of DNPT

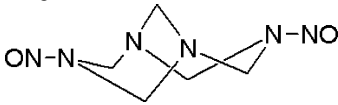
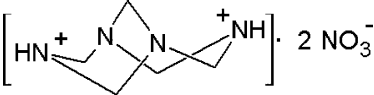
Chemical name	3,7-Dinitroso-1,3,5,7-tetraazabicyclo[3.3.1]nonane (IUPAC); 1,5-endomethylene-3,7-dinitroso-1,3,5,7-tetraazacyclooctane; dinitrosopentamethylenetetramine; code designation DNPT
Structural formula	
Appearance and form [21]	Lemon-yellowish monoclinic crystals (from ethanol) “chair–chair” conformation in preference with <i>trans</i> -orientation of nitroso groups
Theoretical maximal density (TMD, ρ_{TMD})	1522 kg m ⁻³ [32]
Melting point	207 °C, decomposition [21]
Heat of formation, ΔH_f	53.6 kcal mol ⁻¹ [18] (i.e. 224.3 kJ mol ⁻¹); 57.7 kcal mol ⁻¹ [32] (i.e. 241.4 kJ mol ⁻¹)
Heat of combustion, ΔH_c	4663.7 kcal kg ⁻¹ [32] (i.e. 19512.9 kJ kg ⁻¹)
Heat of decomposition	Minimum 491.05 kJ mol ⁻¹ , i.e. maximum 2637 kJ kg ⁻¹ [20]; 537.50 kJ mol ⁻¹ , i.e. 2887 kJ kg ⁻¹ [22]; 610.30 kJ mol ⁻¹ , i.e. 3278 kJ kg ⁻¹ [23]
Onset of thermal decomposition by DTA	116–152 °C (389–425 K) [29]
Vacuum stability test (STABIL, in cm ³ g ⁻¹ 1 h ⁻¹)	0.060–0.105 at 125 °C for technical DNPT [36]
Kinetic parameters of thermal decomposition (by DSC)	$E_a = 144.2$ kJ mol ⁻¹ and $\log A = 13.9$ s ⁻¹ for temperature range 470–485 K [30]
Solubility in 100 g of:	Methyl alcohol: 1.70 g at 15 °C [25]; acetone: 0.30 g at 15 °C [25]; water: 0.15 g at 15 °C and 0.83 g at 45 °C [24] (DNPT could have a slight odor of formaldehyde under its longer contact with an aerial humidity); mineral acids: DNPT decomposes explosively under contact with them
Oxygen balance	
Impact sensitivity (5 kg hammer, detection by noise) [27]	14.6 J ($h_{50} = 29.6$ cm) for sample containing of 2.7 wt.% TMTA and 0.3 wt.% water (for 1,3-dinitrobenzene it is 17.7 J); 30.4 J ($h_{50} = 61.6$ cm) for sample containing of 2.2 wt.% TMTA and 6.5 wt.% water
Performance (in Pb block, Trauzl test)	10 g DNPT + detonator No. 8: 185 cm ³ [26]
Characteristics of detonation	D -value calculated: 6531 m s ⁻¹ for TMD; 5756 m s ⁻¹ for $\rho = 1260$ kg m ⁻³ ; D -value experimental [4]: 5553 m s ⁻¹ for $\rho = 1267$ kg m ⁻³ , 5573 m s ⁻¹ for $\rho = 1280$ kg m ⁻³ ; heat of explosion, Q_{max} : 4584 kJ kg ⁻¹ ; heat of explosion, Q_{real} : 3942 kJ kg ⁻¹ for TMD, 3686 kJ kg ⁻¹ for $\rho = 1260$ kg m ⁻³ ; detonation pressure, P : 17.0 GPa for TMD, 11.5 GPa for $\rho = 1260$ kg m ⁻³ ; volume of gaseous products of detonation: 783 dm ³ kg ⁻¹ ; Gurney energy (theor. calc. for TMD): 2193 m s ⁻¹

