



## Electric Spark Sensitivity of Polynitro Arenes. Part II. Aspects of the Molecular Structure with Utilization of the Net Charges of Nitro Groups

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*

Zdeněk FRIEDL

*Faculty of Chemistry, Brno University of Technology  
CZ-612 00 Brno, Czech Republic*

Jiří KOČÍ

*Austin Detonator, Ltd., CZ-755 01 Vsetín, Czech Republic*

**Abstract:** An ESZ KTTV instrument of a new, relatively simple construction has been applied to the determination of electric spark sensitivity ( $E_{ES}$ ) of 31 polynitro arenes and their derivatives. Results obtained are compared with the theoretical DFT B3LYP/6-31G(d,p) Mulliken net charges of nitro groups,  $Q_{NO_2}$ , which primarily react in the initiation by the spark. On the basis of analysis of the results obtained it is shown that intermolecular interaction plays in this initiation a considerable role. However, generally accepted presumption, that most positive  $Q_{NO_2}$  value represents a sensitivity of the given molecule, is not valid without reserve. If the polynitro aromatic molecule contains several potential reaction centres, the proper initiation might then be realized selectively (depending on the kind of initiation impulse).

**Keywords:** electric spark, Mulliken net charges, sensitivity, polynitro arenes

## Introduction

In our recent papers [1, 2] attention was focused on mutual comparison of results of the measurements of sensitivity of polynitro compounds to electric spark performed on two different types of apparatus. It was shown [1, 2] that the apparatus developed in a financial support from Czech Ministry of Industry and Commerce [3] (referred to as ESZ KTTV [4-6]) provides results that are more closely connected with molecular structure.

It is well known that nitro groups in a molecule of polynitro compound are not equivalent from the standpoint of their initiation reactivity [7, 8]. One of the methods of specification of the nitro group reacting as the first, consists in finding the direct correlation between initiation characteristics and electron charges at the nitrogen atoms of the said nitro group [1, 7, 8]. Some authors found that the theoretical Mulliken net charges of nitro groups,  $Q_{NO_2}$ , calculated by means of DFT BLYP/DNP method, can be regarded as structural parameters that can be used to estimate the impact sensitivity [8-11]. This finding was extended to molecular structure vs. electric spark sensitivity correlations of nitramines [1].

The present paper forms a continuation of our earlier work [1] and shows the molecular structure vs. electric spark sensitivity correlations of polynitro arenes with utilization of the mentioned above net nitro groups charges,  $Q_{NO_2}$ .

## Experimental

### The compounds studied

A survey of the tested polynitro arenes and their derivatives is given in Table 1. All the compounds were purified by crystallization in motion, and often by precipitation crystallization (with a good stirring) from organic solvents. The crystallization was carried out in such a way as to obtain the product appearing as individual in thin layer chromatography. However, the granulometry of the substances investigated was not specified.

**Table 1.** A survey of the studied polynitro arenes and their derivatives, their code designation and electric spark sensitivity (designed as a spark energy  $E_{ES}$ ) [2, 12].

