Crystal Lattice Free Volume in a Study of Initiation Reactivity of Nitramines: Friction Sensitivity.

Svatopluk Zeman[a*], Ning Liu[b], Marcela Jungová[a], Ahmed K. Hussein[a], Qi-Long Yan[c]

[a] *Institute of Energetic Materials, Faculty of Chemical Technology, University of Pardubice, CZ-532 10 Pardubice, Czech Republic (Czechia);*
[b] *Xi'an Modern Chemistry Research Institute,Xi'an, Shaanxi, 710065, China;*
[c] *School of Astronautics, Northwestern Polytechnical University, Xi'an 710072 Shaanxi, China;*

Abstract

The relationship between friction sensitivity (FS) and the crystal lattice free space per molecule, ΔV, of thirteen nitramines is described by a linear equation, divided into a number of the partial relationships with strong limitations by their molecular structure characteristics. Increasing FS due to raising of the ΔV values is not clearly confirmed. The influence of the ΔV values on friction sensitivity of nitramines is similar to that of their aza atoms which influence the mutual orientations of nitro groups in neighboring molecules. The dipole-dipole interaction of the oxygen and nitrogen atoms of nitro groups in neighboring nitramine molecules has a major effect on their own FS. In accordance with this interaction, a directly proportional relationship was derived between FS and the intrinsic gas phase molecular volume, V_{int}, of the nitramines mentioned, which is divided also into several straight lines according to relatively tight molecular structure similarity. The relationships found again confirm a level of disorder in the distribution of the forces in the crystal lattice of the "common" quality of ε–2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane, in comparison with its reduced sensitivity (RS) or chemically pure analogue.

Keywords: Crystal lattice; Friction; Initiation reactivity; Nitramines;

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*Corresponding author: svatopluk.zeman@upce.cz

1. Introduction

Over the last 30 years, the main interest in initiation of high energy materials has been focused on studies of shock and impact sensitivities [1, 2]. In comparison with these, no similar attention has been paid to the friction sensitivity (FS) of such materials. We have dealt with FS intensely over the last five years [3 – 8]. Our experience shows that the results of the FS determination can be heavily

influenced by “human variability”. Nevertheless, careful measurements [3] by a single researcher provide results showing relationships which correlate with the output of other sensitivity parameters [4 - 8], with ^{15}N NMR chemical shifts of the key nitrogen atoms in the reaction center of the molecule [7] or with the DFT calculation outputs [8]. Therefore, it should not be without interest to use in the FS outputs analysis recent knowledge about free spaces in crystal lattice of energetic materials (EMs), ΔV, and about their influence on the EMs' impact sensitivity [9 - 13]. Recently we have analyzed a relationship between the ΔV values and impact sensitivity of eighteen nitramines [13]. In the present paper, which can be taken as a continuation of those studies [4 – 8], we use the same approach in analyzing similar relationships for friction sensitivity of thirteen nitramines.

