Military Technical College
Kobry El-Kobbah,
Cairo, Egypt

6th International Conference
on
Chemical & Environmental
Engineering
29 -31 May, 2012.

ENMC-2

SENSITIVITY AND DETONATION PARAMETERS OF 4, 6-DIAZIDO-*N*-NITRO-1, 3, 5-TRIAZIN-2-AMINE

Tomáš Musil*, Robert Matyáš*, Ondřej Němec*, Martin Künze*

Abstract

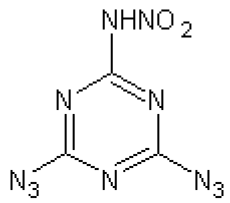
Highly dense nitrogen-rich compounds are potential high performance energetic materials for use in industrial scene or military. 4,6-Diazido-N-nitro-1,3,5-triazin-2-amine (DANT) is relatively a new substance on which characterization and detonation parameters were tested. The sensitivity of DANT to impact, friction and electric discharge was also determined. Sensitivity to impact is between PETN and RDX, sensitivity to friction is higher as PETN. DANT´s relative strength is 108 % of TNT. We also calculated and measured detonation parameters such as pressure and detonation velocity. Theoretical detonation parameters are 8 205 $m.s^{-1}$ and 30.3 GPa. Temperature of autoignition is 156 °C.

Keywords:
4,6-Diazido-N-nitro-1,3,5-triazin-2-amine; DANT, detonation parameters, sensitivity

* Institute of Energetic Materials, Faculty of Chemical Technology, University of Pardubice, Studentska 95, 532 10 Pardubice, Czech Republic. st13233@student.upce.cz

1. Introduction

4,6-Diazido-*N*-nitro-1,3,5-triazin-2-amine (DANT, see scheme 1) – this relatively simple molecule was first reported only four years ago by Fronabarger et al. *[1]*. The more extensive study of this molecule focused on its synthesis, analysis, structure and its sensitivity to mechanical stimuli was published recently by us *[2]*. Cesium and rubidium salt of DANT were suggested as green primary explosives *[1]*; salts of DANT with nitrogen bases (e. g. aminoguanidium, 4-amino-1,2,4-triazolium, guanizinium) were patented as a high performance energetic salts for military and industrial use *[3]*. Not all explosive properties of DANT (primarily performance or detonation velocity) have been published yet. Therefore the present study is focused on explosive parameters and sensitivity of DANT.

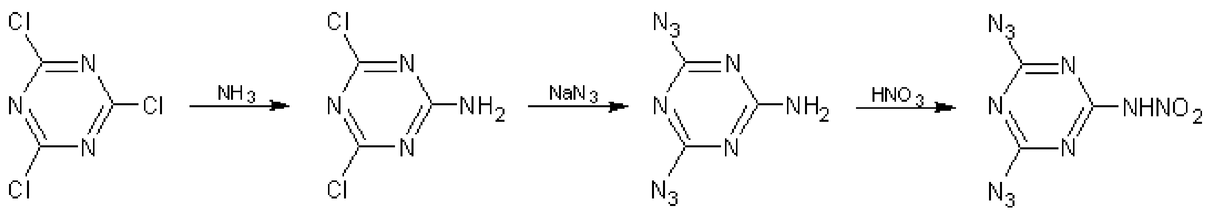


Scheme 1 DANT molecule

2. Experimental

2.1 Synthesis of DANT

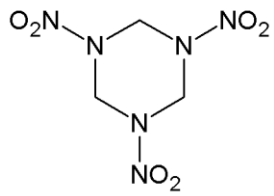
DANT was prepared by a three step synthesis (see scheme 2). The 2-amino-4,6-dichloro-1,3,5-triazine (first intermediate) was prepared by adding the cyanuric chloride into aqueous ammonia according to published procedure *[4]*. The second intermediate is formed by reaction of aqueous sodium azide with 2-amino-4,6-dichloro-1,3,5-triazine in an ethanol suspension *[5]*. Nitration is the last step of the synthesis. 2,4-Diazido-*N*-nitro-1,3,5-triazin-2-amine was nitrated by a cooled nitric acid according to Fronabarger and Williams procedure [1] to yield DANT. The product was recrystallized from methanol (product does not melt). The whole three step synthesis including the analysis of intermediates is described in detail in our pervious paper *[2]*.



