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Publisher *Taylor & Francis*

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## Journal of Energetic Materials

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713770432>

### A New View of Relationships of the N-N Bond Dissociation Energies of Cyclic Nitramines. Part III. Relationship with Detonation Velocity

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**To cite this Article** Zeman, Svatopluk and Atalar, Taner(2009) 'A New View of Relationships of the N-N Bond Dissociation Energies of Cyclic Nitramines. Part III. Relationship with Detonation Velocity', *Journal of Energetic Materials*, 27: 3, 217 – 229

**To link to this Article:** DOI: 10.1080/07370650802640374

**URL:** <http://dx.doi.org/10.1080/07370650802640374>

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## A New View of Relationships of the N–N Bond Dissociation Energies of Cyclic Nitramines. Part III. Relationship with Detonation Velocity

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*The values of bond dissociation energies, BDE, of the weakest N–N bonds and total energies,  $E_{total}$ , of molecules have been calculated for 14 cyclic nitramines by means of the UB3LYP/6-31G\* and UB3LYP/6-31+G\* // PM3 methods. Ambiguous relationships were found between the logarithms of detonation velocities and BDE/ $E_{total}$  ratios of these nitramines. The reason of this found ambiguity mainly lies in a real conformation of the respective molecules and intermolecular force effects in real molecular crystals, which are included in neither of the two calculation methods. However, partial relationships of this type can be used for evaluation of effectiveness of the method of designing molecular structures of energetic cyclic nitramines for obtaining products with the maximum possible performance.*

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**Keywords:** bond dissociation energy, cyclic nitramines, detonation velocity

## Introduction

Over the last 10 years the study of problems of sensitivity (i.e., initiation reactivity) of energetic materials has accelerated thanks to theoretical methods based on quantum chemistry. Impact and shock sensitivities have been in the center of interest [1]. The dissociation energy of the weakest bond in the molecule of energetic material is thought to play an important role in the initiation events. However, in the case of the impact sensitivity some authors accept the idea that the correlation between bond strength and this sensitivity is not generally limited within certain classes of molecules [2,3]. Using a set of nitramines, we have confirmed that there exists a semi-logarithmic relationship between the impact and electric spark sensitivities and characteristics of the weakest bond in the molecule, but this relationship is not unambiguous [4–6]. A simplification in the case of impact sensitivity should have resulted from Fried's et al. modification [3] of the characterization of impact sensitivity (impact reactivity) on the basis of the introduction of the ratio of bond dissociation energy ( $BDE$ ) and total energy content,  $E_d$ , calculated by means of CHEETAH [3]. Song et al. [7] modified this characteristic by replacing the  $E_d$  values by the total energy of molecule,  $E_{\text{total}}$  (calculated by means of B3LYP 6-31G\*). The said modifications did not bring any simplification in the case of the impact sensitivity [5]; however, the application of the  $BDE/E_{\text{total}}$  ratio provided higher quality partial semi-logarithmic relationships between this sensitivity and the said ratios [5].

The weakest bond in a molecule is also connected with the ability of energetic materials to undergo detonation [1,8]; however, the above-given approach was not applied to its course. Therefore, the present article pays attention to the relationship between the  $BDE/E_{\text{total}}$  ratios and detonation velocities.

## Substances and Data Sources

Table 1 presents a set of the cyclic nitramines whose values of detonation velocity,  $D$ , were taken from literature [8–11] in which they were calculated by means of the well-known Kamlet & Jacobs method [12] for a theoretical maximum crystal density (TMD). For *cis*-1,3,4,6-tetranitrooctahydroimidazo[4,5-*d*]imidazole (BCHMX) the calculation was realized in this article using its TMD value, namely,  $1.86 \text{ g cm}^{-3}$  [13], and the value of its heat of formation, namely,  $49.3 \text{ kcal mol}^{-1}$  [14]; the common values, i.e., the TMD of  $1.96 \text{ g cm}^{-3}$  and the heat of formation of  $-48.59 \text{ kcal mol}^{-1}$  [15], were used in the first approach for 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (TNIW5) and 4,8,10,12-tetranitro-2,6-dioxa-4,8,10,12-tetraaza-isowurtzitane (TNIW6). Table 1 also presents nitramines tetrogen and decagon, which have not been synthesized yet; their properties were predicted earlier (see Zeman [9] and references therein).