2. Data Sources

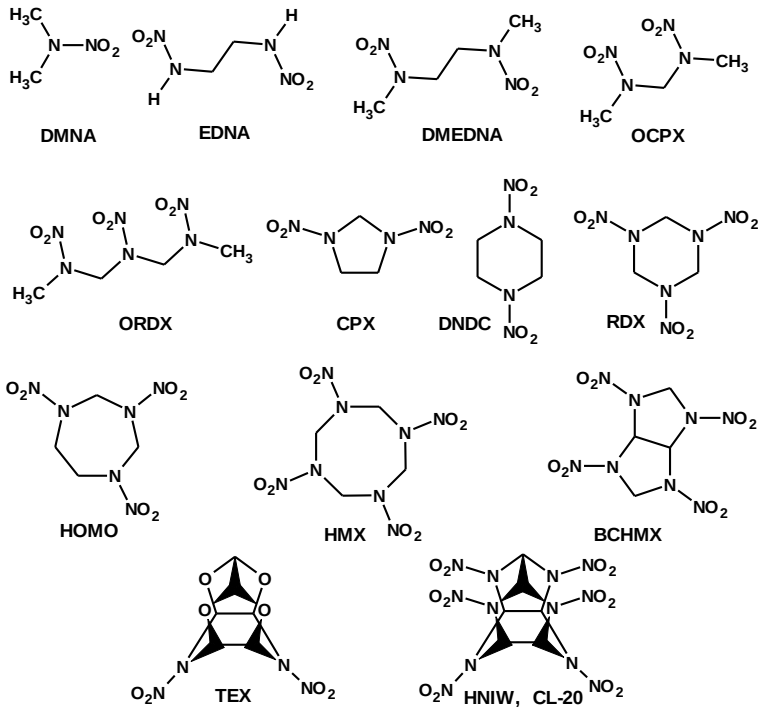
2.1. Nitramines under study

Chemical names, code designations and impact sensitivity, expressed as friction energy of the nitramines studied are summarized in Table 1. For a better illustrative view, structural formulas of these nitramines are presented in Scheme 1.

Table 1. A review of the nitramines studied and their friction sensitivities (FS) from papers [4, 7]

Data No.	Chemical name of nitramine	Code designation	FS [4, 7] (N)
1	2-Nitro-2-azapropane	DMNA	82.4
2	1,4-Dinitro-1,4-diazabutane	EDNA	47.4
3	2,5-Dinitro-2,5-diazahexane	DMEDNA	57.9
4	2,4-Dinitro-2,4-diazapentane	OCPX	74.9
5	2,4,6-Trinitro-2,4,6-triazaheptane	ORDX	147.7
6	1,3-Dinitroimidazolidine	CPX	57.7
7	1,4-Dinitropiperazine	DNDC	122.3
8	1,3,5-Trinitro-1,3,5-triazinane	RDX	148.5
9	1,3,5-Trinitro-1,3,5-triazepane	HOMO	119.9
10	β–1,3,5,7-Tetranitro-1,3,5,7-tetrazocane	β–HMX	154.4
11	*cis*-1,3,4,6-Tetranitrooctahydroimidazo[4,5-d]-imidazole	BCHMX	66.1
12	4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane	TEX	161.3
13.1	ε–2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane	RS-ε–HNIW	84.4[a]
13.2		ε–HNIW	69.0

Note: [a] determined in the present paper; RS–ε–HNIW is a product with reduced sensitivity prepared according to patent [14].



Scheme 1: Structural formulas of the nitramines studied

2.2. Friction Sensitivity

The friction sensitivities of all the nitramines studied were determined [4, 7] by means of the BAM friction test apparatus operated under standard test conditions [15] with evaluation of the output by Probit analysis [16] (only the normal force at which 50% of initiations occur is reported in Table 1).

2.3. Results of Calculation for Crystal Lattice Free Volume of Nitramine Explosives

The object molecules were optimized at computational level of B3LYP/6-311+g(d,p) by using the Gaussian 09 package [17]. All of the optimized structures were characterized to be true local energy minima on the potential energy surfaces without imaginary frequencies. The crystal volume [$V(0.003)$] was calculated by using the Multiwfn [17 - 19] software. The effective volume per molecule (V_{eff}) is calculated as:

$$V_{\text{eff}} = M/d \qquad (1)$$

where M is molecular mass, and d is crystal density. The intrinsic gas phase molecular volume (V_{int}) is calculated by the 0.003 au surface according to Ref. 13, $V_{int} = V(0.003)$. Therefore, the free space per molecule (ΔV) is:

$$\Delta V = V_{eff} - V_{int} = V_{eff} - V(0.003) \qquad (2)$$

Results of these calculations are summarized in Table 2, together with crystal densities of the nitramines studied.

Table 2. A survey of the molecular mass, *M,* crystal densities, *d*, effective volume per molecule, V_{eff}, intrinsic gas phase volume, V_{int}, and free space per molecule, ΔV

Comp.	Mol. mass	M $\times 10^{-24}$ (g)	d (g cm^{-3})	V_{eff} (Å^3)	V_{int} (Å^3)	ΔV (Å^3)
DMNA	90.1	149.67	1.36	110.05	81.72	28.33
EDNA	150.1	249.34	1.65	151.12	119.69	31.43
DMEDNA	178.1	295.85	1.45	204.03	153.19	50.84
OCPX	164.1	272.59	1.50	181.73	135.88	45.85
ORDX	238.2	395.68	1.66	238.36	189.56	48.80
CPX	162.1	269.27	1.65	163.19	126.03	37.16
DNDC	176.1	292.52	1.63	179.46	142.23	37.23
RDX	222.1	368.94	1.81	203.83	161.97	41.86 (46)
HOMO	236.1	392.19	1.77	221.58	178.06	43.52
HMX	296.2	492.03	1.91	257.61	214.79	42.82 (49)
BCHMX	294.2	488.70	1.92	254.53	206.06	48.47
TEX	262.2	435.55	1.99	218.87	179.33	39.54
ε-HNIW	438.2	727.91	2.04	356.82	290.84	65.98

