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Overview on Theoretical Prediction of 3,6-Bis-(3,5-dinitro-1,2,4-triazolyl)-1,2,4,5-tetrazine as a High Performance Explosive

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Abstract: This work presents various aspect of properties of 3,6-bis-(3,5-dinitro-1,2,4-triazolyl)-1,2,4,5-triazine or BDTT, that has not been synthesized yet, as a novel energetic heterocyclic compound. Crystal density, condensed phase heat of formation, detonation temperature, impact sensitivity, shock sensitivity based on small-scale gap test, adiabatic exponent and heat of detonation as well as detonation pressure and velocity that are important properties for explosive users are investigated. It is shown that sensitivity of BDTT as a high performance explosive is less than HMX and RDX. Moreover, high oxygen content of BDTT can introduce it as suitable oxidizer to use in solid propellants.

Key words: 3,6-bis-(3,5-dinitro-1,2,4-triazolyl)-1,2,4,5-triazine; detonation performance; sensitivity; monopropellant

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1 Introduction

The determination of detonation performance, sensitivity and thermochemical properties of a new energetic compound prior of its actual synthesis is appreciated to explosive user because they can help to reduce the costs associated with its synthesis, test and evaluation as well as to eliminate poor candidate. Some properties such as crystal density, heat of formation, detonation pressure, detonation velocity and sensitivity would permit the selection of only the most promising substances for laboratory synthesis, scale-up, testing, etc. Theoretical studies of energetic materials can also predict a considerable insight into understanding of factors affecting their behavior. However, maximizing performance with minimizing sensitivity is highly desirable in designing and formulating of energetic materials.

Since heterocyclic compounds generally have a higher heat of formation, density and oxygen balance than their carbocyclic analogous, they have attracted a great amount of interest[1-4]. Moreover, the synthesis of nitrotriazoles as energetic materials and as intermediates to energetic materials has received a great deal of attention[5]. Lee and coworkers[6] synthesized 3,6-bis(5-amino-3-nitro-1,2,4-triazolyl)-1,2,4,5-tetrazine or BANTT by reacting the sodium salt of 5-amino-3-nitro-1,2,4-triazole with 3,6-dichlorotetrazine and cyanuric chloride in refluxing CH_3CN. BANTT has density of 1.78 $g \cdot mL^{-1}$ and DTA exotherm at 240 ℃[6]. Although this compound is thermally stable, it seems to hold no advantages over well-known explosive namely 1,3,5-triamino-2,4,6-trinitrobenzene or TATB.

The purpose of this work is to present various aspect of properties of 3,6-bis-(3,5-dinitro-1,2,4-triazolyl)-1,2,4,5-tetrazine or BDTT that can be considered as a novel heterocyclic energetic compound with some advantages over BANTT. Detonation pressure, temperature, heat, velocity and adiabatic exponent of BDTT are calculated and compared with BANTT by some new methods. It will be shown that BDTT can be supposed as one of the interesting explosive with high performance. Crystal density, condensed phase heat of formation and sensitivity of BDTT and BANTT explosive are also evaluated and discussed by using some new correlations. Since BDTT has a good oxygen content as compared to BANTT, its application as monopropellant is also investigated.

2 Properties of BDTT

Various aspects of BDTT and BANTT including of thermochemical properties, detonation performance and sensitivity are calculated and discussed by new methods. The results are given in Table 1 and described in the following sections.

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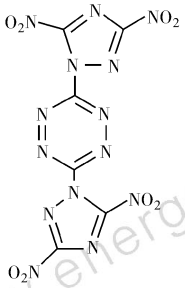
Table 1 Comparison of various aspects of BDTT and BANTT

properties	BDTT	BANTT
molecular structure		
crystal density/g · cm^{-3}	1.91[8]	1.78[6]
heat of formation in solid phase/kcal · mol^{-1}	182[12]	170[12]
heat of detonation/kJ · g^{-1}	5.023[13]	3.428[13]
detonation temperature/K	6184[22]	4409[22]
velocity of detonation/km · s^{-1}	8.69[29]	7.79[29]
detonation pressure/kbar	353[13]	262[13]
adiabatic exponent	3.08[32]	2.98[32]
impact sensitivity/cm	70[34]	321[34]
P_{98}/kbar	21.03[36]	119.91[36]
I_{sp}/(N · s) · g^{-1}	2.418[38]	2.246[38]

2.1 Crystal density and heat of formation

As seen in Table 1, predicted crystal density of BDTT is 7.3% higher than BANTT, which has predominant effect to increase the performance of BDTT.

Since condensed phase heat of formation is usually needed to evaluate detonation properties by a computer code or empirical methods[7], the ability to estimate condensed phase heat of formation of a new explosive from a given molecular structure is a problem of the utmost importance. Two methods can be used to predict condensed phase heat of formation of energetic compounds, which include quantum mechanical methods[9] and empirical procedures[10-12]. As indicated in Table 1, predicted solid phase heat of formation of BDTT is higher than BANTT[12], that is consistent with their molecular structures.