Table 2 presents calculated total energies,  $E_{\text{total}}$ , of the investigated nitramines and their fragments as a result of N–NO<sub>2</sub> bond rupture and the value of the bond dissociation energies ( $BDEs$ ) of the weakest N–N bonds in the molecules of the nitramines studied. The calculations of  $BDEs$  were performed by means of the UB3LYP/6-31G\* and UB3LYP/6-31+G\* // PM3 (UHF) methods [16, 17]; the values obtained by these two methods are denoted by the codes  $BDE^a$  and  $BDE^b$ , respectively. All the calculations were performed using the Spartan 06 package program. Table 2 also includes the dimensionless ratios  $DBE/E_{\text{total}}$ , denoted as *Ratio*.

## Results and Discussion

In a detonation, primary fission of molecules of energy material continuously by action of the shock caused by detonation wave takes place. Both experimentally and computationally, the best accessible characteristic of this transformation is its velocity,  $D$ . It is well known that the detonation rate of stable detonation does not depend upon the concentration of a given explosive

**Table 1**

A survey of the studied cyclic nitramines and their calculated detonation velocities,  $D$ , for theoretical maximum density (TMD) of their crystals

Data no.	Chemical name of nitramine	Code designation	Detonation velocity calculated	
			$D$ ( $\text{km s}^{-1}$ )	Ref.
1	1,3-Dinitro-1,3-diazetidine	Tetrogen	8.46	9
2	1,3,3-Trinitroazetidine	TNAZ	8.62	11
3	1,3-Dinitroimidazolidine	CPX	7.76	9
4	1,4-Dinitropiperazine	DNDC	6.75	9
5	1,3,5-Trinitro-1,3,5-triazinane	RDX	8.89	9
6	1,3,5-Trinitro-1,3,5-triazepane	HOMO	8.23	9
7	1,3,5,7-Tetranitro-1,3,5,7-tetrazocane	HMX	9.13	9
8	<i>cis</i> -1,3,4,6-Tetranitrooctahydroimidazo[4,5-d]imidazole	BCHMX, Bicyclo- HMX	9.05	<sup>a</sup>

9	<i>trans</i> -1,4,5,8-Tetranitrodecahydro- pyrazino[2,3- <i>b</i> ]-pyrazine	TNAD	8.52	10
10	1,3,5,7,9-Pentanitro-1,3,5,7,9-pentazecane	Decagen	8.96	9
11	2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12- hexaazaisowurtzitane	HNIW	9.62	9
12	4,8,10,12-Tetranitro-2,6- dioxo-4,8,10,12-tetraaza-isowurtzitane	TNIW-5, Aurora-5	8.94	<sup>a</sup>
13	4,6,10,12-Tetranitro-2,8- dioxo-4,6,10,12-tetraaza-isowurtzitane	TNIW-6, Aurora-6	8.94	<sup>a</sup>
14	4,10-Dinitro-2,6,8,12-tetraoxa-4,10- diazaisowurtzitane	TEX	8.47	9

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<sup>a</sup>The value calculated in this article (see text in the paragraph 2).

**Table 2**

A survey of the results of calculations by means of the UB3LYP/6-31G\* and UB3LYP/6-31+G\* // PM3 (UHF) methods; total energies,  $E_{total}$ , of molecules of the considered nitramines and of fragments R and bond dissociation energy values,  $BDE$ , of the weakest N–N bonds

Nitramine	UB3LYP/6-31G* method			UB3LYP/6-31+G* // PM3 method		
	Total molecular energy $E_{total}$ (a.u.)	$BDE^a$ (kJ mol <sup>-1</sup> )	$Ratio^a$ (10 <sup>-5</sup> )	Total molecular energy $E_{total}$ (a.u.)	$BDE^b$ (kJ mol <sup>-1</sup> )	$Ratio^b$ (10 <sup>-5</sup> )
1. Tetrogen 1 R	-598.145870 -393.026959	145.794	9.284	-598.250756 -393.112507	147.742	9.406
2. CPX 2 R	-637.462307 -432.344596	142.643	8.544	-637.592981 -432.459870	134.252	8.020
3. TNAZ 3 R (N–N) 3 R (C–N)	-786.600738 -581.476374 -581.474480	160.111 165.084	7.753 7.994	-786.727902 -581.585436 -581.580755	158.814 171.104	7.689 8.284
4. DNDC 4 R	-676.756808 -471.628279	171.046	9.627	-676.921350 -471.771150	179.119	10.078
5. RDX 5 R	-897.265511 -692.143645	153.552	6.537	-897.418043 -692.281040	144.471	6.132

