Friction Sensitivity of Nitramines Part IV: Links to Surface Electrostatic Potentials

Zdeněk Friedl[1], **Marcela Jungová**[1], **Svatopluk Zeman**[1], **Adéla Husárová**[2]

(1. *Faculty of Chemistry*, *Brno University of Technology*, *CZ*-612 00 *Brno*, *The Czech Republic*；2. *Institute of Energetic Materials*, *Faculty of Chemical Technology*, *University of Pardubice*, *CZ*-532 10 *Pardubice*, *The Czech Republic*)

Abstract：The friction sensitivity (FS) of five aliphatic linear and eight cyclic nitramines has been determined and correlated with DFT B3LYP/6-31-G(d,p) // 6-311 + G(d,p) positive ($V_{S,max}$) and negative ($V_{S,min}$) extremes of molecular surface electrostatic potentials $V_S(r)$. While there is an ambiguous relationship between the $V_{S,max}$ values and FS values, the decrease of FS is connected (more or less) with increase in $V_{S,min}$ values.

Key words：physical chemistry；electrostatic potential；friction；nitramines；sensitivity

---

1 Introduction

The reasons of our interest in study of friction sensitivity (FS) were mentioned in the previous parts of this series[1-3]. One of the applied characteristics for evaluation of sensitivity of energetic materials (EMs) is their electrostatic surface potentials $V_S(r)$ (ESP)；Politzer and co-workers[4-6] established correlations between the features of the quantum chemically determined ESP surrounding an isolated molecule and many of its condensed-phase properties. The most sensitive molecules have high levels of the imbalance between the positive ($V_{S,max}$) and negative ($V_{S,min}$) extremes of surface potentials[5]. Politzer et al. use the $V_{S,max}$ values for dealing with the problems of impact sensitivity of EMs[4-6]. This strong positive ESP is concentrated on the surface, more or less near the centre of the molecule, while the weaker negative ESP is on the periphery of the molecule (it is connected with the charges at oxygen atoms of nitro groups)[5]. In this present work we have focused our attention on the relationship between FS and both extremes of ESP；it must be stated that we have used the $V_{S,max}$ and $V_{S,min}$ as the most simple features of the surface electrostatic potentials which are accessible from the standard output of DFT surface calculations.

2 Substances and Data Sources

Table 1 presents a set of nitramines and their FS data (see also papers[1-3]). The purity of the nitramines tested was the same as in the case of previous parts[1-3]. The friction sensitivity of all the nitramines studied was determined by means of the BAM friction test apparatus operated at standard test conditions[7] with evaluation of the outputs by Probit analysis[8] (only the normal force at which 50% of initiations occur is reported as the friction sensitivity[1-3] as in Table 1). The equilibrium geometries of all nitramines studied were optimized at the DFT B3LYP/6-311 + G(d,p) level and the electron energies obtained were refined by the not-scaled ZPE correction. The molecular surface electrostatic potentials $V_S(r)$ were calculated at DFT B3LYP/6-31G(d,p) // 6-311 + G(d,p) level and the molecular surface was taken to be 0.001 e·au^{-3} contour of the electron density. The results are shown in Table 1.

Table 1 A table of the nitramines studied, their surface electrostatic potentials and friction sensitivities (50% probability of initiation)[1-3]

data No.	chemical name of nitramine	code design	surface electrostatic potential/kJ·mol^{-1}		friction sensitivity[1-3]/N
			$V_{S,max}$	$V_{S,min}$	
1	2-nitro-2-azapropane	DMNA	111.74	−154.75	82.4
2	1,4-dinitro-1,4-diazabutane	EDNA	227.35	−126.16	47.4
3	2,4-dinitro-2,4-diazapentane	OCPX	113.14	−122.50	74.9
4	2,4,6-trinitro-2,4,6-triazaheptane	ORDX	145.50	−140.31	147.7
5	2,5-dinitro-2,5-diazahexane	DMEDNA	146.56	−159.54	57.9
6	1,3-dinitroimidazolidine	CPX	131.87	−116.94	57.7
7	1,4-dinitropiperazine	DNDC	109.00	−121.98	122.3
8	1,3,5-trinitro-1,3,5-triazinane	RDX	182.51	−89.44	148.5
9	1,3,5-trinitro-1,3,5-triazepane	HOMO	151.30	−117.63	119.9
10	β-1,3,5,7-tetranitro-1,3,5,7-tetrazocane	ε-HMX	232.85	−114.68	154.4
11	*cis*-1,3,4,6-tetranitrooctahydroimidazo[4,5-*d*]-imidazole	BCHMX	212.09	−83.86	66.1
12	ε-2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane	ε-HNIW	229.23	−67.84	69.0
13	4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane	TEX	136.93	−98.04	161.3

