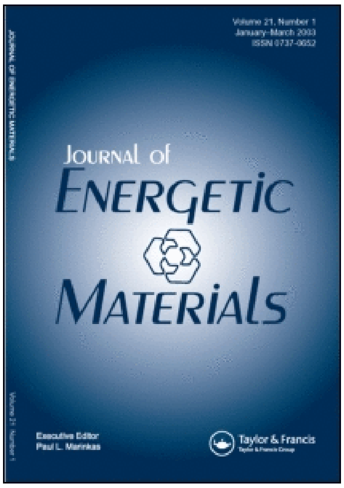

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Taner Atalar[a]; Svatopluk Zeman[b]
[a] Department of Chemistry, Middle East Technical University, Ankara, Republic of Turkey [b] Institute of Energetic Materials, Faculty of Chemical Technology, University of Pardubice, Pardubice, Czech Republic

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A New View of Relationships of the N−N Bond Dissociation Energies of Cyclic Nitramines. Part I. Relationships with Heats of Fusion

TANER ATALAR[1] and
SVATOPLUK ZEMAN[2]

[1]Department of Chemistry, Middle East Technical University, Ankara, Republic of Turkey
[2]Institute of Energetic Materials, Faculty of Chemical Technology, University of Pardubice, Pardubice, Czech Republic

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. The relationships found between the BDE values and values of heat of fusion, $\Delta H_{m,tr}$, of these nitramines are not unambiguous. More unambiguous and logical relationships result from comparison of the BDE/E_{total} ratio and the $\Delta H_{m,tr}$ values. The dependences found appear suitable for prediction of the $\Delta H_{m,tr}$ values for cis-1,3,4,6-tetranitrooctahydroimidazo[4,5-d]imidazole (31.89 kJ mol^{-1}), 4,8,10,12-tetranitro-2,6-dioxa-4,8,10,12-tetraazaisowurtzitane (41.73 kJ mol^{-1}), and 4,6,10,12-tetranitro-2,8-dioxa-4,6,10,12-tetraazaisowurtzitane (41.67 kJ mol^{-1}); the predicted values of $\Delta H_{m,tr}$ are within the expected limits and can represent a stabilizing effect of crystal lattice in*

Address correspondence to Svatopluk Zeman, Institute of Energetic Materials, Faculty of Chemical Technology, University of Pardubice, CZ-532 10 Pardubice, Czech Republic. E-mail: svatopluk.zeman@upce.cz

decomposition reactions of the studied compounds in their molecular crystals.

Keywords: bond dissociation energy, cyclic nitramines, heat of fusion, N–N bond

Introduction

Studies on the relationship between molecular structure of energetic materials and their sensitivity to impact, shock, electric spark, and heat represent an important starting point for study of chemical micromechanism governing detonation initiation of these materials [1–5]. From the results of studies of this type it follows that both the intensity of intermolecular interactions [1–6] and dislocations [7] in the corresponding crystal represent two of the factors influencing the transfer of initiation energy into the reaction center of the molecule. The influence of these intermolecular interactions has been studied most reliably on the example of thermal decomposition of polynitro compounds, where it is known as a stabilizing effect of crystal lattice [8,9] or as a retardation effect of crystal lattice (REL) [10]; the said effect acts against formation of the activated complex of the reaction and, as it were, increases the strength of the weakest (the most reactive) bond in the molecule. Hence, a relationship could exist between the bond dissociation energy of the weakest bond in the molecule and the intensity of intermolecular interactions in its molecular crystal and the work needed for formation of defects in crystal lattice. This work can be represented by heat of fusion, $\Delta H_{m,tr}$ [2–5]; the heat is defined as a sum of heats of all the polymorphous transitions and of the heat of melting [11]. It is desirable to mention that relationships between the heat of fusion and impact and electric spark sensitivities of explosives were found and interpreted [2–5].

The presumption stated has been verified in this work on a set of 14 cyclic nitramines, making use of the published $\Delta H_{m,tr}$ values and bond dissociation energies (*BDE*s) of the weakest N–N bonds in their molecules. This article is a continuation of a recent study [12] in which relationships between the $\Delta H_{m,tr}$ values and lengths of the longest N-N bonds of nitramines were used for a prediction of the heats of fusion for 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW) and 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane (TEX).

Substances and Data Sources

Table 1 presents a set of the cyclic nitramines whose $\Delta H_{m,tr}$ values were taken from Zeman [13] and Sućeska et al. [14]; part was obtained by means of DSC-7 [13,14] and another part on the basis of prediction [12,13].