Note: The ΔV values listed in brackets are taken from Ref. 11

3. Results and Discussion

In papers [4, 7] we found a semi-logarithmic relationship between impact and friction sensitivities of the nitramines which, in the case of individual compounds, is divided into a number of partial relationships in close correlation with the molecular structure characteristics of these compounds [7]. If we also take into account our findings in paper [13], it should be clear that friction sensitivity is in a semi-logarithmic relationship with the crystal lattice free volume per molecule, ΔV, of the nitramines studied, as shown in Figure 1.

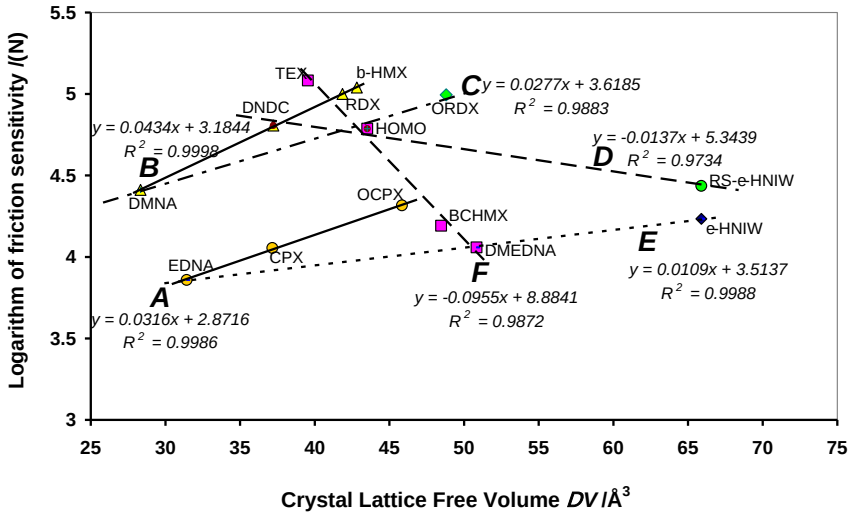


Figure 1: Molecular structure analysis of the relationship between friction sensitivity and free space per molecule, *ΔV.*

This relationship is broken into the partial straight lines which are strongly limited by the molecular structure similarity. Only straight lines D and F correspond to the expected trend of increase in friction sensitivity with the increase in *ΔV* values; in molecular skeletons of all the nitramines, the data for which are associated with these lines, it is possible to find the molecular skeleton of DMEDNA (or part of it).

Data for compounds which can theoretically be generated from the DMNA molecule are associated with the straight lines B and C. The OCPX molecule on the straight line A is as if it is an "opened" molecule of 1,3-dinitroimidazolidine (CPX) in the skeleton of which one can find the ethylene dinitramine grouping.

The position of ε–HNIW in Fig. 1 is interesting. Its data correlate well with those of DMEDNA and EDNA using the straight line E. Comparison with the nitramines associated with the straight line D clearly shows that the difference between ε–HNIW and its RS-analogue rests in the difference in the intensity and uniformity of intermolecular interactions in their crystals. From this comparison it seems as if in the ε–HNIW crystals only the nitro groups in positions 2,4,6, and 8 have a major part to play in the intermolecular force in its crystals – in so doing, the most reactive nitramino grouping is in position 2 of this particular nitramine [1, 7, 20, 21].