---

3   Results and Discussion

Figure 1 gives a comparison of the FS values of studied nitramines with their strong positive ($V_{S,max}$) ESPs. The trend of the indicated relationships is not unequivocal here. A relatively close molecular-structural similarity exists in each of the groups. The most reactive group is that containing the nitramines CPX-DMEDNA-BCHMX-HNIW like in the previous parts of this series[1-3]. This might be due to the bond configuration of the aza atoms carrying the nitro group that is primarily leaving in the initiation. It is known that pyramidal configuration at these atoms is connected with increased reactivity of the nitramines as compared with the nitramines of planar configuration[9]. The pyramidal configuration at the aza atoms was found in the CPX molecules in gaseous phase[10]. Crystallographic studies of BCHMX[11] and HNIW[12] show that the aza atoms corresponding with the longest N—NO$_2$ bonds have pyramidal bond configuration too. However, the DMEDNA molecule does not contain this kind of nitrogen atoms, and dihedral angle between planes CCN—NO$_2$ in its molecule is $15°$[16]. Imaginary transition from the DMEDNA skeleton into others molecules of the mentioned group brings into each of them corresponding conformational increment and reaction center. This transition must connect with change not only of the mentioned dihedral angle but also with change of corresponding "surrounding of the reaction center" (steric and inductive effects there); these effects should change of the configuration on aza atoms. The second straight line with positive slope in Fig. 1 includes the data of ORDX, RDX and HMX; the crystallographic studies of RDX (see the references in Ref. [13]) and HMX[14,15] show that the aza atoms in these molecules have planar bond configurations. Logically, the nitramines mentioned possess a lower reactivity, i. e. a lower FS. Hence the trends with positive slope in Fig. 1 are predominantly determined by the configuration at the reaction centre of the molecules of studied nitramines.
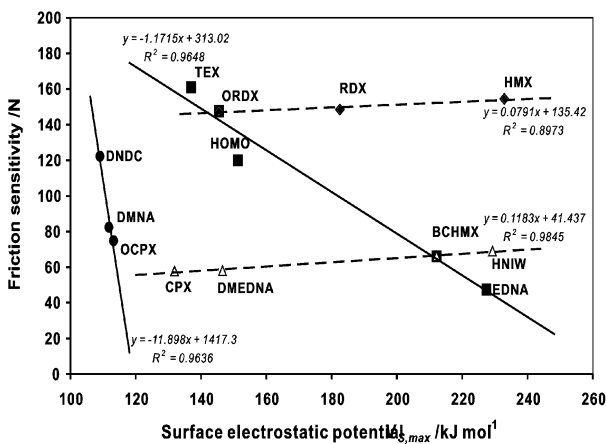

Fig. 1   Comparison of friction sensitivity of the studied nitramines with their maximum positive surface electrostatic potentials $V_{S,max}$

The interpretation of the trends with negative slope in Fig. 1 is more problematic. With respect to the definition of the $V_{S,max}$ values, the interpretation might lie in the dominant effect of molecular conformation upon the shear module of the respective nitramines. What has been said can be demonstrated

on the example of EDNA: in its molecular crystal there exist weak intermolecular hydrogen bonds[16], which sort of cross-link the molecular crystal (increase its shear resistance); however, the EDNA skeleton brings into the imaginary derived molecules BCHMX, HOMO and TEX basic conformational increment and reaction center; but here the increment differs from those of DMEDNA. It must be stated that beside BCHMX TEX has the pyramidal configuration at its aza atoms[17]; "tetraacetal's super-structure" in its molecule operates here as a lubricant.
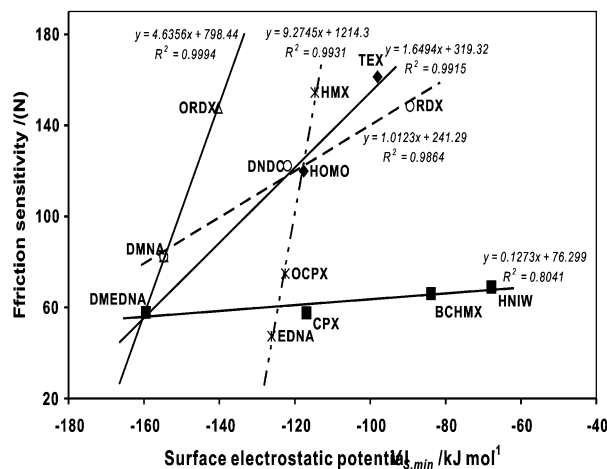