Table 2 presents calculated total energies, E_{total}, of the investigated nitramines and their fragments as a result of N–NO$_2$ bond rupture and the value of the bond dissociation energies (*BDE*s) of the weakest N–N bonds in the molecules of the nitramines studied. The calculations of *BDE*s were performed by means of the UB3LYP/6-31G* and UB3LYP/6-31+G* // PM3 (UHF) methods [15, 16]: the values obtained by these two methods are denoted by the codes BDE^a and BDE^b, respectively. All the calculations were performed using Spartan 06 package program.

Some authors used for the correlation between the bond strength and impact sensitivity the ratio of bond dissociation energy (*BDE*) and energy content, E_d, calculated by Fried et al. [17] using CHEETAH or, in the modified form, the ratio with replacing the E_d values by the total energy of molecule, E_{total} (calculated by means of B3LYP 6-31G) [18]. These approaches might be legitimate in the case when the heat of decomposition plays a decisive role in the corresponding reaction (first of all in detonation). However, the dimensionless ratio DBE/E_{total}, denoted in Table 2 as *Ratio*, is used also in this article.

Results and Discussion

It is well known that intra- and intermolecular interactions in crystals affect the conformation of molecules as compared with the conformation of the same isolated molecules (conditions of the *BDE*s calculation) or in solution or melt (some N–N bonds

Table 1
A survey of the studied cyclic nitramines and their heats of fusion, $\Delta H_{m,tr}$

Data no.	Chemical name of nitramine	Code designation	Heat of fusion $\Delta H_{m,tr}$ (kJ mol^{-1})	Ref.
1	1,3-Dinitro-1,3-diazetidine	Tetrogen	26.32	10
2	1,3,3-Trinitroazetidine	TNAZ	30.31	13
3	1,3-Dinitroimidazolidine	CPX	22.57	10
4	1,4-Dinitropiperazine	DNDC	33.82	10
5	1,3,5-Trinitro-1,3,5-triazinane	RDX	33.01	10
6	1,3,5-Trinitro-1,3,5-triazepane	HOMO	27.73	10
7	1,3,5,7-Tetranitro-1,3,5,7-tetrazocane	HMX	32.10	10
8	*cis*-1,3,4,6-Tetranitrooctahydroimidazo[4,5-d]imidazole	BCHMX, bicyclo-HMX	31.89	[a]
9	*trans*-1,4,5,8-Tetranitrodecahydropyrazino[2,3-*b*]-pyrazine	TNAD	46.40	10
10	1,3,5,7,9-Pentanitro-1,3,5,7,9-pentazecane	Decagen	34.93	10
11	2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane	HNIW	43.03	14
12	4,8,10,12-Tetranitro-2,6-dioxa-4,8,10,12-tetraaza-isowurtzitane	TNIW-5, Aurora-5	41.73	[a]
13	4,6,10,12-Tetranitro-2,8-dioxa-4,6,10,12-tetraaza-isowurtzitane	TNIW-6, Aurora-6	41.67	[a]
14	4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane	TEX	36.10	14

[a] The value found in this article; see Table 3.

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

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

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_2	−205.063381			−205.081977		

$Ratio = BDE/E_{\text{total}}$ and $BDE = [E(\mathrm{RNO_2}) + E(\mathrm{NO_2})] - E(\mathrm{R{-}NO_2})$.

in crystals of nitramines can be compressed [19]). In the case of nitramino grouping acting as a carrier of orientation interaction in nitramine crystals, one of the N–N bonds is usually the longest one [19–21]. The said fact can be the reason for the complicated relationship between the *BDE* values and heat of fusion in Figs. 1 and 2. The *BDE* values should be proportional to the N–N bond lengths; however, the relationship between the experimental N–N bond lengths and the $\Delta H_{m,tr}$ values is more unambiguous [12].

Figures 3 and 4 represent logical relationships between the values of DBE/E_{total} ratios and the $\Delta H_{m,tr}$ values. Classification of the nitramines studied in individual groups in the sense of these figures is connected with similarity of conformations of their molecules in the individual groups. Figures 3 and 4 confirm the possibility of existence of a relationship between the weakest N-N bond in the molecule of the given energetic material and the work needed to create the crystal defects. Zeman and Jalový [12] stated that the nitramino groupings in the 1,3,5-trinitro-1,3,5-triazepane (HOMO), 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (HNIW), and 4, 10-dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane (TEX)

