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ELECTRON DENSITY, BOND LENGTH AND SELECTED PROPERTIES OF CHNO EXPLOSIVES

Miroslav POSPÍŠIL[a] and Pavel VÁVRA[b1]
[a]Faculty of Mathematics and Physics, Charles University, CZ–121 16 Prague
[b]Institute of Energetic Materials,
The University of Pardubice, CZ–532 10 Pardubice

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The electron densities in a selected set of explosives with composition C-H-N-O were calculated (i) for individual molecules and (ii) for molecules placed in crystal cell. Indirect linearity between difference of absolute partial charges for bonds C–NO_2, N–NO_2 and O–NO_2 versus the bond lengths was found in both cases. The influence of non-covalent hydrogen bonds causing distinctly decreasing impact sensitivity was confirmed. Possibilities of sensitivity prediction of new energetic materials are discussed on the basis of the results obtained from impact sensitivity (the values taken from literature) and from theoretical methods, such a molecular mechanics, and the electron density for a set of twenty explosives.

[1] To whom correspondence should be addressed.

Introduction

Structure-properties relationship for CHNO explosives was described in detail in many publications and also their review was recently published [1]. The highest attention is focused on the power, sensitivity and stability of investigated explosives. It is well known that increasing value of detonation energy is usually connected with increasing sensitivity [2]. The rule does not apply generally here because of a lot of exceptions existing in both directions. While detonation energy E_d for selected explosive can be calculated, sensitivity of a newly proposed structure is not. The reason of this fact lies in sensitivity. Sensitivity of explosives is influenced by many factors, such as structure of the molecule, type of bonds in the molecule, position of nitro groups in the molecule, non-bond interactions related to one molecule, non bond-interactions among individual molecules in crystal, charge distribution etc.

Bond is an interesting factor that plays role between nitro group ($-NO_2$) and the rest of molecule in the case of nitro compounds. This bond is important as documented by recently supported idea based on experiments, calculation and molecular simulations, namely that this bond is primarily interrupted [3] under influence of detonating (shock) wave.

Nitro groups are usually connected to carbon, nitrogen or oxygen but these bonds have quite different properties. Moreover, in many explosives nitro groups are connected to different atoms in one molecule, e.g. to carbon and nitrogen, or to nitrogen and oxygen. This creates different potential places for primary decomposition of molecule. In addition, the influence of neighbor molecules and their position in the crystal must also be taken into account.

The value and distribution of partial charges in the molecule is one of the factors, which influence the strength of the bond between nitro group and other atoms. This fact influences not only the bond length but also sensitivity and molecular stability. The density and also the amount of energy per volume unit of the base cell is influenced by intra- and intermolecular interactions.

For these reasons, we tried to find a relationship for sensitivity of explosives. This relationship is derived on the basis of electron density calculation and experimentally (X-ray analysis) determined bond length $X–NO_2$ (where X = C, N and O). Moreover, contribution of hydrogen bonds as a part of van der Waals forces was reflected.

Calculations

The equation for calculation of volume detonation energy E_d can be derived from polytrophic state equation for detonation products [4]

$$E = \frac{PV}{\gamma - 1} - Q \tag{1}$$

in the form

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

where

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

where ρ, P_{CJ}, D_{CJ} and Q are density, detonation pressure, detonation velocity and detonation heat, respectively. Parameters P_{CJ} and D_{CJ} can simply be calculated from Kamlet–Jacobs equations [5].

The results of electron density for individual molecules were calculated in WinMOPACv.2.0 by AM1 method for bonds X–NO_2 (where X = C, N, O) and summa $\Delta 1$ of absolute values of partial charges δ (see Eq. (4))

$$\Delta = |\delta^+| + |\delta^-| \tag{4}$$

The electron density of molecules bonded in crystal structures [6-25] were calculated in *Cerius*^{2} modeling environment [26]. The charge distribution in the crystal structures was calculated by charge equilibrium approach (Qeq) method [27]. The crystal structures were built on the basis of published X-ray and neutron diffraction data in *Crystal Builder module*. These structures were built in agreement with published data and no changes in atom position were made during subsequent calculation. The total crystal energy of the selected energetic materials was calculated in Universal force field (UFF) [28] in *Minimizer module*. The values of detonation energy, impact sensitivity described as a height h_{50} in cm with 50 % probability of explosion [3], and the value of non-covalent hydrogen bonds HB (Expressed in per cent of van der Waals energy E_{vdW}. HB energy in this case was calculated in *Crystal Packer module*, under Universal force field) for selected set of explosion are shown in Table I.