Table 3
A survey of the data of HEXADI

Chemical name	1,3,5,7-Tetraazabicyclo[3.3.1]nonane dinitrate (IUPAC); hexamethylenetetramine dinitrate; code designation HEXADI
Appearance and form	White crystals
Structural formula	
Theoretical maximal density (TMD, ρ_{TMD})	1570 kg m ⁻³ [33]
Melting point	160–165 °C [34]
Heat of formation, ΔH_f	-92.8 kcal mol ⁻¹ [18] (i.e. -388.3 kJ mol ⁻¹)
Heat of combustion, ΔH_c	3583 kcal kg ⁻¹ [18] (i.e. 14991.3 kJ kg ⁻¹)
Onset of thermal decomposition by DTA	160–173 °C (433–446 K) [5]
Vacuum stability test (STABIL, in cm ³ g ⁻¹ 20 h ⁻¹)	0.0024 at 40 °C and 0.0178 at 70 °C for pure HEXADI
Solubility [35] in 100 g of:	Water: 11.4 g at 0 °C, 17.5 g at 15 °C, 18.9 g at 20 °C (formaldehyde is liberated in the presence of moisture in HEXADI especially above 20 °C); 1.06 wt.% nitric acid: 8.2 g at 0 °C, 14.3 g at 15 °C, 15.5 at 20 °C; 10.4 wt.% nitric acid: 0.8 g at 0 °C, 3.8 g at 15 °C, 3.9 g at 20 °C; methyl alcohol: slightly soluble; diethylether or acetone: insoluble
Oxygen balance	-78.1%
Impact sensitivity	Slightly more sensitive than TNT [35] (ca. 1.07 times by means of Picatiny Arsenal Apparatus)
Performance (in Pb block, Trauzl test)	65% of TNT [34] (i.e. ca. 195 cm ³)
Characteristics of detonation	D -value calculated: 6895 m s ⁻¹ for TMD, 5214 m s ⁻¹ for $\rho = 1000$ kg m ⁻³ ; D -value experimental (this paper): maximum 3192 m s ⁻¹ for $\rho = 799$ kg m ⁻³ ; heat of explosion, Q_{max} : 4210 kJ kg ⁻¹ ; heat of explosion, Q_{real} : 3637 kJ kg ⁻¹ for TMD, 3150 kJ kg ⁻¹ for $\rho = 1000$ kg m ⁻³ ; detonation pressure, P : 19.3 GPa for TMD, 7.8 GPa for $\rho = 1000$ kg m ⁻³ ; volume of gaseous products of detonation: 800 dm ³ kg ⁻¹ ; Gurney energy (theor. calc. for TMD): 2321 m s ⁻¹