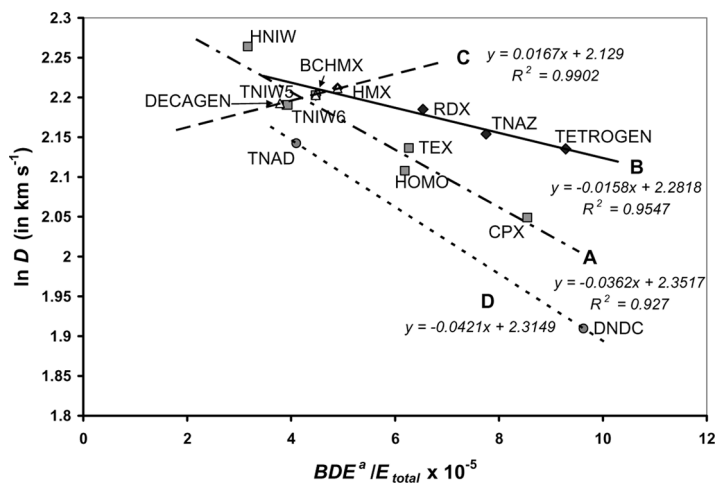
6. HOMO	-936.551276	152.158	6.188	-936.730074	145.353	5.910
6 R	-731.429941			-731.592735		
7. HMX	-1196.354948	153.715	4.894	-1196.546670	135.599	4.316
7 R	-991.233020			-991.413046		
8. BCHMX	-1195.165324	140.291	4.471	-1195.339070	131.892	4.203
8 R	-990.048509			-990.206858		
9. TNAD	-1273.722908	137.001	4.097	-1273.923260	98.359	2.941
9 R	-1068.607346			-1068.803820		
10. Decagen	-1495.444899	148.648	3.786	-1495.663440	107.496	2.738
10 R	-1290.324901			-1290.540520		
11. HNIW	-1790.961447	148.895	3.167	-1791.187680	139.947	2.976
11 R	-1585.841355			-1586.052400		
12. Aurora-5	-1421.779884	146.101	3.914	-1421.982960	165.414	4.431
12 R	-1216.660856			-1216.837980		
13. Aurora-6	-1421.778269	146.805	3.933	-1421.978700	152.419	4.083
13 R	-1216.658973			-1216.838670		
14. TEX	-1052.595046	173.133	6.265	-1052.775060	166.801	6.035
14 R	-847.465722			-847.629552		
NO <sub>2</sub>	-205.063381			-205.081977		

$$\text{Ratio} = \text{BDE}/E_{\text{total}} \text{ and } \text{BDE} = [E(\text{RNO}_2) + E(\text{NO}_2)] - E(\text{R-NO}_2).$$

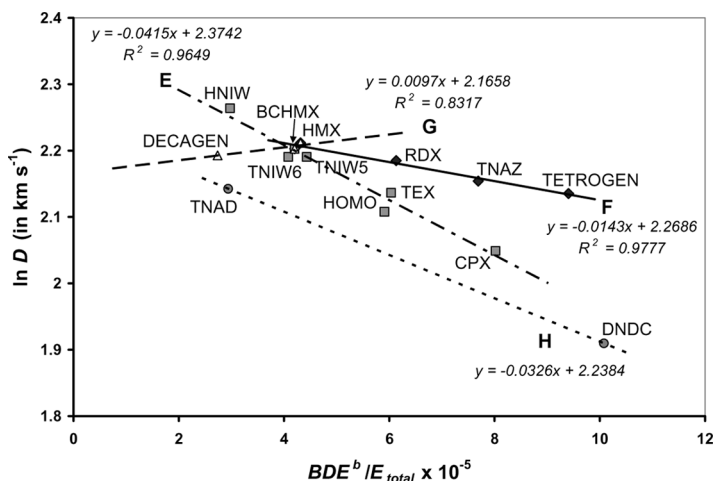


in the given space [8]. Therefore, from the point of view of the classical reaction kinetics, the chemical change of a one-component explosive in the detonation might be taken as a zero-order reaction. The ease of initiation of this reaction depends on bond energy of the weakest bond in the molecule (for a discussion of reaction centers of molecule in this context, see Zeman [1]). Being a specific type of exothermic decomposition reaction, detonation has a velocity that very distinctly depends upon the energy content per volume unit of the given explosive (or expressed in another way: upon the charge density) [8]. For this reason, and with reference to Atalar et al. [5], we have applied—for the purposes of this work—the approach described by Fried et al. [3] and modified by Song et al. [7]; i.e., the characterization of sensitivity of the studied nitramines by the  $BDE/E_{\text{total}}$  ratios from Table 2.