Chemical name of polynitro arene	Code designation	$E_{ES}$ (mJ)
1,3-Dinitrobenzene	1,3-DNB	256.7
1,4-Dinitrobenzene	1,4-DNB	403.3
1,3,5-Trinitrobenzene	TNB	108.2
2,2',4,4',6,6'-Hexanitro-1,1'-biphenyl	HNB	286.7
2,4,6,4',6',2'',4'',6''-Octanitro[1,1',3',1'']terphenyl	ONT	128.9 <sup>a</sup>
2,4,6,2',4',6',2'',4'',6''-Nonanitro[1,1',3',1'']terphenyl	NONA	158.2
2,4,6,2',4',6',2'',4'',6'',2''',4''',6'''-Dodecanitro[1,3',1',1'',3'',1''']-quaterphenyl	DODECA	157.8 <sup>a</sup>
1,5-Dinitronaphthalene	1,5-DNN	180.0
1,8-Dinitronaphthalene	1,8-DNN	238.2
1,4,5-Trinitronaphthalene	TNN	210.0
1,4,5,8-Tetranitronaphthalene	TENN	95.0
2,4,6-Tris(2,4,6-trinitrophenyl)-[1,3,5]triazine	TPT	283.3
<i>N,N</i> -Bis(2,4-dinitrophenyl)-2,4,6-trinitroaniline	NTFA	50.2
5,7-Dinitro-1-(2,4,6-trinitrophenyl)-1 <i>H</i> -1,2,3-benzotriazole	BTX	135.0
2-Methyl-1,3,5-trinitrobenzene	TNT	111.8
2,4,6-Trimethyl-1,3,5-trinitrobenzene	TNMs	292.7
2-Amino-1,3,5-trinitrobenzene	PAM	156.7
2,4-Diamino-1,3,5-trinitrobenzene	DATB	175.0
2,4,6-Triamino-1,3,5-trinitrobenzene	TATB	293.3
2-Chloro-1,3,5-trinitrobenzene	CTB	101.0
2-Hydroxy-1,3,5-trinitrobenzene	PA	115.5
2,4,6-Trinitro- <i>N</i> -(2,4,6-trinitrophenyl)aniline	DPA	103.0
1,1'-Methylenebis(2,4,6-trinitrobenzene)	DPM	136.4
1,1'-Ethane-1,2-diylbis(2,4,6-trinitrobenzene)	DPE	167.0
3,3'-Dimethyl-2,2',4,4',6,6'-hexanitro-1,1'-biphenyl	BITNT	206.7
Bis(2,4,6-trinitrophenyl) sulfide	DIPS	125.5
Bis(2,4,6-trinitro-3-methylphenyl) sulfone	DIPSO	186.7
Bis(2,4,6-trinitro-3-methylphenyl) sulfide	DMDIPS	112.7
( <i>E</i> )-Bis(2,4,6-trinitrophenyl)diazene	HNAB	112.0
( <i>E</i> )-Bis(3-methyl-2,4,6-trinitrophenyl)diazene	DMHNAB	118.2
1,3,7,9-Tetranitro[1,2,3]benzotriazolo[2,1- <i>a</i> ][1,2,3]benzotriazole-5,11-diium-6,12-diide	TACOT-Z	883.0 <sup>a</sup>