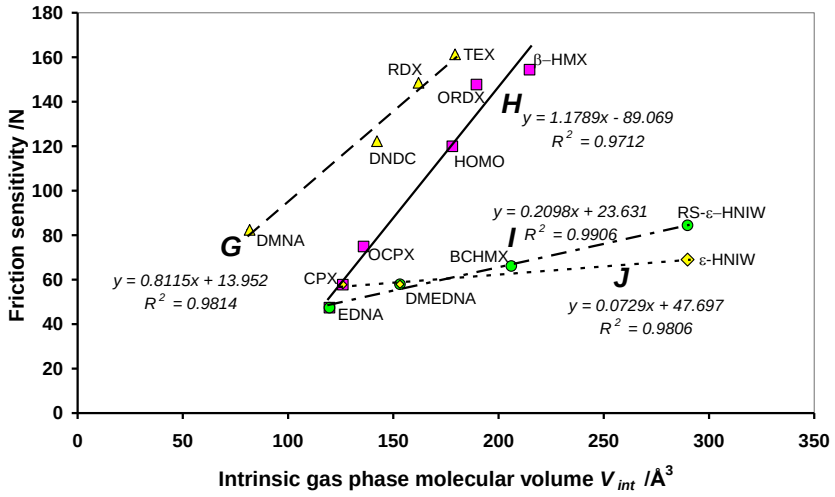


Figure 2: Molecular structure analysis of the relationship between friction sensitivity and intrinsic gas phase molecular volume, V_{int}, in the nitramines studied.

For all the nitramines studied a direct proportionality exists between their intrinsic gas phase volume, V_{int} (V(0.003)), and corresponding friction sensitivity, as shown in Fig. 2. This is understandable because the friction force during shearing is proportional to the contact area. Also here it is possible to observe a limitation by molecular structure similarity. In this case, the difference in the crystals of both kinds of HNIW is demonstrated by comparison of the straight lines I and J, with the same possible explanation as in the case of Fig. 1. In each case it demonstrates that ??HNIW (technical or "common" quality) gives the impression of disorder in the distribution of the forces in its crystal lattice in comparison with its RS or chemically pure analogue [13].

It is interesting that the composition and sequence of nitramines associated with straight line I are the same as in the corresponding partial relationship between FS and the ^{15}N NMR chemical shifts of nitrogen atoms in the most reactive nitro groups of these nitramines [7]. The oxygen atoms of nitro groups, by their dipole-dipole interactions, contact the oxygen and nitrogen atoms of nitro groups in neighboring nitramine molecules in the crystal [22 – 24], which is the decisive factor governing the crystal structure of nitramines. The type of interaction mentioned will act against the shear slide during friction. Aza atoms (i.e. bearers of these nitro groups) influence the mutual orientations of nitro groups in neighboring molecules by means of conformation of molecular skeletons. This conformation has a determining influence on the crystal lattice free volume. As aza atoms are "inner" atoms of the nitramines' molecular skeleton, their effect on the intermolecular potential will be lower than that of the nitro groups attached to them [7]. Therefore, the crystal lattice free volumes should have a similar

influence on this potential. This has already been shown in the case of the relationship between impact sensitivity and crystal lattice free volumes in paper [13].

4. Conclusion

The relationship between friction sensitivity (FS, shear slide with fixed volume) and the crystal lattice free space per molecule, ΔV, of the nitramines studied is described by a linear equation which is divided into a number of partial relationships with a strong limitation created by the molecular structure characteristics of such compounds. It is not possible to say clearly that increasing ΔV values leads to increasing FS and vice versa. It is possible to see some similarity with the influence of aza atoms on FS [7]. These atoms, as part of the molecular skeleton of nitramines, influence the mutual orientations of nitro groups in neighboring molecules by means of conformation of the nitramine molecules and thus determine simultaneously the crystal lattice free space per molecule. Also, in friction sensitivity, the dominating influence is thus the dipole-dipole interaction on the base of mutual contacts of the oxygen and nitrogen atoms of nitro groups in neighboring nitramine molecules. In agreement with this interaction, a directly proportional relationship was found between FS and the intrinsic gas phase molecular volume, V_{int}, of the nitramines mentioned, which is divided into several straight lines according to relatively tight molecular structure similarity. Both types of friction sensitivity relationships found again confirm the disorder in distribution of the forces in the crystal lattice of the "common" quality of □□□2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane, in comparison with its RS or chemically pure analogue.

Acknowledgement

The work described in this paper partially received financial support from the Students Grant Projects No. SGSFCHT_2016002 of the Faculty of Chemical Technology at the University of Pardubice, partially it was created in the framework of the six month trainee-ship of Dr. LIU Ning in Institute of Energetic Materials at University of Pardubice in 2016 under financial support of the Chinese State Administration of Foreign Experts Affairs

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