Fig. 2   Comparison of friction sensitivity of the studied nitramines with their minimum negative surface electrostatic potentials $V_{S,min}$

The initiation reactivity of poly nitro compounds is most often due to the nitro group[18-20]: either through the homolysis of its bond to the rest of molecule (i. e. C—NO$_2$, N—NO$_2$ or O—NO$_2$ bonds) or through the interactions of its oxygen atoms with the substituents at ortho-position (the case of "trinitrotoluene mechanism" of primary fragmentation)[18-21]. As already stated, the electron configuration of oxygen atoms in nitro groups corresponds with the weaker negative surface electrostatic potentials, i. e. $V_{S,min}$ values. A comparison of these ESP with FS is presented in Fig. 2. Here the increasing $V_{S,min}$ values are (more or less) connected with decreasing FS values. In this context we should mention the work by Zhang et al. [22-23] in the field of application of DFT computation methods to the study of sensitivity: the authors found that the net charges of nitro groups in isolated molecules can be regarded as structural parameters to estimate the impact sensitivity, and the most negative charge values being connected with the lowest impact sensitivity[22-23]. It was shown that increasing FS corresponds with decreasing impact sensitivity[1]—or in other words, the trends shown in Fig. 2 correspond with the mentioned finding of Zhang et al. [22-23]. The groups of nitramines in Fig. 2 are notionally derived mainly from DMEDNA, and to a lesser degree from DMNA and EDNA. The molecular-structural kinship in the individual groups is also reflected by the similarity of intermolecular interactions in molecular crystals of the respective nitramines and, hence, the similarity of their sensitivities to mechanical stimuli (sensitivity as a function of intermolecular interactions, see Refs [1,21,24,]). The mentioned interactions (their effect upon the initiation reactivity) might be the reason for the classification of nitramines in the sense of Fig. 2.

4 Conclusion

The relationship between the maximum positive surface electrostatic potentials ($V_{S,max}$) and friction sensitivity (FS) is not unequivocal. In the groups of nitramines in which its increase is connected with a decrease (not very distinct) in FS, the dominant role in the initiation reactivity is most likely played by the bonds configuration of aza nitrogen atoms; the conformation of molecules might perhaps play the dominant role in the group of nitramines exhibiting the opposite trend in the relationship of FS versus the $V_{S,max}$ values. The trend of the relationship between minimum negative surface electrostatic potentials ($V_{S,min}$) and the FS values stands in relatively good accordance with the evaluation of initiation reactivity by means of the net charges of nitro groups; in this case, FS more or less decreases with increasing $V_{S,min}$ values. It can be seen that the $V_{S,min}$ values correspond better than the $V_{S,max}$ values with the initiation reactivity. This conjecture agrees well with the fact that nitro group is the centre of initiation reactivity of nitro compounds.

References:

[1] Jungová M, Zeman S, Husáová A. Friction Sensitivity of Nitramines. Part I. Comparison with Impact Sensitivity and Heat of Fusion[J]. *Chinese Journal of Energetic Materials* (*Hanneng Cailiao*), in press.

[2] Jungová M, Zeman S, Husáová A. Friction Sensitivity of Nitramines. Part II. Comparison with Thermal Reactivity[J]. *Chinese Journal of Energetic Materials* (*Hanneng Cailiao*), in press.

[3] Zeman S, Jungová M, Husáová A. Friction Sensitivity of Nitramines. Part III. Comparison with Detonation Characteristics[J]. *Chinese Journal of Energetic Materials* (*Hanneng Cailiao*), in press.

[4] Politzer P, Murray J, Sensitivity Correlations[C/M], Politzer P., Murray J. (Eds) Theoret. Comput. Chem., Vol. 13, Energetic Materials, Part 2, Detonation, Combustion. Elsevier B. V., Amsterdam, 2003, p. 5.