Note: <sup>a</sup>) the data obtained in this paper

**Table 2.** A survey of the net charges of nitro groups in molecules of polynitro arenes studied

Polynitro arene	Net charge at nitro group		Polynitro arene	Net charge at nitro group	
	position in molecule	$Q_{\text{nitro}}$ (e)		position in molecule	$Q_{\text{nitro}}$ (e)
1,3-DNB	<b>1,3-</b>	<b>-0.3603</b>	TPT	<b>2-</b>	<b>-0.3073</b>
1,4-DNB	<b>1,4-</b>	<b>-0.3484</b>		4-	-0.3352
TNB	<b>1,3,5-</b>	<b>-0.3335</b>	TNT	<b>1-</b>	<b>-0.3529</b>
HNB	2-	-0.3433		3-	-0.3516
	<b>4-</b>	<b>-0.3384</b>	TNMs	<b>1,3,5-</b>	<b>-0.3738</b>
NONA	2-	-0.3375	PAM	<b>1-</b>	<b>-0.3852</b>
	4-	-0.3290		3-	-0.3764
	6 <sup>+</sup>	-0.3514	DATB	1-	-0.4717
	2 <sup>+</sup>	-0.3407		<b>3-</b>	<b>-0.4205</b>
ONT	6-	-0.3333	TATB	<b>1,3,5-</b>	<b>-0.5042</b>
	2-	-0.3313	PA	<b>1-</b>	-0.3388
	4-	-0.3390		3-	-0.3482
	6 <sup>++</sup>	-0.3331	CTB	<b>1-</b>	<b>-0.3146</b>
	2 <sup>++</sup>	-0.3322		3-	-0.3360
	4 <sup>++</sup>	-0.3388	DIPS	<b>2-</b>	<b>-0.3167</b>
	4 <sup>+</sup>	-0.3423		4-	-0.3384
	6 <sup>+</sup>	-0.3434		6-	-0.3313
DODECA	6-	-0.3352	DMDIPS	<b>2-</b>	<b>-0.3265</b>
	4-	-0.3369		4-	-0.3543
	2-	-0.3388		6-	-0.3555
	2 <sup>+</sup>	-0.3232	DIPSO	<b>2-</b>	<b>-0.2851</b>
	6 <sup>+</sup>	-0.3367		4-	-0.3251
	4 <sup>+</sup>	-0.3375		6-	-0.3086
	2 <sup>++</sup>	-0.3417	DPA	2-	-0.3441
	6 <sup>++</sup>	-0.3334		4-	-0.3485
	4 <sup>++</sup>	-0.3427		6-	-0.3404
	6 <sup>+++</sup>	-0.3312	DPM	<b>2-</b>	<b>-0.3218</b>
	4 <sup>+++</sup>	-0.3335		4-	-0.3405
	2 <sup>+++</sup>	-0.3323		6-	-0.3504
NTFA	2-	-0.2977	DPE	2-	-0.3428
	4-	-0.3400		4-	-0.3459
	6-	-0.2985		6-	-0.3404
	4 <sup>+</sup>	-0.3560	BITNT	<b>2-</b>	<b>-0.3506</b>
	2 <sup>+</sup>	-0.3545		4-	-0.3538
	2 <sup>++</sup>	-0.3540		6-	-0.3450
	4 <sup>++</sup>	-0.3560		4-	-0.3459
1,8-DNN	1,8-	-0.3523		6-	-0.3404
1,5-DNN	<b>1,5-</b>	<b>-0.3796</b>	HNAB	<b>2-</b>	<b>-0.3007</b>
TNN	1-	-0.3574		4-	-0.3386
	4-	<b>-0.3289</b>	DMHNAB	<b>2-</b>	<b>-0.3077</b>
	5-	-0.3456		4-	-0.3534
TENN	<b>1,4,5,8-</b>	<b>-0.3218</b>		6-	-0.3331
BTX	<b>2-(in picryl)</b>	<b>-0.3242</b>	TACOT-Z	1,7-	-0.3346
	4-(in picryl)	-0.3279		3,9,-	-0.3593
	6-(in picryl)	-0.3328			
	5-(on benzo-)	-0.3549			
	7-(on benzo-)	-0.3626			

Note: data written by boldface were used for the Figures 1 and 2 construction

### Specification of the electric spark sensitivity

The method using the instrument ESZ KTTV [4-6] was described in Ref. [1, 2, 12]: the instrument is designed for small-scale sensitivity tests of energetic materials [4-6]. A method of measurement of the studied compounds is described in Ref. [2, 12]. The results obtained expressed as the spark energies,  $E_{ES}$ , are presented in Table 1.

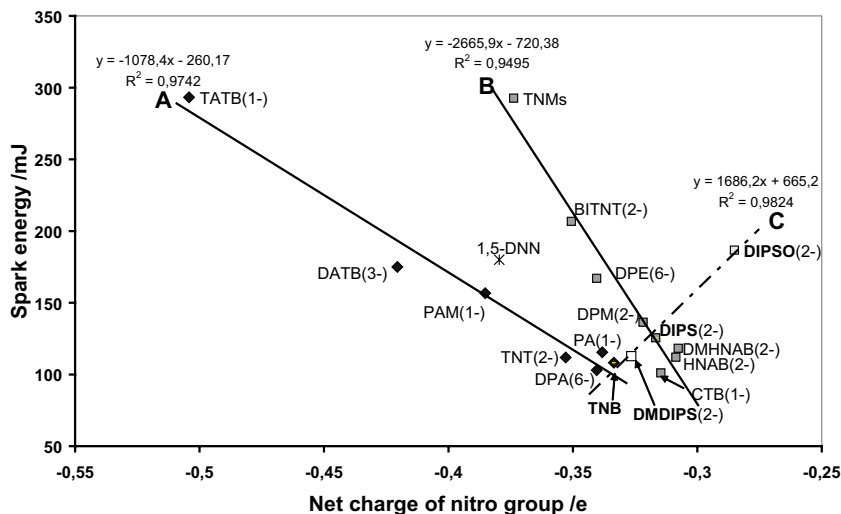
### Molecular structure characteristics

The net charges of nitro groups,  $Q_{nitro}$ , of the polynitro arenes investigated were obtained by means of Mulliken population analysis of the electron densities obtained at *ab initio* level by DFT B3LYP/6-31G(d,p) method [13] without frequency analysis. The relevant data are summarized in Table 2.

