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Characterization of C-NO₂ Bonds in Nitroaromatic Compounds: A Bond Disproportionation Approach

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Abstract: Homolytic dissociation of $C\text{-}NO_2$ bond represents the primary fission process of nitroaromatic compounds under thermal, impact, shock and electric spark initiation stimuli. Homolytic bond dissociation energies BDE($C\text{-}NO_2$) describe the $C\text{-}NO_2$ bond fission. Theoretical calculations of BDEs are substantially influenced by inadequate treatment of electron correlation. Recently the alternative method was suggested to overcome this substantial drawback – an isodesmic reaction $RC\text{-}NO_2 + SC\text{-}H \rightarrow RC\text{-}H + SC\text{-}NO_2$ where $SC\text{-}NO_2$ is standard nitroaromatic compound. This reaction is characterized by bond disproportionation energy DISP($C\text{-}NO_2$), which inherently cancels the electron correlation effect accompanying homolytic bond dissociation energies. The bond disproportionation energies DISP($C\text{-}NO_2$) and bond dissociation energies BDE($C\text{-}NO_2$) were evaluated for 11 nitro benzenes and 19 nitro toluenes at DFT B3LYP/6-311+G(d,p) level and correlated with their detonation velocities, D, and with charge of the most reactive nitro group, Q(NO_2).

Keywords: bond dissociation energy, bond disproportionation energy, nitro benzenes, nitro toluenes, detonation velocity

Introduction

Recently computational chemistry is widely used in energetic materials evaluation [1-3]. There are many methods to predict various explosive properties, e.g. heat of explosion, heat of detonation, detonation velocity or sensitivity [4-8]. The study of primary cause of initiation reactivity is in the centre of attention [9, 10]. The idea of fundamental role of nitro group in fission mechanism is greatly accepted. Polynitro compounds are generally known as high energetic materials [11]. The R-NO_2 (R can be oxygen, nitrogen, carbon) bond included there is, excluding few cases, the most unstable bond in molecule of polynitro compound. Consequently, the homolytic dissociation of R-NO_2 bond represents the primary fission process of nitroaromatic compounds under thermal, impact, shock and electric spark initiation stimuli.

In case of polynitro compounds as nitroaromatics, nitramines and nitramides the C-NO_2 or N-NO_2 bond fission is mostly characterized by homolytic bond dissociation energies *BDE*(C-NO_2) [10, 12, 13]. Theoretical calculations of homolytic *BDE*s are substantially influenced by inadequate treatment of electron correlation. This substantial drawback was overcome in previous studies by the isodesmic reaction approach [14, 15]. Isodesmic reactions which are generally used in different type of studies (bond separation reactions, energies of proton-transfer reactions, absolute and relative acidities, etc.) inherently cancel the electron correlation effects accompanying homolytic bond dissociation. The using of closed shells reactants guarantee, that the electron correlation in *DISP* energy is unimportant. In view of the difference in cost between theoretical calculations of open shell or neutral molecules, the latter seems the perspicuous choice for this purpose.

The concept of isodesmic reaction, which describes C-NO_2 bond fission leads to disproportionation energy *DISP*(C-NO_2) by the following series of reactions:

$$\mathrm{RC\text{-}NO_2} \rightarrow \mathrm{RC\cdot} + \mathrm{NO_2\cdot} \quad BDE(\mathrm{RC\text{-}NO_2}) \tag{1}$$
$$\mathrm{RC\text{-}H} \rightarrow \mathrm{RC\cdot} + \mathrm{H\cdot} \quad BDE(\mathrm{RC\text{-}H}) \tag{2}$$

Eq. (1) and Eq. (2) represent the homolytic bond dissociation reaction *BDE* of specific nitroaromatic and related aromatic compound.

$$\mathrm{RC\text{-}NO_2} + \mathrm{H\cdot} \rightarrow \mathrm{RC\text{-}H} + \mathrm{NO_2\cdot} \quad BSE(\mathrm{RC\text{-}NO_2}) \tag{3}$$
$$\mathrm{SC\text{-}NO_2} + \mathrm{H\cdot} \rightarrow \mathrm{SC\text{-}H} + \mathrm{NO_2\cdot} \quad BSE(\mathrm{SC\text{-}NO_2}) \tag{4}$$

The difference between Eq. (1) and Eq. (2) gives an isodesmic reaction described by Eq. (3) which can be denoted as homolytic bond separation energy BSE(C-NO_2). The same sequence of dissociation reaction for standard nitroaromatic molecule SC-NO_2 and related aren SC-H leads to homolytic bond separation energy *BSE*(SC-NO_2), Eq. 4.

$$\mathrm{RC\text{-}NO_2} + \mathrm{SC\text{-}H} \rightarrow \mathrm{SC\text{-}NO_2} + \mathrm{RC\text{-}H} \quad DISP(\mathrm{C\text{-}NO_2}) \tag{5}$$

Finally the difference between homolytic bond separation energies *BSE*(RC-NO_2) and *BSE*(SC-NO_2) represents the isodesmic reaction which has already been denoted as *bond disproportionation energy DISP*(C-NO_2) described by Eq. (5) [14,15]. In this paper 30 nitroaromatic compounds were studied by quantum chemical DFT method B3LYP/6-311+G(d,p) and B3LYP/6-31G(d,p) respectively. The evaluated *BDE*(C-NO_2) and *DISP*(C-NO_2) energies were correlated with detonation velocities and charge of the most reactive nitro group.