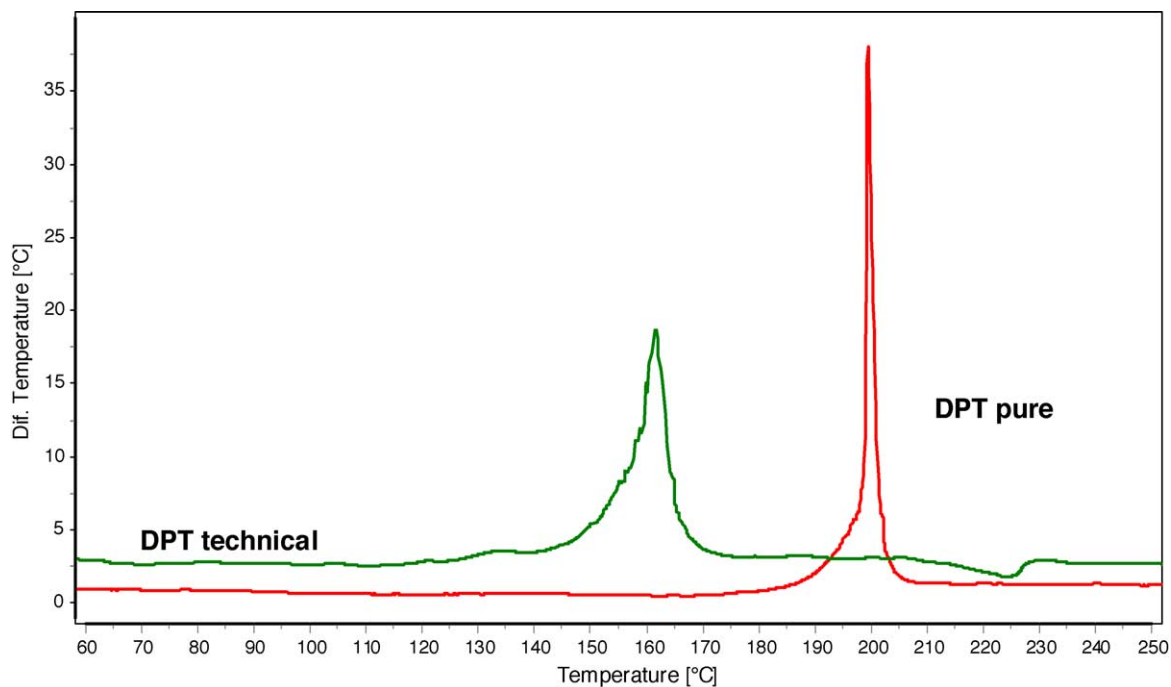


Fig. 1. A comparison of the DTA record of DPT prepared at the pilot-plant conditions (designated DPT technical) with those of the pure DPT.

2.3. Vacuum stability test

We used a modernized apparatus STABIL 16-Ex [7] (manufactured by OZM Research; the original apparatus is described in [8]). The amount of DPT or HEXADI was 2 g. Tests were performed for 24 h at temperatures of 40 and 70 °C. The

dried samples in evacuated glass test tubes were placed into the heating block and heated to the desired temperature. Pressure transducers continuously estimated the pressure increase in the glass tubes. The results were in the form of time dependence of the gas volume evolved from 1 g sample and corrected to standard conditions. The samples of the techni-

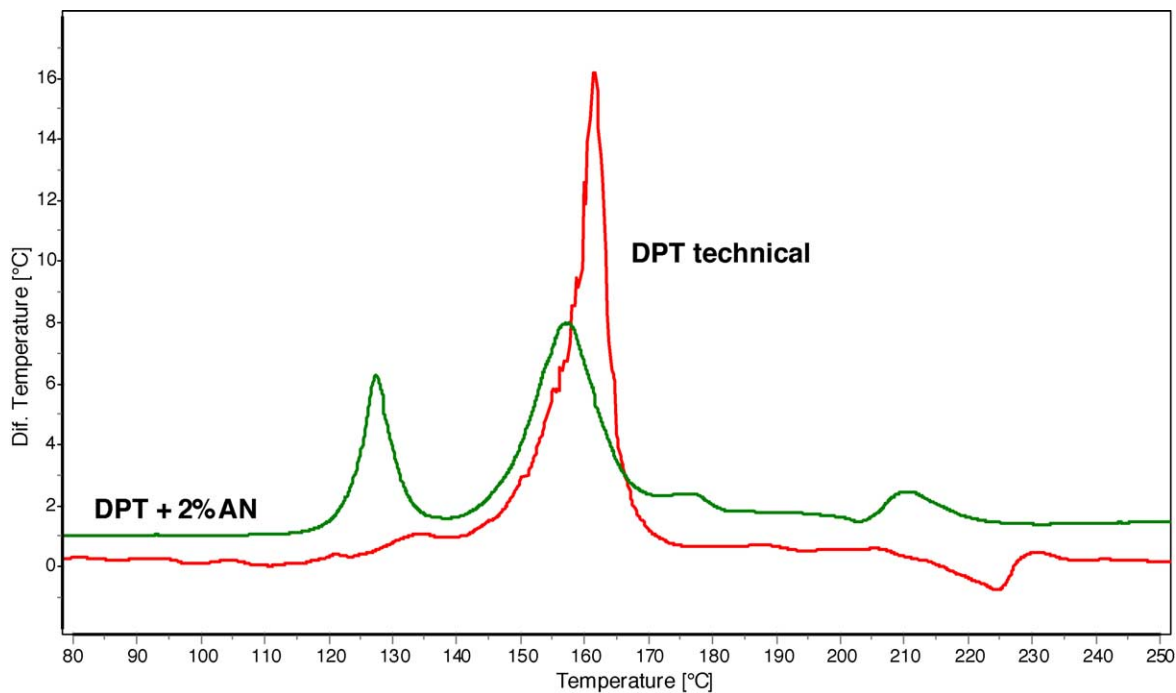


Fig. 2. A comparison of the DTA record of DPT prepared at the pilot-plant conditions (designated DPT technical) with those of the mixture of pure DPT with 2 wt.% of ammonium nitrate (AN).