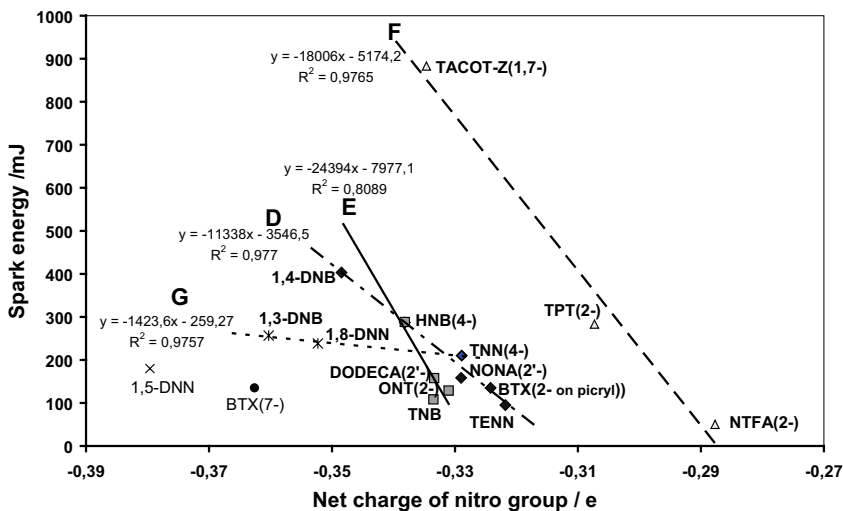
## Discussion

The analysis of mutual relationship between the  $E_{ES}$  and  $Q_{NO_2}$  values of the studied polynitro compounds led to Figures 1 and 2. According to Ref. [8-11], the sensitivity of a given polynitro compound is characterized by the most positive  $Q_{NO_2}$  value, which means that the nitro groups in molecules of these compounds are not equivalent from the standpoint of initiation reactivity [7-11] (see Figure 1 and also Table 2). However, Figure 1 shows that this need not always be the case. This Figure includes compounds exhibiting the primary low-temperature fragmentation by the trinitrotoluene mechanism [7, 8] (for this mechanism, see also Ref. [14-16]) and those exhibiting this fragmentation *via* a five-membered transition state (interaction of *ortho*-nitro group with bridge heteroatom), which applies to DIPS and DMDIPS, respectively; (see Ref. [7, 8, 17]).

Both Figures compare theoretical data of isolated molecules with experimental results obtained from real samples. The division of studied compounds in Figure 1 into subgroups A and B can thus be connected not only with the chemism of primary fragmentation in the initiation but also with the effect of intermolecular interactions upon the respective sensitivity: in the case of nitramines it was found [1] that the  $E_{ES}$  values also correlate with heats of fusion of these compounds, probably due to influence of dislocations in their crystals on electric spark sensitivity. Straight line C (which includes TNB and derivatives of DIPS) is not connected with the mechanism of primary fragmentation of the molecules in question (from this point of view, this is a heterogeneous group); in this case the behavior might be governed by intermolecular interactions in the compounds investigated.



**Figure 1.** Relationship between outputs from ESZ KTTV instrument (spark energy  $E_{ES}$ ) for derivatives of polynitro arenes with “trinitrotoluene mechanism” as the primary low-temperature thermal fission of their molecules (the numbers in parenthesis denote the position in molecule according to Table 2).



**Figure 2.** Relationship between outputs from ESZ KTTV instrument (spark energy  $E_{ES}$ ) for “genuine” polynitro arenes and for two azaarenes (the numbers in parenthesis denote the position in molecule according to Table 2).

Figure 2 supports the presumption of cooperation between the mechanism of primary fragmentation (the homolysis of C–NO<sub>2</sub> bond in this case) and intermolecular interactions in their effects upon the electric spark sensitivity. The point of intersection of straight lines D and E corresponds to the data for HNB. The data for 1,5-DNN do not correlate in Figure 1 due to structural reasons (different distribution of intermolecular interactions), and in Figure 2 due to difference in mechanism of primary fragmentation (interaction between oxygen atom of nitro group and hydrogen atom at the *peri*-position [17]). Straight line G logically combines the data for 1,3-DNB, 1,8-DNN and TNN. The line F is an analogy of the relationship between impact sensitivity of NTFA, TPT and TACOT-Z and net charges of the most reactive nitro groups in their molecules [18]: the line combines data of the spatially condensed derivatives of the polynitro arenes.