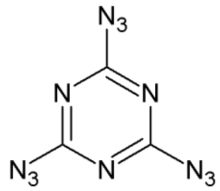
Scheme 2 Synthesis of DANT

2.2 Characterization of other used explosives

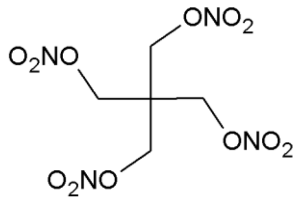
Pentrit and hexogen (see Scheme 3) were used for comparison with DANT sensitivity. Pentrit with trade name “Pentrit NS” (with particles lower than 200 μm) and was provided by Explosia a. s. company; hexogen was provided by Chemko Strazke company.



RDX



TTA



PETN

Scheme 3 Examples of common explosives.

2.3 Temperature of autoignition

The autoignition point was measured with the DTA 551-Ex by OZM Research. The 25 mg samples were measured in test tubes, which were in a special furnace filled with Wood´s metal. The heating rate was 5°C min^{-1}. Each sample was tested at three independent measurements.

2.4 Hygroscopicity evaluation

Samples of DANT were dried over phosphorus pentoxide for 1 day. Then the samples were weighed (to within 0.1 mg) and quickly placed to a desiccator containing 18.6 % sulphuric acid (relative humidity of 90 % is thus obtained). During the following 7 days, the samples were weighted.

2.5 Sensitivity to impact

The fall hammer apparatus (produced by Reichel and Partner) was applied for determination of impact sensitivity with a 0.5 kg heavy hammer for lead azide, a 1 kg hammer for PETN and DANT, and a 2 kg hammer for RDX. Both; piston and cylinders; were produced by OZM Research.

2.6 Sensitivity to friction

The sensitivity to friction was determined using BAM type friction apparatus FSKM-08 for DANT, PETN and RDX samples; lead azide was measured on small BAM friction apparatus FSKM-PEx. Porcelain plates type no. BFST-Pn-200 and porcelain plates type BFST-Pt-100S were used. The apparatus, porcelain plates and pegs were produced by OZM Research. The probit analysis was used for determination and calculation of sensitivity of all samples.

2.7 Relative strength

The relative explosive strength was measured by a ballistic mortar. Values are reported as a relative performance of TNT. For each measurement, 5 g DANT was wrapped in a polyethylene foil and inserted into the mortar enclosed by a steel projectile and then fired using a non-electric detonator (No. 8, provided by Sellier & Bellot Company). Three tests were carried out.

3. Results and discussion

3.1 Temperature of autoignition

The temperature of autoignition of DANT is 156°C. This value corresponds with value 149°C determined at DTA in our previous study (heating rate 5°C.min^{-1}, sample weight 10 mg) *[2]*. Fronabarger et al. published onset at 175°C and 179°C for peak on DSC measurement.

However the heating rate was higher (20°C.min^{-1}) *[1]*. In comparison; autoignition temperature of RDX is 204°C and for PETN is 192°C *[6]*.

3.2 Hygroscopicity

The hygroscopicity of DANT was measured at 30°C during 7 days (at 24 hour period). After exposing the sample for a time period it was removed from desiccator and the weight gain was recorded. It was determined that DANT is non-hygroscopic, gaining 0.02% surface moisture.

3.3 Sensitivity of DANT to impact

Dependence of probability of ignition on impact energy is presented on Figure 1. Sensitivity of DANT to impact is between PETN and RDX. Values of PETN and RDX are lower than commonly reported. This phenomenon can be caused by distinct apparatus, sets (pistons and cylinders) or methodology used for measuring in various laboratories.

3.4 Sensitivity to friction

Sensitivity of DANT to friction was determined on BAM friction apparatus and compared with other common explosives (PETN and RDX). Sensitivity of DANT to friction is high; it exceeds PETN (see Figure 2).

3.5 Relative strength

Despite the high content of nitrogen molecules of DANT its relative strength is 108 % TNT. It is slightly less than PETN (119 % TNT) and RDX (122 % TNT).

