Performance, Sensitivity and Non-covalent Hydrogen Bonds of Explosives

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Abstract: A set of 30 different molecular structures generally confirms that the sensitivity usually increases with increasing the value of detonation energy. This can be influenced by several factors depending on the type of crystal structure and on the properties depending on mutual interactions among the molecules in the crystal. In this work, the influence of hydrogen bond interactions on decreasing sensitivity of energetic materials was especially confirmed in cases where amine head group is a donor of proton. The knowledge of basic crystal structure properties relationship in detail may allow to predict new structures of energetic materials with low sensitivity and high detonation energy per unit volume by molecular simulation methods.

Keywords: energetic materials, detonation energy, molecular simulations

Introduction

Many properties of energetic materials (EM) are intensively investigated due to their usefulness for civil and military industry. The performance, the sensitivity and the stability are in the centre of interest due to their big influence on the possible synthesis of new structures of energetic materials and on their resultant useful properties. Since a development and synthesis of these materials

is time consuming and usually materially expensive, it is purposeful to predict properties of these materials from calculated or designed structures. Many articles were published in this research area and their review is possible to see in Ref. [1, 2]. It is known that the performance of explosives can be calculated on the base of structure data. On the other hand the calculation of sensitivity is not still enough precise. The reason of this situation is the influence of several factors on sensitivity, which we can describe as (i) space group of structure and composition of energetic material (ii) value of releasable detonation energy (iii) density, compression and crystal packing of material with creation of "hot spots" [3].

In this work, the relations between the performance, sensitivity and presence of hydrogen bond (HB) interactions in the structure were checked on the set of 30 energetic materials with different structure. Accessible and published data about the relationship of crystal structure properties of energetic materials were used in our investigation and calculations.

Materials and Methods

The Kamlet-Jacobs equations [4] allow calculating the detonation velocity D_{CJ} and the pressure P_{CJ} on the base of composition, density and detonation heat of energetic material with using polytrophic state equation for gas detonation products

$$E = \frac{P \cdot V}{\gamma - 1} - Q \tag{1}$$

where $E = E_c + E_d$ (E_c is compression and E_d is detonation energy), P, V, Q and γ are pressure [Pa], volume [m^3], detonation heat [kJ/mol] and adiabatic coefficient for products of detonation, respectively. The form for detonation energy per unite – E_d [5]

$$E_d = \frac{P_{CJ}}{2 \cdot (\gamma - 1)} \tag{2}$$

where

$$\gamma = \frac{\rho \cdot D_{CJ}^2}{P_{CJ}} - 1 \tag{3}$$

and where D_{CJ}, P_{CJ}, Q, ρ and γ are detonation velocity [km/s], detonation pressure [GPa], detonation heat [kJ/mol], density [g/cm³] and adiabatic coefficient, respectively.

The sensitivity value **h_{50}** (in cm) were taken over from the literature [6, 7] except of the value for DNAF, which was estimated on the base [8]. On the base of published X-ray diffraction data [9] and its references, the models for individual crystal structures were built in *Crystal Builder module* in *Cerius²* modeling environment [10]. The built structures were not optimized and minimized except some structures where hydrogen bond positions were not published. The positions of hydrogen atoms were optimized in *Minimizer module*, other atoms were fixed on the coordinates that had been published. Several energetic materials, which do not create hydrogen bond, the energies were not calculated due to missing crystallographic data or due to their liquid state. Charges were calculated by charge equilibration approach (Qeq) method [11]. Non-bond interactions were calculated in *Crystal Packer module* under Universal force field [12]. The results for ratio of calculated HB energies with respect to value of van der Waals energy E_{vdW} (in %) together with E_d and h_{50} values are presented in Table 1. On the base of these results the volume detonation energy versus the sensitivity described by hammer drop (2.5 kg, cm) is presented in Figure 1.
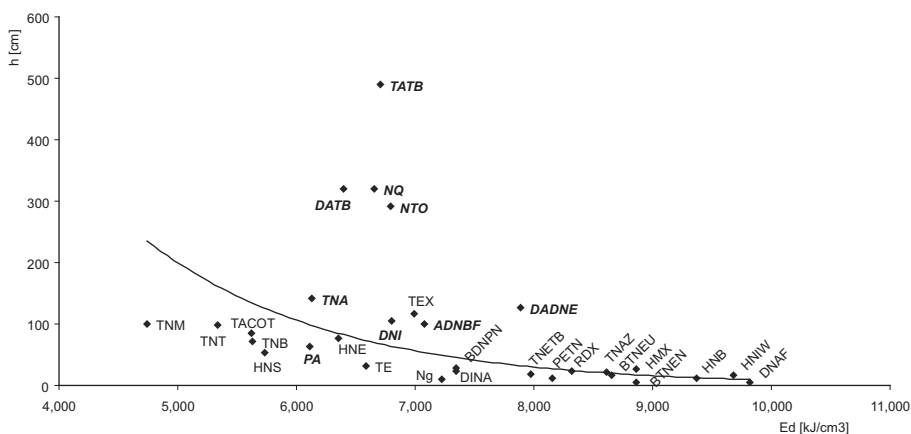

Figure 1.   Relation between volume energy of detonation and impact sensitivity (compounds with HB are bold and italic).