The total crystal energy and its valence and non-bond energy components were calculated from following compounds: (i) valence components are bond, angle, torsion and inversion energy terms and (ii) non-bond components are van der Waals and Coulomb energy terms. Van der Waals energy terms are calculated with Lenard-Jones potential functional form [29] and Coulomb energy terms are calculated on the basis of Coulomb principle. The hydrogen bond energy terms are

Table I Basic parameters of selected explosives

Number	EM	ρ g cm^{-3}	H_f kcal mol^{-1}	E_d kJ cm^{-3}	h_{50} cm	*HB* %
1	e-HNIW	2.03	99.2	9.684	17	0
2	b-HMX	1.90	17.8	8.858	26	0
3	BTNEN	1.96	–175.9	8.861	5	0
4	BTNEU	1.86	–71.7	8.657	17	0
5	TNAZ	1.84	3.0	8.614	21	0
6	RDX	1.80	14.7	8.321	24	0
7	PETN	1.77	–129.0	8.157	12	0
8	DADNE	1.88	–32.0	7.889	126	32.6
9	DINA	1.67	–74.0	7.348	23	0
10	BDNPN	1.73	–65.3	7.343	29	0
11	NG	1.59	–118.7	7.224	10	0
12	2.4DNI	1.76	4.9	6.806	105	9.9
13	TATB	1.94	–33.3	6.710	490	3.3
14	NQ	1.77	–22.0	6.650	320	27.3
15	TE	1.73	8.0	6.590	32	0
16	DATB	1.84	–23.6	6.394	320	5.5
17	TNA	1.77	–18.0	6.131	141	7.5
18	HNS	1.74	16.1	5.731	54	0
19	TNB	1.68	–24.6	5.631	71	0
20	TNT	1.65	–18.0	5.336	98	0

Abbreviations:
1. 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
2. β-HMX 1,3,5,7-tetranitro-1,3,5,7-tetrazocane
3. BTNEN bis(2,2,2-trinitroethyl)nitroamine
4. BTNEU *N,N'*-bis(2,2,2-trinitroethyl)urea
5. TNAZ 1,3,3-trinitroazetidine
6. RDX 1,3,5-trinitro-1,3,5-triazinane
7. PETN pentaerythritol tetranitrate
8. DADNE 2,2-dinitroethylene-1,1-diamine
9. DINA bis(2-nitrooxyethyl)nitroamine
10. BDNPN bis(2,2-dinitropropyl)nitroamine
11. NG glycerol trinitrate
12. 2,4DNI 2,4-dinitroimidazole
13. TATB 1,3,5-triamino-2,4,6-trinitrobenzene
14. NQ nitroguanidine
15. TE *N*-methyl-*N*-nitro(2,4,6-trinitropfenyl)amine
16. DATB 1,3-diamino-2,4,6-trinitrobenzene
17. TNA 2,4,6-trinitroaniline
18. HNS 2,2',4,4',6,6'-hexanitrostilbene
19. TNB 1,3,5-trinitrobenzene
20. TNT 2,4,6-trinitrotoluene

calculated as a part of non-bond energy terms and they are not evaluated individually in *Minimizer module* [26,30]. The values of D1, D2, length of bonds,

E_w and E_s related to one molecule in crystal structure and impact sensitivity for different types of nitro-groups are shown in Table II.