3.6 Detonation parameters

Detonation velocity D (m.s^{-1}) and detonation pressure P (GPa) of DANT was calculated using Kamlet and Jacobs equations *[7]*. Results are summarized in Table 1. The density and heat of formation were taken from literature.

Table 1 Detonation parameters

	M_r (g.mol^{-1})	ρ [A] (g.cm^{-3})	ΔH_f [B] (kJ.mol^{-1})	D_{max} [C] (m.s^{-1})	P_{max} [D] (GPa)	OB [E] (wt. %)
DANT	223.1	1.849 *[2]*	723.7 *[2]*	8 205	30.3	-32.37
PETN	316.1	1.760 *[8]*	-538.9 *[8]*	8 652	32.8	-10.12
RDX	222.1	1.820 *[8]*	67.1 *[8]*	8 862	35.1	-21.61
TTA	204.1	1.720 *[9]*	1053 *[10]*	7 639	25.2	-47.03

[A] Theoretical maximum density, [B] Heat of formation, [C] Calculated detonation velocity. [D] Calculated detonation pressure, [E] Oxygen balance.

Detonation parameters of DANT are slightly lower than for PETN. However it exceeds cyanuric triazide.

4. Conclusion

The sensitivities and explosive properties of 4,6-diazido-*N*-nitro-1,3,5-triazin-2-amine were reported. Final survey of the main explosive properties of DANT in comparison with those for RDX and PETN is summarized bellow:

	DANT	RDX	PETN
Temperature of autoignition (°C)	156	204	192
Impact energy for 50% probability of initiation (J)	1.68	3.59	1.33
F of I for 50% probability of initiation	37	80	30
Friction force for 50% probability of initiation (N)	40.7	75.5	127
Calculated detonation velocity ($m.s^{-1}$)	8 205	8 862	8 652
Calculated detonation pressure (GPa)	30.3	35.1	32.8
Relative explosive strength (% TNT)	108	122	119

References

[1] J. Fronabarger, M. E. Sitzmann, M. D. Williams, Method for azidotriazole, nitrosoguanazine, and related compounds, *US patent 7 375 221 B1*, **2008**.

[2] T. Musil, R. Matyáš, : 4,6-Diazido-*N*-nitro-1,3,5-triazin-2-amine (DANT) - synthesis and characterization, *Propellants, Explos., Pyrotech.*, in print.

[3] Y. Huang, Y. Zhang, J. M. Shreeve, Nitrogen-rich salts based on energetic nitroaminodiazido[1,3,5]triazine and guanazine, *Chem. Eur. J.*, **2011**, 17, 1538-46

[4] J. T. Thurston, J. R. Dudley, D. W. Kaiser, I. Hechenbleikner, F. C. Schaefer, D. Holm-Hansen, Cyanuric chloride derivates. I. Aminochloro-*s*-triazines, *J. Am. Chem. Soc.*, **1951**, 73, 2981-2983.

[5] Yu. A. Azev, O. L. Guselnikova, N. A. Klyuev, C. V. Shorshnev, V. L. Rusinov, O. N. Chupakhin, Produkty prevrashchenii azidoproizvodnykh *s*-triazina s nekotorymi *O*- i *N*-nukleofilami, *Zh. Org. Khim. Russian*, **1995**, 31, 1566-1572.

[6]. D. Klasovitý, S. Zeman, A. Růžička, M. Jungová, M. Roháč, *cis*-1,3,4,6-tetranitrooctahydroimidazo-[4,5-d]imidazole (BCHMX), its properties and initiation reactivity, *J. Hazard. Mater.*, **2009**, 164, 954–961.

[7] M. J. Kamlet, S .J .Jacobs, *J. Chem. Phys.*, **1968**, 48, 23-25.

[8] R. Meyer, J. Köhler and A. Homburg Explosives, 6th edit., VCH publishers, Weinheim, Germany **2007**.

[9] T. C. Sutton, Structure of cyanuric triazide $C_3N_3(N_3)_3$, *Philos. Mag.*, **1933**, 15, 1001-1018.

[10] E. G. Gillian, Synthesis of nitrogen-rich carbon nitride networks from an energetic molecular azide precursor, *Chem. Mater.*, **2000**, 12, 3906-3912.