Table 1.   Some parameters of selected explosive

No.	compound	ρ g/cm^3	H_f kJ/mol	E_d kJ/cm^3	h_{50} cm	HB %
1	DNAF	2.00	581.9	9.822	5	0.00
2	ε-HNIW	2.03	415.3	9.684	17	0.00
3	HNB	2.00	196.7	9.372	11	0.00
4	β−HMX	1.90	74.9	8.858	26	0.00
5	BTNEN	1.96	-736.3	8.861	5	0.00
6	BTNEU	1.86	-300.1	8.657	17	0.00
7	TNAZ	1.84	12.6	8.614	21	0.00
8	RDX	1.80	61.5	8.321	24	0.00
9	PETN	1.77	-540.0	8.157	12	0.00
10	TNETB	1.78	-496.0	7.976	18	0.00
11	DADNE	1.88	-134.0	7.889	126	32.60
12	DINA	1.67	-309.8	7.348	23	0.00
13	BDNPN	1.73	-293.3	7.343	29	0.00
14	NG	1.59	-496.9	7.224	10	0.00
15	ADNBF	1.90	154.0	7.074	100	9.75
16	TEX	1.99	-540.8	6.991	117	0.00
17	2.4DNI	1.67	20.5	6.806	105	9.95
18	NTO	1.93	-129.8	6.791	291	0.00
19	TATB	1.94	-139.4	6.711	490	3.31
20	NQ	1.77	-92.1	6.651	320	27.34
21	TE	1.73	33.5	6.590	32	0.00
22	DATB	1.84	-98.8	6.394	320	5.54
23	HNE	1.85	119.7	6.350	77	0.00
24	TNA	1.77	-75.3	6.131	141	7.50
25	PA	1.76	-239.9	6.108	64	1.50
26	HNS	1.74	67.4	5.731	54	0.00
27	TNB	1.68	-103.0	5.631	71	0.00
28	TACOT	1.77	460.5	5.624	85	0.00
29	TNT	1.65	-75.3	5.336	98	0.00
30	TNM	1.63	38.5	4.741	100	0.00

Abbreviations:

DNAF   4,4´-dinitro-3,3´-diazenofuroxane

ε-HNIW   2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{5,9}.0^{3,11}] dodecane

HNB   hexanitrobenzene

β-HMX   1,3,5,7-tetranitro-1,3,5,7-tetrazocane
BTNEN   bis(2,2,2-trinitroethyl)nitramine
BTNEU   N,N´-bis(2,2,2-trinitroethyl)urea
TNAZ   1,3,3-trinitroazetidine
RDX   1,3,5-trinitro-1,3,5-triazinane
PETN   pentaerythritol tetranitrate
TNETB   (2,2,2-trinitroethyl)-4,4,4-trinitrobutyrate
DADNE   2,2-dinitroethylene-1,1-diamine
DINA   bis(2-nitrooxyethyl)nitramine
BDNPN   bis(2,2-dinitropropyl)nitramine
NG   glycerol trinitrate
ADNBF   7-amino-4,6-dinitrobenzofuroxane
TEX   4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo[5.5.0.0^{5,9}.0^{3,11}] dodecane
2,4DNI   2,4-dinitroimidazole
NTO   3-nitro-1,2,4-triazol-5-one
TATB   1,3,5-triamino-2,4,6-trinitrobenzene
NQ   nitroguanidine
TE   N-methyl-N,2,4,6-tetranitrophenylaniline
DATB   1,3-diamino-2,4,6-trinitrobenzene
HNE   hexanitroethane
TNA   2,4,6-trinitroaniline
PA   2,4,6-trinitrophenole
HNS   2,2´,4,4´,6,6´-hexanitrostilbene
TNB   1,3,5-trinitrobenzene
TACOT   tetranitro-2,3,5,6-dibenzo-1,3a,4,6a-tetraazapentalene
TNT   2,4,6-trinitrotoluene
TNM   tetranitromethane