The semi-logarithmic relationship between the  $D$  values and the  $BDE/E_{\text{total}}$  ratios is represented by Fig. 1 for the calculations using the UB3LYP/6-31G\* method and by Fig. 2 for the results of UB3LYP/6-31+G\* // PM3 method. It can be



**Figure 1.** Semi-logarithmic relationship between detonation velocity,  $D$ , and the  $BDE^a/E_{\text{total}}$  ratio obtained by UB3LYP/6-31G\* method for the studied nitramines.



**Figure 2.** Semi-logarithmic relationship between detonation velocity,  $D$ , and the  $BDE^3/E_{total}$  ratio, obtained by UB3LYP/6-31+G\* // PM3 method for the studied nitramines.

seen that as in the case of impact sensitivity [5] this relationship is not unambiguous. The straight line A in Fig. 1 and analogous straight line E in Fig. 2 correspond to an imaginary construction of globular skeletons of aza-wurtzitane molecules from skeletons of molecular types of CPX and HOMO. The course of both straight lines documents that such way of construction of molecules of energetic nitramines, together with accumulation of nitro groups in them, is a very efficient method for obtaining substances exhibiting high detonation velocities; also the high density and higher thermal stability are attributed to these caged structures [15,18].

The straight line B in Fig. 1 and analogous straight line F in Fig. 2 cover the data of monocyclic nitramines, predominantly those containing a methylenenitramine grouping in the molecule. Also, decagen structurally belongs among these substances; however, its data correlate with straight line C in Fig. 1 and straight line G in Fig. 2. These two last mentioned straight lines cover the data of nitramines in the order of decreasing maximum density of their crystals: HMX

(1.96 g cm<sup>-3</sup> [18])–BCHMX (1.86 g cm<sup>-3</sup> [13])–decagen (1.79 g cm<sup>-3</sup> [19]). The next (not yet synthesized) homologue of this series, 1,3,5,7,9,11-hexanitro-1,3,5,7,9,11-hexaazacyclododecane (BCX), has the predicted density of 1.84 g cm<sup>-3</sup> [19]. From the said facts it follows that HMX is the cyclic nitramine (having a methylenenitramine grouping in its molecule) of the highest performance; in the case of higher (not yet synthesized) homologues of this series the increasing size of the molecule should correspond with a decrease in detonation velocity below the level of detonation velocity of HMX (probably in the sense of straight lines C and G). The intermolecular force effects in the crystal and the therewith connected real conformation of molecules determine the crystal density of the nitramines studied (see the densities of HMX polymorphs [18]). However, the results obtained from the UB3LYP calculation methods used apply to isolated molecules. The difference mentioned can be the main reason for the ambiguity of the relationship between logarithms of detonation velocities and the  $BDE/E_{\text{total}}$  ratios.

The indicated straight lines D in Fig. 1 and H in Fig. 2 signal a possibility of increase in detonation parameters by accumulation of dinitropiperazine building units in the molecule; from both figures it can be seen that this approach should be less efficient compared with the construction of nitramine molecules in the sense of straight lines A, B, E, and F.

## Conclusions

The relationship between detonation velocities and ratios of bond dissociation energies ( $BDEs$ ) of the weakest N–N bonds and total energies ( $E_{\text{total}}$ ) of cyclic nitramines is not unambiguous. The main reason can lie in the intermolecular force effects and real molecular configuration of these substances in their crystals, which are not involved in the applied calculation methods of the  $BDE/E_{\text{total}}$  ratios. However, partial relationships of this type make it possible to evaluate the effectiveness of the way of construction of molecules of cyclic nitramines with the aim of achieving a high performance; in this respect in the

given case it is most advantageous to combine skeletons of cyclopentane and cycloheptane types into wurtzitane arrangements; the cyclic accumulation of methylenenitramine building units gives the maximum effect in the case of HMX; any further increasing of size of molecules of this type should lead to a decrease in explosive parameters of such (not yet synthesized) homologues.

## Acknowledgements

The work was supported by the Ministry of Education, Youth & Sports of the Czech Republic, as a part of its research project No. MSM 0021627501. Participation of T. Atalar in dealing with this project was supported by the Scientific & Technological Council of Turkey (TÜBİTAK) as a part of its program 2214.

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