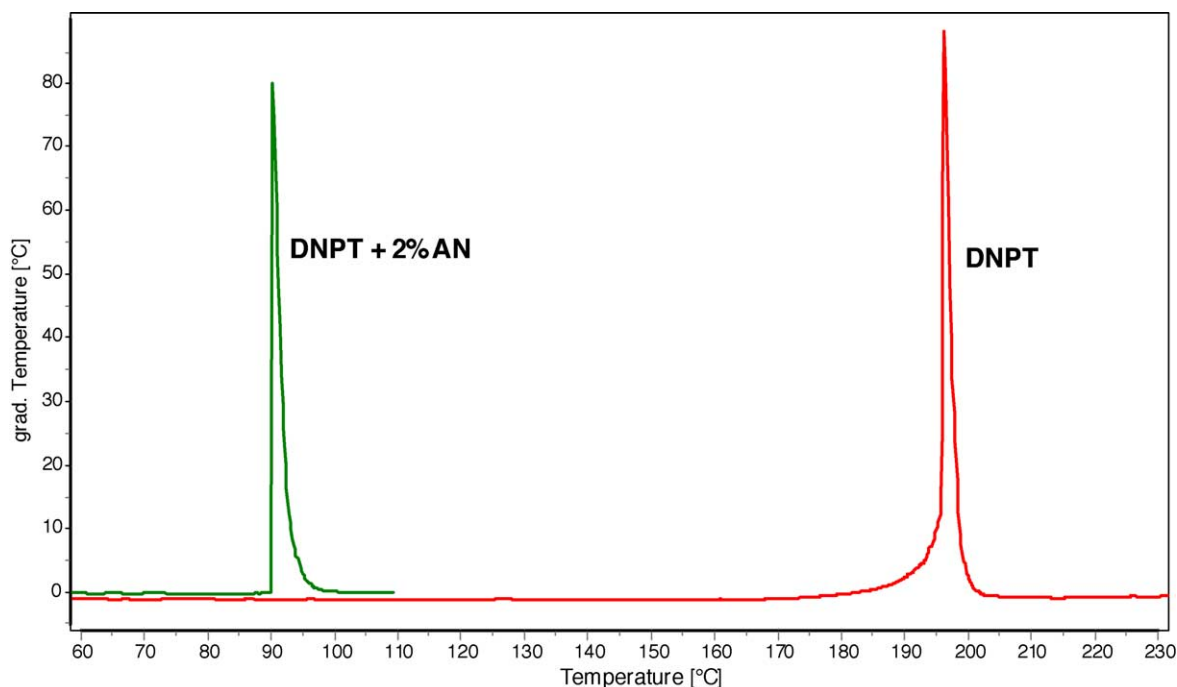


Fig. 3. A comparison of the DTA record of pure DNPT with those of the mixture of pure DNPT with 2 wt.% of ammonium nitrate (AN).

cal DNPT (i.e. products of the Chemko Co., Strážske) were measured earlier by means of the original STABIL apparatus [8]; the tests in this case were performed at 125 °C for 5 h. Results of all the tests are presented in Tables 1–3.

2.4. Thermal sensitivity

The procedure for determination of thermal sensitivity (small-scale cook-off test KTTV, see Ref. [45]) was devel-

oped in our department. The procedure can be carried out in miniaturized version as well as in accordance with standard STANAG 4491 or UN standards. The testing set-up consists of a steel pipe with 21 mm internal diameter, 90 mm length and 2.5 mm wall thickness (see Fig. 5). The pipe is closed at both sides by cap nuts with 20 mm long thread. The internal volume of closed pipe is approximately 32 cm³. The pipe is filled with 27–32 g powdered substance tested. A gas