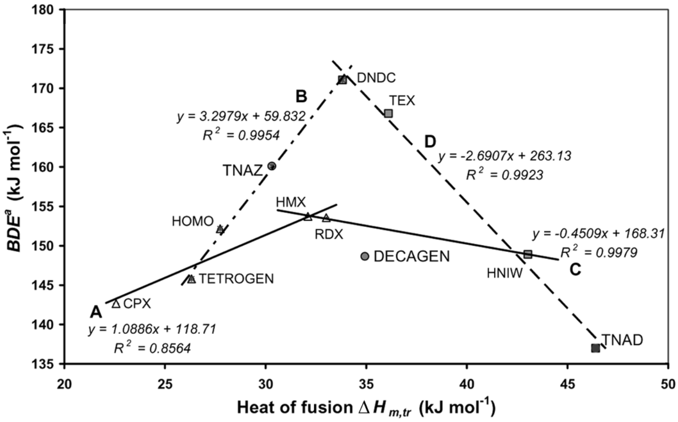


Figure 1. Relationship between *BDE*^{a}, obtained by UB3LYP/6-31G* method, and heats of fusion.

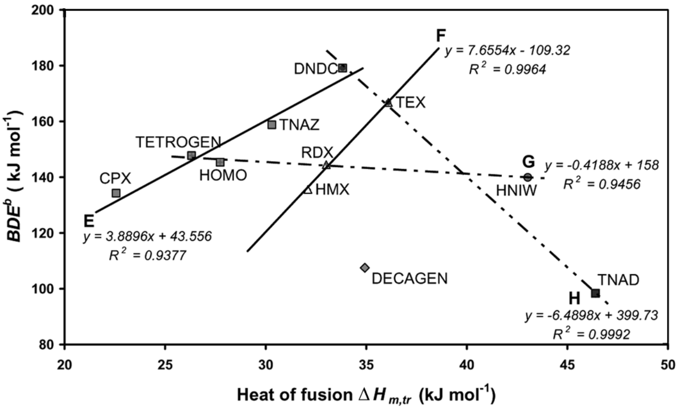


Figure 2. Relationship between BDE^b, obtained by UB3LYP/6-31+G*// PM3 method, and heats of fusion.

molecules, which play the decisive role in orientation interaction in their molecular crystals, are the first to undergo homolysis during both thermolysis and the initiation of detonation of these substances. The above-given facts document the significance of application of the $\Delta H_{m,tr}$ values to the studies of initiation

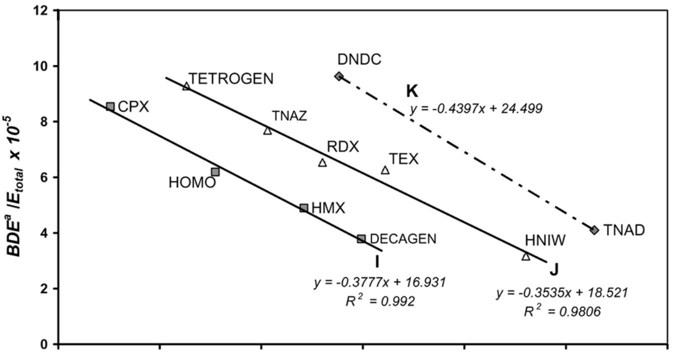


Figure 3. Relationship between the BDE^a/E_{total} ratio, obtained by UB3LYP/6-31G* method, and heats of fusion.

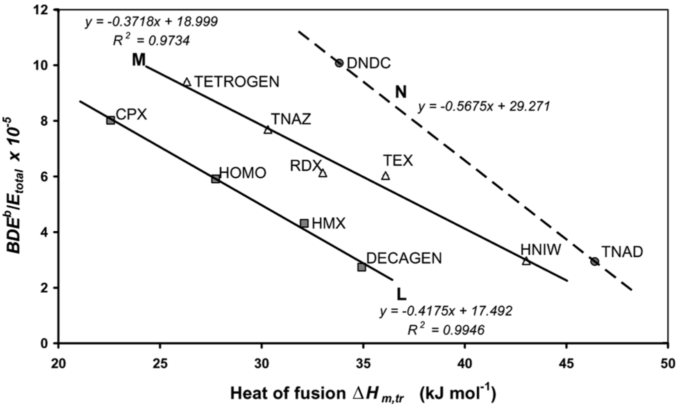


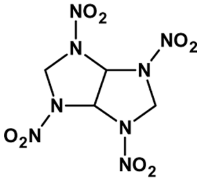
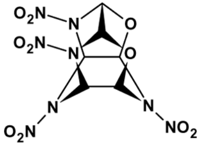
Figure 4. Relationship between the BDE^b/E_{total} ratio, obtained by UB3LYP/6-31+G*// PM3 method, and heats of fusion.

reactivity of individual energetic materials (see also Zeman [2,3,5] and Zeman et al. [4]).