Table II Selected properties for investigated set of explosives

EM	delta Δ1 e	Bond length pm	Impact sensitivity cm	*Ew* kcal mol^{-1}	*Es* kcal mol^{-1}	delta Δ2 e
Nitro-amines N–NO_2						
ε-HNIW	0.965	142.4	17	47.60	150.17	0.4397
β-HMX	0.921	137.3	26	37.85	–60.20	0.4397
BTNEN	0.999	137.5	5	34.25	587.75	0.5469
TNAZ	0.845	135.1	21	–0.22	162.20	0.4886
RDX	0.852	139.8	24	31.80	79.15	0.4403
DINA	0.925	135.7	23	11.50	58.00	0.4368
BDNPN	1.018	136.7	29	22.50	155.20	0.5090
NQ	0.958	133.5	320	35.44	96.06	0.3724
TE	0.904	134.8	32	16.20	41.45	0.4667
Nitro-aliphatic C–NO_2						
BTNEN	0.686	154.4	5	34.25	587.75	0.2702
BTNEU	0.692	153.0	17	20.55	187.80	0.3158
TNAZ	0.682	151.7	21	–0.22	162.20	0.1115
DADNE	1.124	142.6	126	25.75	89.87	0.2611
BDNPN	0.594	153.0	29	22.50	155.20	0.0850
Nitrates O–NO_2						
PETN	0.926	140.4	12	4.50	294.25	0.8062
DINA	0.906	140.5	23	11.50	58.00	0.7382
Ng	0.893	141.4	10	6.90	201.75	0.7136
Nitro-aromatic C–NO_2						
TE	0.697	149.7	32	16.20	41.45	0.0104
TATB	1.009	142.2	490	376.90	480.75	0.1524
DNI	0.747	147.1	105	56.38	162.88	0.3208
DATB	0.889	151.0	320	135.10	214.60	0.0647
TNA	0.819	147.4	141	56.77	84.82	0.0384
HNS	0.716	147.1	54	32.02	28.42	0.0453
TNB	0.728	149.3	71	58.75	20.85	0.0059
TNT	0.730	147.4	98	4.61	48.18	0.0486

Discussion

By comparing detonation energy E_d and value of drop height h_{50} (impact sensitivity) we can conclude that high values of E_d are usually associated with low values of h_{50}. This is not valid generally because of existence of important exception – DADNE. In the case of DADNE the low sensitivity is most probably caused by the influence of hydrogen bond upon increasing stability of structure. Other energetic materials containing a hydrogen bond also show higher value h_{50}

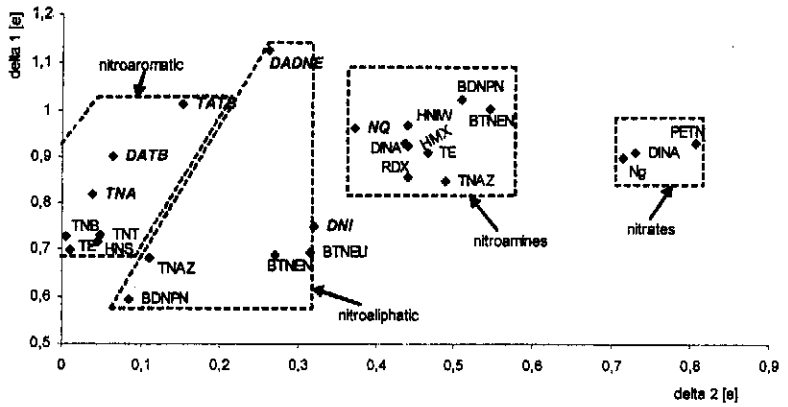

Fig. 1 Relation between Δ1 and Δ2

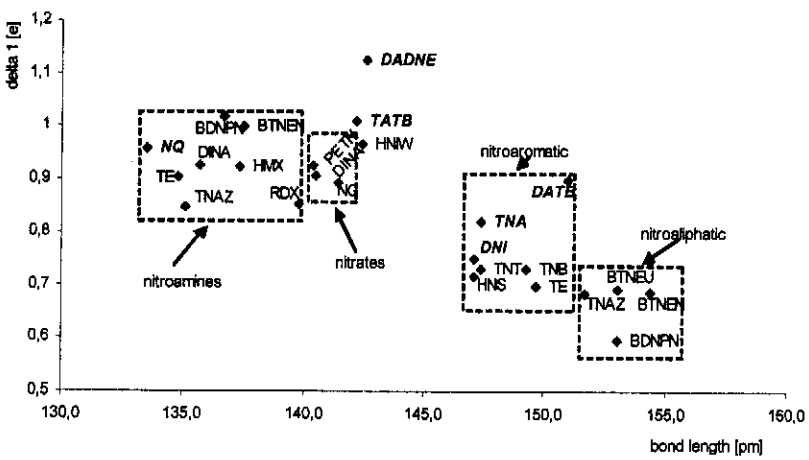

Fig. 2 Relation between Δ1 and bond length X–NO_2 (X = C, H, O)

of impact sensitivity as compared with energetic materials without hydrogen bond. It is possible to conclude that non-covalent hydrogen bonds increase the stability of EM.