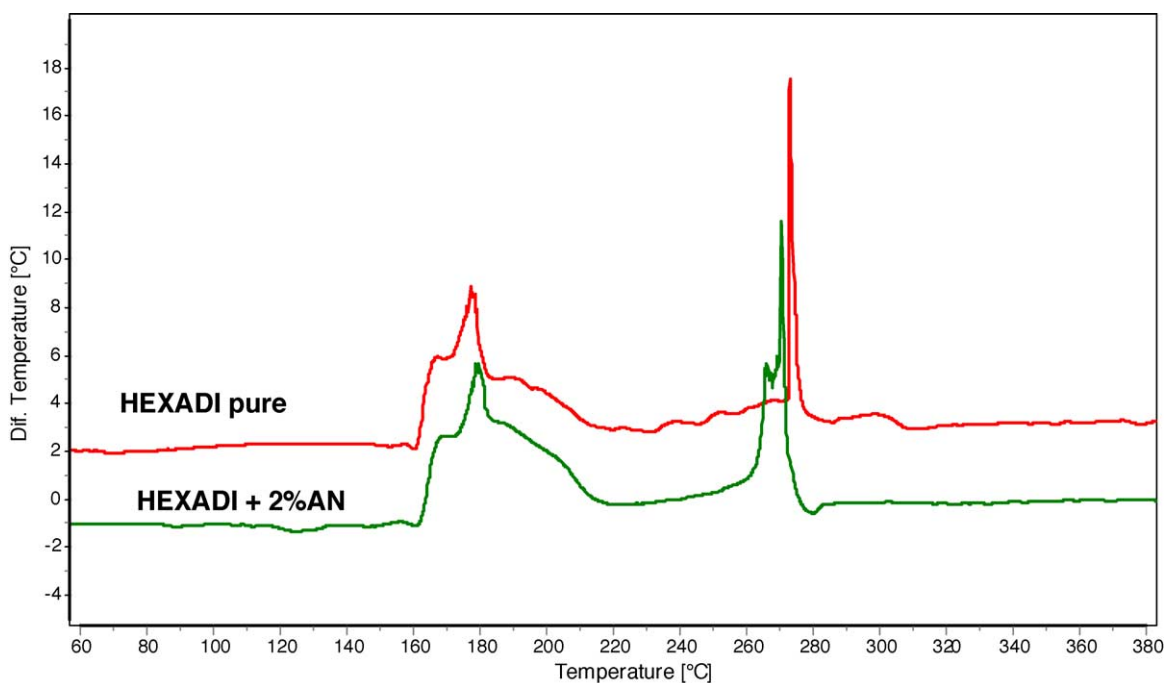


Fig. 4. A comparison of the DTA record of pure HEXADI with those of the mixture of pure HEXADI with 2 wt.% of ammonium nitrate (AN).

Table 4
A survey of the small scale cook-off test

Substance	Weight of sample (g)	Density of charge (kg m^{-3})	Weight of stainless pipe (g)	Number of pipe fragments	Fragments found (wt.%)	Time till explosion (s)	Figure number
DPT	29.1	851	289.6	3	94.0	24	6
	27.0	789	285.1	7	96.4	24	
DNPT	25.6	486	375.1	1	100	24	7
	25.9	491	382.6	1	100	24	
HEXADI	30.4	988	397.6	4	100	26	8
	30.6	933	414.1	3	100	28	

burner was used as a heat source for fast cook-off. A linear temperature increase of 3.3 K min^{-1} for slow cook-off was provided by an electric oven of 50 mm internal diameter and 200 mm length. In all the cases, the tests of the compounds studied were accompanied by explosion and complete reaction of the starting sample. The results are presented in Table 4 and Figs. 5–8.

2.5. Characteristics of detonation

The values of detonation velocity, D , the maximum explosion heat, Q_{max} , detonation pressure, P , and the Guernsey energy, G , of the substances studied were calculated using the known relationships of Kamlet and Jacobs [9] for the maximum theoretical densities, TMD, of crystals (ρ_{TMD} , i.e. for monocrystal) and for $\rho = 1000 \text{ kg m}^{-3}$. The Q_{max} values were recalculated to real heats of explosion, Q_{real} , for monocrystals by means of semi-empirical relationships devised by Pepekin et al. [10]. The experimental D -values for DNPT were taken from report [5] those for DPT and

HEXADI were determined by “HandiTrap” device [11] with the charges placed in PVC tubes of 37 mm inner diameter (wall thickness 1.5 mm). The performance data of the substances studied were taken from literature too. All the above-mentioned data are presented in Tables 1–3.

2.6. Initiation ability [12]

The sensitivity of an explosive to initiation by a shock wave is exactly specified by means of the so-called GAP tests [46]. In current practice it is of fundamental importance to know first of all the initiation sensitivity of the explosive to the standard initiation impulse generated by a detonator. In the case of energetic materials that are less sensitive to initiation, such as DPT, DNPT and HEXADI, the initiation impulse of detonator is usually amplified by means of special charges of primary explosives (the so-called boosters), in our case 50 g plastic explosive derived from RDX (trade name TVAREX, produced by Chemza Ltd., Strážske).