Mutual differences between the lines from Figs. 3 and 4 are caused by a difference in the trends of intermolecular interactions in the crystals of nitramines belonging to each from these individual lines. Similar differences were found in the case of a study of relationships between the heats of fusion, on the one hand, and molecular weights or ^{15}N NMR chemical shifts of nitrogen atoms in the primary reacting nitramino groupings in nitramines [12].

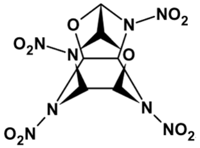
At present, defense-oriented research in particular is focused on syntheses of polycyclic nitramines *cis*-1,3,4,6-tetranitrooctahydroimidazo[4,5-*d*]imidazole (BCHMX), 4,8,10,12-tetranitro-2,6-dioxa-4,8,10,12-tetraazaisowurtzitane (TNIW-5), and 4,6,10,12-tetranitro-2,8-dioxa-4,6,10,12-tetraazaisowurtzitane (TNIW-6) [22]. In the case of these nitramines it is impossible to experimentally determine their heats of fusion, because they decompose in the temperature regions of their melting points; a similar situation is encountered in the case of HNIW and TEX, whose $\Delta H_{m,tr}$ values were predicted [12]. Also, the relationships found in this present work invite one to predict the respective $\Delta H_{m,tr}$; hence, using the

Table 3
A survey of the predicted heats of fusion, $\Delta H_{m,tr}$

Data no.[a]	Nitramine	Prediction of $\Delta H_{m,tr}$ in kJ mol^{-1}, by means of			Averaged $\Delta H_{m,tr}$ in kJ mol^{-1}	Structural formula
		Fig.	Line	$\Delta H_{m,tr}$ value		
8	BCHMX	1	[b]		31.89 ± 0.73	
		2	F	31.508		
		3	I	32.989		
		4	L	31.188		
12	TNIW-5	1	D	43.494	41.73 ± 1.17	
		2	[b]			
		3	J	41.336		
		4	M	40.373		

(*Continued*)

Table 3
Continued

Data no.[a]	Nitramine	Prediction of $\Delta H_{m,tr}$ in $\mathrm{kJ\,mol^{-1}}$, by means of			Averaged $\Delta H_{m,tr}$ in $\mathrm{kJ\,mol^{-1}}$	Structural formula
		Fig.	Line	$\Delta H_{m,tr}$ value		
13	TNIW-6	1	D	43.232	41.67 ± 1.03	
		2	[b]			
		3	J	41.283		
		4	M	40.521		

[a] Numbering according to Table 1.
[b] Any correlation has not been found.

values from Table 2 and dependences from Figs. 1–4 we obtained the values of heats of fusion summarized in Table 3. As it follows from the survey given in Table 1, these predicted $\Delta H_{m,tr}$ values correspond with the expectation.

Conclusions

The results presented show that there exists a relationship between the $\Delta H_{m,tr}$ values and the calculated values of the weakest N-N bond dissociation energies, *BDE*s, for isolated molecules of cyclic nitramines; probably the quantum chemical calculation of the *BDE* values for isolated molecules makes this relationship so complicated. This existence could be connected with fundamental influence of the state of matter on reactivity of polynitro compounds; i.e., with a role of the stabilizing effect of crystal lattice in this reactivity [8–10]. More unambiguous is the logical relationship between the $\Delta H_{m,tr}$ values and the BDE/E_{total} ratio, where the E_{total} values are calculated total energies of molecules of the nitramines considered. These facts fully agree with earlier findings obtained from studies of mutual relationship of the initiation reactivity of individual energetic materials and their heats of fusion, $\Delta H_{m,tr}$ [2–5]. The dependences obtained were found suitable for prediction of the $\Delta H_{m,tr}$ values of technologically attractive new substances, particularly *cis*-1,3,4,6-tetranitrooctahydroimidazo[4,5-*d*]imidazole, 4,8,10,12-tetranitro-2,6-dioxa-4,8,10,12-tetraazaisowurtzitane, and 4,6,10,12-tetranitro-2,8-dioxa-4,6,10,12-tetraazaisowurtzitane. The predicted $\Delta H_{m,tr}$ values are within the expected limits, and thus they can be considered a representatives of intermolecular force interactions in the corresponding crystals; i.e., a representative of the stabilizing effect of crystal lattice.

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