As already mentioned, in some cases the most reactive positions in molecules of the compounds studied (presented in Figures 1 and 2) do not correspond to the most positive  $Q_{NO_2}$  values. This is the case of PAM and TNT, in which probably *ortho*-nitro groups are the first to react (see Ref. [8, 14, 16, 17, 20]), while the most positive  $Q_{NO_2}$  values correspond to the *para*-positions. On the other hand, the correlations in both Figures include the data of 2-positions in DMDIPS, 4-position in HNB, and 2-positions in picryl group of BTX. The most reactive group in DMDIPS molecule should be in its 6-position [17], but straight line C in Figure 1 should not fail to represent the mechanism of primary fragmentation. The C–NO<sub>2</sub> bond lengths at 4-position in some HNB molecules in their crystals are approximately the same as the lengths of these bonds at *ortho*-positions of some of its molecules [21] in the crystal lattice. BTX is an example of polynitro compound with two reaction centers in molecule [22, 23]: the application of <sup>15</sup>N NMR chemical shifts found satisfactory correlation with the initiation by shock in the case of data for both positions, i.e. 2-position in picryl group and 7-position in benzotriazole system [22], while in the case of thermal decomposition the correlation was only found for the data of 7-position of BTX molecule [22]. This can mean a case of selectivity in the initiation reactivity.

## Conclusions

The results of measurements carried out with the apparatus for determination of electric spark sensitivity (type code ESZ KTTV) correlate with molecular structure (represented here by theoretical Mulliken net charges of nitro group,  $Q_{NO_2}$ ) of polynitro arenes and their derivatives studied. These data should concern

the nitro groups that would be the first to undergo chemical changes. It has been shown that intermolecular interactions play a non-negligible role in the initiation by electric spark and that the generally accepted presumption that the most positive  $Q_{NO_2}$  value in molecule represents its sensitivity cannot be regarded as universally valid. In the case of polynitro compounds possessing more than one potential reaction center in molecule there the selective initiation reactivity can occur depending on the kind of impulse. It will be useful to adopt findings from crystallographic studies of the respective compounds in an interpretation of this fact.

### Acknowledgements

The work was done under the auspices of the Ministry of Education, Youth & Sports of the Czech Republic as a part of its research project No. MSM 0021627501.

### References

- [1] Zeman S., Pelikán V., Majzlík J., Friedl Z., Electric Spark Sensitivity of Nitramines. Part I. Aspects of Molecular Structure, *Centr. Europ. J. Energ. Mater.*, **2006**, 3(3), 27-44.
- [2] Zeman S., Kočí J., Majzlík J., Electric Spark Sensitivity of Polynitro Arenes. Part I. A Comparison of Two Instruments, *ibid.*, **2007**, 4(3), 15-24.
- [3] "Special Scientific and Development Activity in the Field of Energetic Materials". *Project No. FC-M2/05*, Ministry of Industry and Commerce, Prague, **2000-2002**, solved by University of Pardubice.
- [4] Strnad J., Majzlík J., Determination of Electrostatic Spark Sensitivity of Energetic Materials. *Proc. 4<sup>th</sup> Seminar "New Trends in Research of Energetic Materials"*, Univ. Pardubice, April **2001**, pp. 303-307.
- [5] Jarman D., Prinse W., Bouma R., Electrostatic Discharge Initiation of CL-20: Effect of Discharge Time and Spark Energy, *Proc. 34<sup>th</sup> Int. Annual Conf. ICT Karlsruhe*, June **2003**, pp. 71/1-71/11.
- [6] Martinez Pacheco M., Bouma R., Katgerman L., Electrostatic Discharge Initiation of Ti+C Mixtures and the Thermite Al+MoO<sub>3</sub>, *Proc. 35<sup>th</sup> Int. Annual Conf. ICT Karlsruhe*, June **2004**, pp. 105/1-105/12.
- [7] Zeman S., New Aspects of Initiation Reactivities of Energetic Materials Demonstrated on Nitramines, *J. Hazard. Mater.*, **2006**, 132, 155-164.
- [8] Zeman S., Sensitivities of High Energy Compounds, in: *Structure & Bonding, Vol. 125, High Energy Density Compounds*, Klapoetke T. (Ed.), Springer, New York **2007**, p. 195.
- [9] Zhang C., Shu Y., Huang Y., Zhao X., Dong H., Investigation of Correlation between