Fig. 5. The testing set-up of the small-scale cook-off test KTTV [45].



Fig. 6. Fragments of the testing set-up of the small-scale cook-off test after DPT testing.



Fig. 7. Fragments of the testing set-up of the small-scale cook-off test after DNPT testing.

3. Results and discussion

3.1. Resistance to water

As already mentioned, DPT, DNPT and HEXADI are Mannich *N*-bases. As a consequence, DNPT and HEXADI can smell of formaldehyde, and the DPT crystals lose their original loose character and can smell of methylamines. In terms of the case a statement is convenient that the kinetics of decomposition of DNPT by water was first described in Ref. [38]. Its reactivity in acid medium is higher [38,39] than that of DPT [40]: the more electronegative nitro groups in the DPT molecule can hinder the protonation of aza atoms at 1,5-positions more effectively than the nitroso groups in the DNPT molecule. The hydrolysis rate of DNPT is 2000 times higher than that of hydrolytic splitting of hexamethylenetetramine [41]. Concentrated mineral acids induce an explosive decomposition of DNPT [4]. The hydrolysis kinetics of DNPT [38] and hexamethylenetetramine [42] are affected by the ionic strength of medium. To a certain extent, the findings of Ref. [42] can also be applied to the hydrolysis of HEXADI, whose stability in solutions has not yet been described in open literature. However, it is known that HEXADI undergoes distinct hydrolysis in aqueous solutions at temperatures above 10 °C [35].

3.2. Thermal reactivity

The thermal reactivity of the substances studied is connected with the significant stabilising influence of their crystal lattices. This is particularly obvious with DPT and

DNPT, whose thermal decomposition starts in solid phase (see Figs. 1–3). The said fact makes itself felt by variability of their thermal reactivity depending on the sample history. A study on nitrosation splitting of hexamethylenetetramine to DNPT [29] shows that the source of nitrosating agent affects the nucleation of the product in the reaction mixture. This causes lattice disturbances of the resulting DNPT crystal, as well as the sort and amount of occluded impurities. The kind of source of nitrosating agent and the nucleation velocity also affect the amount of the nitrosolysis by-product, i.e. 1,3,5-trinitroso-1,3,5-triazacyclohexane (TMTA), in final DNPT [29]. TMTA acts as a solvent of DNPT, hence it negatively affects its thermal stability [29]. What has been said corresponds with the range of onsets of exothermic decompositions of DNPT presented in Table 2. A DTA record of a very stable technical sample of DNPT (prepared within this study) is included in Fig. 3.

The relationships between way of synthesis and thermal reactivity of product are more distinct with DPT: while the Hale procedure gives DPT melting from 177–179 [2,16] to 188–193 °C [14], the synthesis at Bachmann's conditions (in acetic anhydride medium) gives a product melting at 205–206 °C [2,17]. Therewith connected is the range of onsets of exothermic decompositions of DPT (see also Figs. 1 and 2) and the corresponding results of vacuum stability tests presented in Table 1.

The decomposition of HEXADI occurs in the vicinity of its melting point. The beginning of exothermic decomposition of the pure product in Fig. 4 (161.4 °C) is lower than the onsets of *N*-alkylammonium nitrates (e.g. *N*-methylammonium nitrate has this onset at 179–182 °C [43]).



Fig. 8. Fragments of the testing set-up of the small-scale cook-off test after HEXADI testing.

From the point of view of synthesis of DPT and HEXADI within the present study it was interesting to verify the effect of ammonium nitrate (AN), one of the chief by-products of this synthesis, upon the thermal stability of final products. An addition of 2% AN to DPT results in a stability decrease of the final mixture (Fig. 2), and the corresponding DTA record somewhat reminds one of the DTA record of technical DPT (see Fig. 2). The distinctly lower thermal stability of DPT produced by Hale synthesis can thus be connected mainly with the AN occluded on its crystals. The same addition of AN to HEXADI has practically no effect upon the basic shape of the corresponding DTA curve but depresses an onset of its second exothermic peak (see Fig. 4). For comparison: a DNPT sample with the same additive exhibits a strongly lowered thermal stability (at 90 °C the sample explodes, see Fig. 3), which was also observed earlier [5] with a sample containing only 0.17 wt.% AN. It should be pointed out that the explosion of DNPT occurred in the region of III–II polymorphous transition of AN (above 84.2 °C, see also Ref. [5]), while the decomposition of DPT is situated in the region of II–I polymorphous transition of AN (125.2 °C). Here again the reactivity of DNPT is higher (as in the case of DPT and for the same reason) as in the case of their hydrolysis (acidolysis). On the other hand, the reaction centres in the HEXADI molecule (i.e. the aza atoms) are deactivated by protonation in this case.