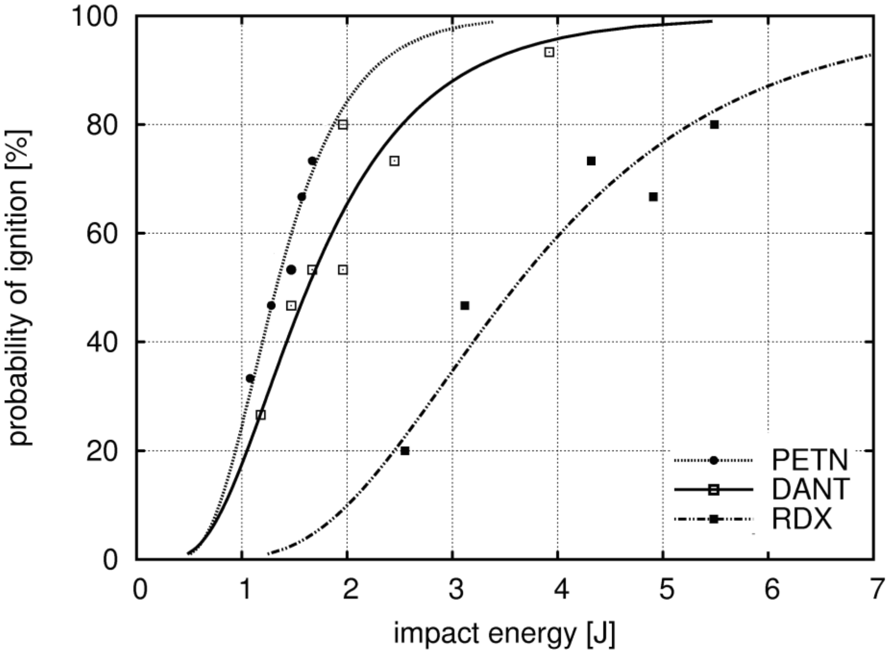


Figure 1 A comparison of impact sensitivity of DANT, PETN and RDX.

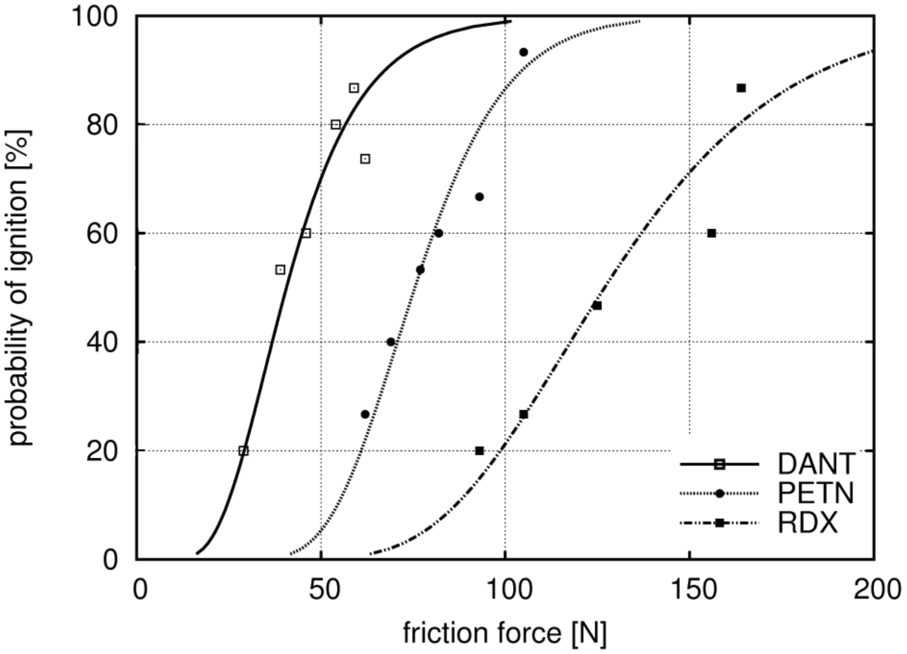


Figure 2 A comparison of friction sensitivity of DANT, PETN and RDX.