- Impact Sensitivities and Nitro Group Charges in Nitro Compounds, *J. Phys. Chem.*, **2005**, B109, 8978- 8982.
- [10] Zhang C., Shu Y., Wang X., Theoretical Investigation of the Relationship between Impact Sensitivity and the Charges of the Nitro Group in Nitro Compounds, *J. Energet. Mater.*, **2005**, 23, 107-119.
- [11] Xu X., Xiao H., Wang G., Ju X., Theoretical studies on structures and relative stability for polynitrohexaazaadamantanes, *J. Chem. Phys.*, **2006**, 19(5), 395-400.
- [12] Kočí J., Zeman S., Majzlík J., Strnad J., Notices to Determination of the Electric Spark Sensitivity of Energetic Materials, *Proc. 5<sup>th</sup> Seminar „New Trends in Research of Energetic Materials“*, Univ. Pardubice, April **2002**, pp. 110-126.
- [13] TITAN v.1.0.8. Wavefunction, Schrödinger, Inc., USA, **2001**.
- [14] Matveev V.G., Dubikhin V.V., Nazin G.M., Soglasovanyi mekhanizm razlozheniya aromaticseskikh nitrosoedinii v gazovoy faze (Thermolysis Mechanism of the Aromatic Nitrocompounds in the Gas Phase), *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1978**, 474-477.
- [15] Bulusu S., Einstein D.I., Autera J.R., Anderson D.A., Velicky R.W., Deuterium Kinetic Isotope Effect: An Experimental Probe for the Molecular Processes Governing the Initiation of RDX, HMX and TNT, *Proc. 8<sup>th</sup> Int. Symp. on Detonation*, Albuquerque, NM, July, **1985**.
- [16] Manelis G.B., Nazin G.M., Rubtso Yu. I., Strunin V.A., *Thermal Decomposition and Combustion of Explosives and Powders* (Russ.), Izdat. Nauka, Moscow **1996**.
- [17] Zeman S., Krupka M., Study of the Impact Reactivity of Polynitro Compounds, Part II. Impact Sensitivity as the First Reaction of Polynitro Arenes, *Propellants Explos. Pyrotech.*, **2003**, 28, 249-255.
- [18] Zeman S., Friedl Z., Roháč M., Molecular Structure Aspects of Initiation of some Highly Thermostable Polynitro Arenes, *Thermochim. Acta*, **2006**, 451, 105-114.
- [19] Zeman S., Varga R., Decomposition of some Polynitro Arenes Initiated by Heat and Shock. Part I. 2,4,6-Trinitrotoluene, *J. Hazard. Mater.*, **2006**, 132, 165-170.
- [20] Zeman S., Varga R., Decomposition of some Polynitro Arenes Initiated by Heat and Shock. Part II. Several N-(2,4,6-trinitrophenyl)-substituted amino derivatives, *J. Hazard. Mater.*, **2006**, 137, 1345-1351.
- [21] Roháč M., Zeman S., Růžička A., Crystallography of 2,2',4,4',6,6'-hexanitro-1,1'-biphenyl and its relation to initiation reactivity, *Chem. Mater.*, **2008** – in press.
- [22] Zeman S., Pešková M., A Relationship between <sup>15</sup>N NMR Chemical Shift and Detonation Characteristics of Polynitro Derivatives of Arenes and Polyazaarenes, *Centr. Europ. J. Energ. Mater.*, **2005**, 2(3) 71-84.
- [23] Zeman S., A study of Chemical Micro-mechanism of the Organic Polynitro Compounds Initiation, in: *Energetic materials, Detonation, Combustion*, P. Politzer and J. S. Murray (Eds.), Elsevier, Amsterdam **2003**, Part 2, pp. 25-52.