2.2 Detonation performance

Since decomposition of an explosive is extremely fast in detonation process, the heat librated will raise the temperature of gaseous detonation products. This process will in turn cause them to expand and work on surroundings[7]. As indicated in Table 1, predicted heat of detonation of BDTT is larger than BANTT, which is consistent with determined values of the other detonation parameters. Of different approaches for predicting heat of detonation[13-15], simple method of Keshavarz and Pouretedal[13] is used to determine heats of detonation of BDTT and BANTT.

Detonation temperature is an important property which can be predicted by computer codes or theoretical methods[16-19]. If the quantities and the nature of the gaseous products as well as heat of formation of explosive are assumed, detonation temperature can be calculated via molar heat capacities of detonation products[16-19]. However, it has been recently indicated that gas phase heat of formation of explosive as well as some parameters can also be used to predict detonation temperature[20-22]. As seen in Table 1, since there is no hydrogen in BDTT which can reduce detonation temperature, calculated detonation temperatures of BDTT is relatively higher than BANTT. Moreover, high detonation temperature of BDTT is consistent with its high oxygen content to force carbon in forming carbon dioxide and carbon monoxide.

Some empirical methods have been recently introduced to determine detonation pressure and velocity of pure and mixture of ideal and non-ideal explosives at any loading density via different approaches[13,16-19,23-30]. Since BDTT has relatively high crystalline density and heat of formation, calculated detonation pressure and velocity of BDTT are much higher than BANTT.

The calculated adiabatic exponent for BANTT and BDTT at their crystal densities are also indicated in Table 1.

2.3 Comparison of sensitivity of BANTT and BDTT

Minimizing sensitivity as well as maximizing performance is highly desirable in designing and formulating of energetic materials. Organic explosives can undergo very rapid and high exothermic reaction for which an understanding of sensitivity is in large part of chemical problem[33] because all explosives are necessarily metastable and sensitive. Drop weight test can be used to evaluate impact sensitivity in which milligram quantities of an explosive material are placed between a flat tool steel anvil and the flat surface of a tool striker. Explosion or nonexplosion is recorded for some drops that are usually made by a 2.5 kg weight for different heights. H_{50} is frequently used to distinguish explosion, the height in centimeter at which the probability of explosion is 50%, for an arbitrarily set level of sound which produced by the explosive on impact. It was recently found that impact sensitivity can be estimated for nitro-heterocyclic aromatic compounds[34]. As seen in Table 1, the predicted values confirm that BDTT is more sensitive than BANTT, which are consistent with higher oxygen content of BDTT. Predicted impact sensitivity of BDTT is lower than high performance well-known explosive such as HMX and RDX which have low values of impact sensitivities 26 and 24 cm, respectively[35].

Different gap tests can be used qualitatively to measure the shock wave amplitude required in initiating detonation of explosives, e.g. at Naval Surface Warfare Center (NSWC) and Los Alamos National Laboratory (LANL). A standard small scale gap test[35] is often used to measure shock sensitivity. To predict shock sensitivity based on small scale gap test, a new method was recently developed so that the pressure required to initiate material pressed to 98% of theoretical maximum density is denoted by P_{98}[36]. Predicted results are consistent with determined impact sensitivities values of BANTT and BDTT. Moreover, predicted P_{98} of BDTT is larger than HMX (P_{98} = 17.49 kbar[35]), which is consistent with their predicted impact sensitivities.

2.4 Application of BDTT in solid propellant

The propellant performance is characterized widely by means of the specific impulse[37]. The specific impulse is defined as the thrust divided by the propellant consumption rate and can be characterized the performance of liquid and solid propellants. Thermodynamically, it is a parameter to identify the energy efficiency of propellant combustion, which can show the effective time to generate thrust and sustain the propellant mass against the gravitational force through energy conversion. The specific impulse of a high explosive, which can be designated as a monopropellant, increases with a high positive heat of formation and the formation of light gases. Since the former leads to a greater release of energy upon combustion and for the next then a greater number of moles are produced per unit weight of propellant. As seen in Table 1, a new method was used to calculate specific impulse of BANTT and BDTT[38]. Higher specific impulse of BDTT shows that it is a suitable crystalline oxidizer for application in solid propellant.

3 Conclusions

Various aspects of BDTT and BANTT including crystal density, condensed phase heat of formation, detonation temperature, impact sensitivity, shock sensitivity based on small-scale gap test, adiabatic exponent and heat of detonation as well as detonation pressure and velocity are calculated and compared with each other. BDTT is a hydrogen free interesting energetic nitroheterocyclic aromatic compound. Due to recent developments in synthesis of energetic nitroheterocyclic compound[1-4], this paper suggests that BDTT can be introduced as a novel interesting energetic compound to explosive industries. High oxygen content of BDTT can introduce it as high energy density explosive as well as suitable oxidizer to use in solid propellants. Moreover, its sensitivity is lower that well-known HMX and RDX explosives.

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