Another very important influence on impact sensitivity depends on the type of atoms to which nitro group (–NO_2) is connected. Figure 1 shows values between the difference of partial charges (Δ1) for individual molecule calculated in WinMOPACv.2.0 by AM1 method versus the difference of partial charges (Δ2) for molecules in the crystal structure calculated in program *Cerius2* by Qeq method. Both methods are numerically different but each group (nitro-aromatic,

nitro-aliphatic, nitro-amines and nitrates) form a distinct area as it is represented in Fig. 1 by dashed line. These results allow a prediction that new, not yet prepared EM's can also be added into group area.

Figures 2 and 3 show the dependences of difference in partial charges (Δ1 and Δ2, respectively) versus related bond length. We can divide the groups into two areas. In the first one there are nitro-amines and nitrates, mostly with higher difference in partial charge and shorter bond, and in the second one there are nitro-aromatic and nitro-aliphatic EM. Moreover in comparison with impact sensitivity in Table II we can see the relation between the type of group and charge difference, which means that the low value of impact sensitivity is usually connected with high charge difference and shorter bond. Of course, apart from EM's with hydrogen bond, it is also necessary to keep in mind that some EM's possess several types of nitro groups but impact sensitivity is due to more reactive bond with nitro group. So these results for less reactive bonds can be calculated for better understanding of destruction mechanism of EM but it is still impossible for example to obtain sensitivity for C–NO_2 bond from TE experimentally. Table II shows very impressive difference between nitro bonds in nitro-amine group and nitro-aromatic group from calculation of both Δ1 and Δ2.

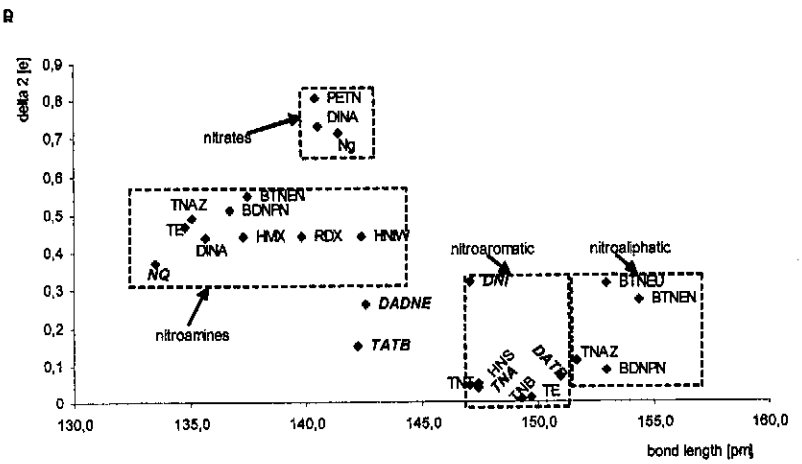

Fig. 3 Relation between Δ2 and bond length X–NO_2 (X = C, H, O)

On the basis of calculated and experimental results from Table II it seems to be true, that nitro groups connected to reactive atoms (O, N) influence the size of impact sensitivity of EM's (BTNEN, DINA, etc.) strongly. Moreover calculations allow us to predict the charge differences for other less reactive types of groups. This could contribute to a better understanding of the structure-properties relationship in development of new energetic materials with desirable properties. But it is necessary to keep in mind that there are a lot of factors and

parameters which influence the behavior of EM's, such as the earlier mentioned non-covalent hydrogen bonds, van der Waals interactions, density, melting temperature, homogeneity, etc. The values of van der Waals energies related to one individual molecule in crystal structure are presented in Table II; they do not show any direct influence upon the impact sensitivity. In the case of energetic crystals with hydrogen bonds (marked bold in Table 2) the van der Waals energy increases because of the hydrogen bond energy is included as a part of *Ew*.

Conclusion

The results presented show possible use of accessible programs suitable for qualitative prediction of impact sensitivity of new EM's with better properties. The non-covalent hydrogen bonds strongly influence increasing impact sensitivity value h_{50} of investigated set of EM's, which is shown especially for NQ and DADNE crystals. The hydrogen bond connection between oxygen and carbon can also play a role in decreasing of impact sensitivity. The bond type and partial charge difference are important factors in decomposition process of EM's. These relations can be more fully specified with knowledge of results for a higher number of EM's based on X-ray and neutron diffraction analysis and with development of computational software or with *ab-initio* calculation methods.

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