[5] Murray J S, Concha M C, Politzer P. Links Between Surface Electrostatic Potentials of Energetic Molecules, Impact Sensitivities and C—NO_2/N—NO_2 Bond Dissociation Energies [J]. *Mol Phys*, 2009, 107:89.

[6] Pospíšil M, Vára P, Concha M C, et al. A Possible Crystal Volume Factor in the Impact Sensitivities of some Energetic Compounds [J]. *J Mol Model*, 2010, 16(5): 895.

[7] Sućeska M. Test Methods for Explosives, Springer, Heideleberg, 1995.

[8] Šelešovský J. and Pachmáň H J. Probit Analysis—a Promising Tool for Evaluation of Explosive's Sensitivity [J]. *Centr Eur J Energet Mater*, 2010, 7(3): 269.

[9] Korsunskii B L, Manelis G B, Nazin G M, et al. Methodological Problems in Determination of the Thermal Stability of Explosives [J]. *Ros Khim Zh*, 1997, 41(4): 49.

[10] Shishkov I F, E > fimova T L, Vilkov L V, et al. Molecular Structure of 1,3-Dinitro-1,3-diazacyclopentane in the Gas Phase [J]. *Zh Strukt Khim*, 1992, 33(1): 35.

[11] Klasovitý D, Zeman S, Růžička A, et al. *cis*-1,3,4,6-Tetranitrooctahydroimidazo-[4,5-*d*]imidazole (BCHMX), its Properties and Initiation Reactivity [J]. *J Hazard Mater*, 2009, 164 (2–3):954.

[12] Ou Y, Jia H, Xu Y. Synthesis and Crystal Structure of β-Hexanitrohexaazaisowurtzitane for Explosives [J]. *Sci in China*, *Series B*: *Chemistry*, 1999, 42(2): 217.

[13] Filhol A, Clement C, Forel M-T. Molecular Conformation of 1,3,5-Trinitrohexahydro-*s*-triazine [J]. *J Phys Chem*, 1997, 75: 2056.

[14] Cady H H, Larson A C, Cromer D T. The Crystal Structure of α-HMX and a Refinement of the Structure of a-HMX [J]. *Acta Cryst*, 1963, 16(7): 617.

[15] Choi C S, Boutin H P. Study of the Crystal Structure of β-Cyclotetramethylenetetranitramine by Neutron Diffraction [J]. Acta. Cryst. B1970, 26:1235.

[16] Atovmyan L O, Golovina N I, Zolotoy A B, et al. Structure and Packing of Primary and Secondary Nitro Amines [J]. *Zh Org Khim*, 1988, 24(9):1848.

[17] Karaghiosoff K, Klapötke T M, Michailovski A, et al. 4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane (TEX): a nitramine with an exceptionally high density [J]. *Acta Cryst*, C2002, 58:o580.

[18] Manelis G B, Nazin G M, Rubtsov Yu I, et al. Thermal Decomposition and Combustion of Explosives and Propellants [M]. Taylor&Francis, New York, 2003.

[19] Shackelford S A. Role of Thermochemical Decomposition in Energetic Materials Initiation, Sensitivity and Explosive Performance [J]. *Centr Eur J Energet Mater*, 2008, 5(1):75.

[20] Zeman S. A study of Chemical Micro-Mechanisms of Initiation of Organic Polynitro Compounds [C/M] Politzer P., Murray J. (Eds) Theoretical and Computational Chemistry, Vol. 13, Energetic Materials, Part 2, Detonation, Combustion. Elsevier B. V., Amsterdam, 2003, p. 25.

[21] Zeman S. Sensitivity of High Energy Compounds[C/M]. In Klapoetke T. (Ed), High Energy Density Materials, Series: Structure & Bonding, 125, Springer, New York, 2003, p. 195.

[22] Zhang C, Shu Y, Wang X, Theoretical Investigation of the Relationship between Impact Sensitivity and the Charges of the Nitro Group in Nitro Ccompounds. [J]. *J Energet Mater*, 2005, 23: 107.

[23] Zhang C, Shu Y, Huang Y, et al. Investigation of Correlation between Impact Sensitivities and Nitro Group Charges in Nitro Compounds [J]. *J Phys Chem*, 2005, B109:8978–8982.

[24] Zeman S, Krupka M. Aspects of Impact Reactivity of Polynitro Compounds, Part III. Impact Sensitivity as a Function of the Intermolecular Interactions. [J]. *Propellants*, *Explos Pyrotech*, 2003, 28(6): 301.