DSC was used to study the exothermic decomposition heat of DPT and DNPT [20]. With DNPT, the value of this heat depends very strongly on the degree of filling up of the volume by the sample [20]. No such dependence was found with DPT [20]. The value of decomposition heat of DNPT in Ref. [23] is close to its detonation heat, Q_{real} , for TMD (see Table 2).

3.3. Explosive decomposition

In the sense of small-scale cook-off test, DPT behaves as a secondary explosive (Fig. 6), HEXADI approaches to such explosive (Fig. 8). The mere opening of the steel tube in the case of DNPT can also be due to its very low bulk density (i.e. respective very low charge density, see Fig. 7).

The impact reactivity of DPT and HEXADI is at the level of that of TNT if it is judged from the point of view of the tests detected on the basis of sound. However, DPT has a relatively low threshold of detection of primary chemical changes induced by impact (the detection as the first reaction, see Table 1). Dry DNPT is more sensitive to impact than 1,3-dinitrobenzene, which can be due to the higher energy content in its molecules (see Tables 1–3 for the heats of formation of the substances studied).

The performance of the substances studied is a function of their energy content and volume of their detonation products. The detonation transformation connected therewith is stable and has a reproducible detonation velocity only in the case of DPT placed in plastic casing (see Table 1). A strong initiator (hexogene primer) can initiate also dry compressed DNPT [5] (see Table 2). A DNPT sample containing 6.5 wt.% water and

2.2 wt.% TMTA, placed in a weld less steel tube of 57 mm diameter, 500 mm length, 3 mm wall thickness (charge density 690 kg m^{-3}), initiated by a charge of 100 g Semtex 1A, underwent a complete detonation too [44]. The detonation of HEXADI at the charge density of 799 kg m^{-3} is unstable [6] (see also Table 3). Hence, from the point of view of initiation ability in the sense of Ref. [12], it can be stated that only HEXADI cannot be brought to stable detonation by standard initiation tools at the charge density and diameter used.

The safety characteristics of DNPT can be summarised as follows [47]: compared with crystalline 1,3-dinitrobenzene (*m*-DNB) it has a lower sensitivity to the compression wave as well as a failure diameter; its impact sensitivity and tendency to explosive burning is somewhat higher, as that of *m*-DNB. However, dry DNPT does not reach such tendency to deflagration as that exhibited by non-small-grain gunpowder [47]. From the point of view of transport, DNPT is classified in Class 4.1, Group B according to the regulation RID and/or ADR [48].

4. Conclusions

The energetic compounds 3,7-dinitro-1,3,5,7-tetraazabicyclo[3.3.1]nonane (DPT), 3,7-dinitroso-1,3,5,7-tetraazabicyclo[3.3.1]nonane (DNPT) and hexamethylenetetramine dinitrate (HEXADI) are typical Mannich *N*-bases. As such, they relatively easily undergo hydrolysis by action of water or even air moisture. The thermal reactivity, particularly that of DPT and DNPT, is somewhat lower than expected on the basis of their molecular structure. This is due to the stabilising influence of their crystal lattice, which in the case of substances of technical purity tends to be disturbed by the presence of the synthesis by-products. In this respect, ammonium nitrate is an undesirable admixture in DPT and DNPT. Reproducible value of detonation velocity was observed with DPT, which substance also has the highest performances according to the Trauzl test. DNPT can be brought to stable detonation by a strong impulse and in firm casing. HEXADI cannot be brought to stable detonation by standard initiation tools. The highest impact sensitivity was found with dry DNPT, the lowest one with HEXADI (in this respect, together with DPT, it approaches to TNT). On the basis of the data gathered, the process safety risks are the lowest with HEXADI.

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