Results and Discussion

The set of tested energetic materials exhibits some similarities and some differences. Some of them include nitro-aromatic, nitro-amines and nitro-esters with linear or cyclic arrangement and with a cage structure (HNIW, TEX). Most of them is composed from CHNO elements but the composition of some of them include only CNO (DNAF, HNB, HNE, TNM). Two of them have "furoxan" functional group (DNAF, ADNBF). Some energetic materials are characterized by nitro group connected to carbon and nitrogen (BTNEN, TNAZ, BDNPN, TE)

or nitrogen and oxygen (DINA). Other explosives have nitrogroup in *gem*-dinitro-arrangement (TNAZ, BDNPN, DADNE) or they have terminal trinitromethyl group (BTNEN, BTNEU, TNETB, HNE, TNM). This set of energetic materials is not too large, but as we can see very varied.

Figure 1 shows dependence of sensitivity versus volume of detonation energy. Decrease of volume detonation energy is connected with decrease of sensitivity (value of h_{50} increase). This effect can be observed in dependence of amount of energy which can be released from structure of energetic materials. In addition molecular structures which create intra and intermolecular HB decrease sensitivity. It is shown in Figure 1 for explosives marked by bold font. Generally, the donor is amine group and acceptor is oxygen from nitrogroup except picric acid (PA). In this case donor is hydroxyl group but its influence is low (1.5%). The sensitivity increases with increase of number of hydroxyl groups connected to aromatic ring (trinitroresorcine, trinitrophloroglucine) [7]. Hydrogen bonds were not calculated for NTO but it is known marked influence of them [3].
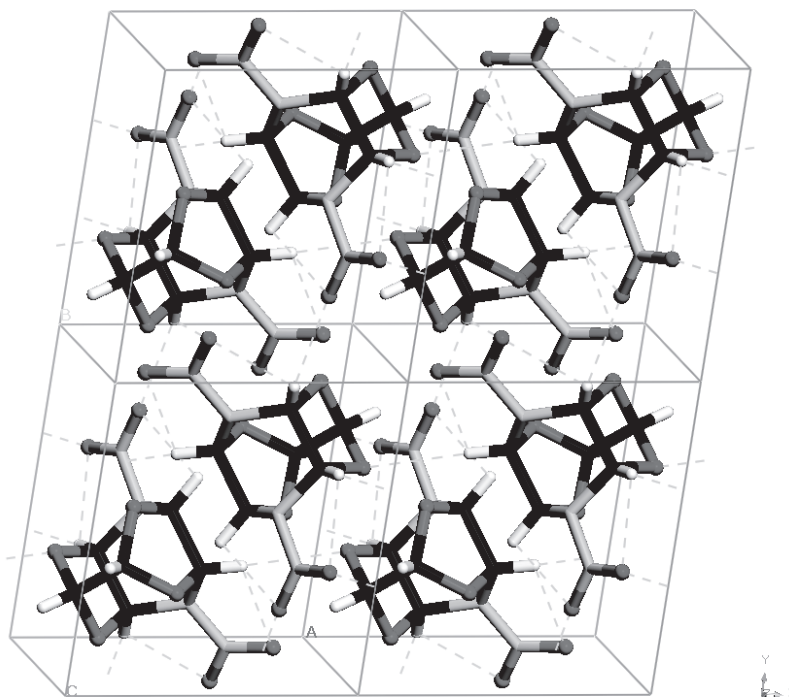

Figure 2.   Crystal structure of TEX with presented possible Hydrogen bonds (dashed line). Carbon is shown as black cylinder, nitrogen is gray cylinder, oxygen is dark gray ball and hydrogen is white.

Special attention could be paid to TEX. In publication [13] the authors mentioned that these explosives have not got hydrogen bonds. On the base of published crystal data, the model of TEX was built in *Cerius²* (see Figure 2). This structure was not minimized or changed from crystal structure data. This model shows possible existence of hydrogen bond in case that donor is carbon of wurtzitane cage –C – H ···· O- (4.58% hydrogen bond energy from total energy, this is not mentioned in Table 1). The sensitivity is dramatically suppressed in contradiction with high value of volume detonation energy. Moreover, similar cage structure of HNIW with nearly the same density lead to high sensitivity (high value of E_d, impossible HB).

Conclusions

The influence of detonation energy versus the sensitivity was verified on the set of energetic materials with different molecular structure. The influence of hydrogen bond on decreasing sensitivity was successfully confirmed, especially for materials containing amine group. These knowledges and relations are possible to be used for prediction of new energetic materials with low sensitivity. With respect to the fact, that all calculations were done on the base of published experimental crystallographic data, the following investigation will be focused for the possibility of calculation of crystal structures for new energetic materials by molecular simulations methods.

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