Calculations

Methods

All calculations were performed by software Titan [16]. The structures of nitroaromatics were optimized by DFT B3LYP/6-311+G(d,p) method and the charges of nitro groups were obtained by DFT B3LYP/6-31G(d,p) method. According to the equations mentioned above and from total energies of molecules the values of *BDE*(C-NO_2) and *DISP*(C-NO_2) were obtained and are shown in Table 1. Chemical structures of all studied compounds are summarized in Figure 1 and 2. The bold emphasized nitro groups are the most reactive and so the fission of this bond is the first step of nitroaromatic compounds decomposition. The reactivity of this nitro group was determined according to the nitro group charge method (NGCM) developed by Zhang [17]. The nitro group charges $Q(NO_2)$ were computed as a summe of respective atomic charges $Q(NO_2) = Q_N + Q_{O1} + Q_{O2}$ derived by Mulliken population analysis and are summarized in Table 1.

Detonations parameters

The value of detonation velocity, *D*, was obtained by empirical Rothstein & Petersen equation [18]. It was chosen because of its good agreement with experimental results and because of its simplicity. The only one disadvantage of this method is the same value of detonation velocity for different isomers. The values of calculated detonation velocities are given in Table 1.

Table 1. Total electron energies *E*, calculated *BDE*(NO_2) energies, *DISP*(NO_2) energies, nitro group charge *Q*(NO_2) and detonation velocities *D*

Nitroaromatic code	*E* [a.u.]	*BDE* [kJ.mol^{-1}]	*DISP* [kJ.mol^{-1}]	*Q*(NO_2) [e]	*D* [mm^2.μs^{-2}]
1,2-DNB	-641.41476	278.17	-57.97	-0.3262	5.84
1,3-DNB	-641.43039	286.66	-16.95	-0.3603	5.84
1,4-DNB	-641.43067	286.95	-16.20	-0.3484	5.84
1,3,5-TNB	-845.98191	276.68	-31.23	-0.3335	7.28
1,2,4-TNB	-845.96766	246.65	-69.38	-0.3091	7.28
1,2,3-TNB	-845.95611	225.24	-98.97	-0.2378	7.28
1,2,4,5-TeNB	-1050.50125	242.46	-78.32	-0.2913	8.13
1,2,3,5-TeNB	-1050.50425	227.85	-107.84	-0.2166	8.13
1,2,3,4-TeNB	-1050.49199	225.17	-102.63	-0.2492	8.13
PNB	-1255.02233	213.90	-111.16	-0.2336	8.70
HNB	-1459.55121	225.25	-90.67	-0.2405	9.10
o-NT	-476.19729	288.24	-10.03	-0.3877	1.63
m-NT	-476.20172	299.89	1.60	-0.3923	1.63
p-NT	-476.20271	304.57	4.20	-0.3956	1.63
2,4-DNT	-680.75588	299.66	-26.89	-0.3703	5.10
2,6-DNT	-680.74875	269.72	-31.39	-0.3731	5.10
3,5-DNT	-680.75918	287.46	-15.65	-0.3651	5.10
2,5-DNT	-680.75513	276.18	-26.26	-0.3597	5.10
3,4-DNT	-680.74448	254.32	-56.84	-0.3305	5.10
2,3-DNT	-680.74339	251.42	-57.09	-0.3042	5.10
2,4,6-TNT	-885.30018	255.22	-50.20	-0.3512	6.67
2,3,5-TNT	-885.29622	242.44	-69.24	-0.2813	6.67
2,3,4-TNT	-885.28481	233.12	-90.54	-0.2630	6.67
2,4,5-TNT	-885.29323	246.91	-68.44	-0.3039	6.67
3,4,5-TNT	-885.28670	235.53	-94.24	-0.2453	6.67
2,3,6-TNT	-885.29085	237.73	-72.73	-0.2965	6.67
2,3,5,6-TeNT	-1089.82880	234.58	-80.96	-0.2751	7.60
2,3,4,6-TeNT	-1089.82718	226.29	-95.60	-0.2439	7.60
2,3,4,5-TeNT	-1089.82300	236.21	-96.30	-0.2543	7.60
PNT	-1294.35404	225.17	-100.25	-0.2592	8.24

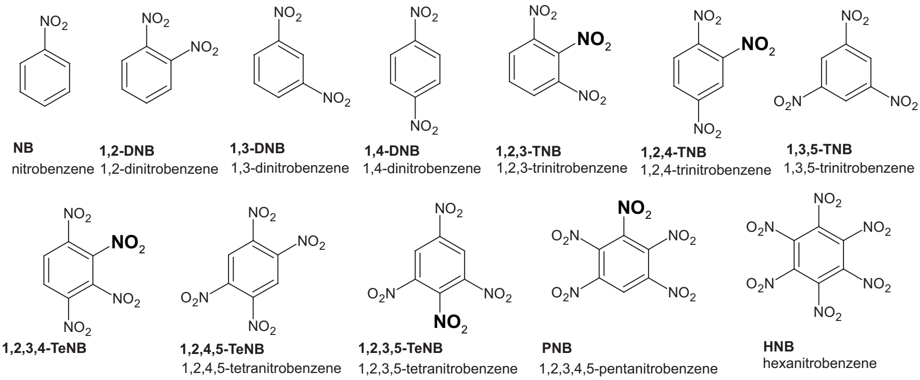

Figure 1. The chemical structures of nitro benzenes with bold emphasized the most reactive nitro group.

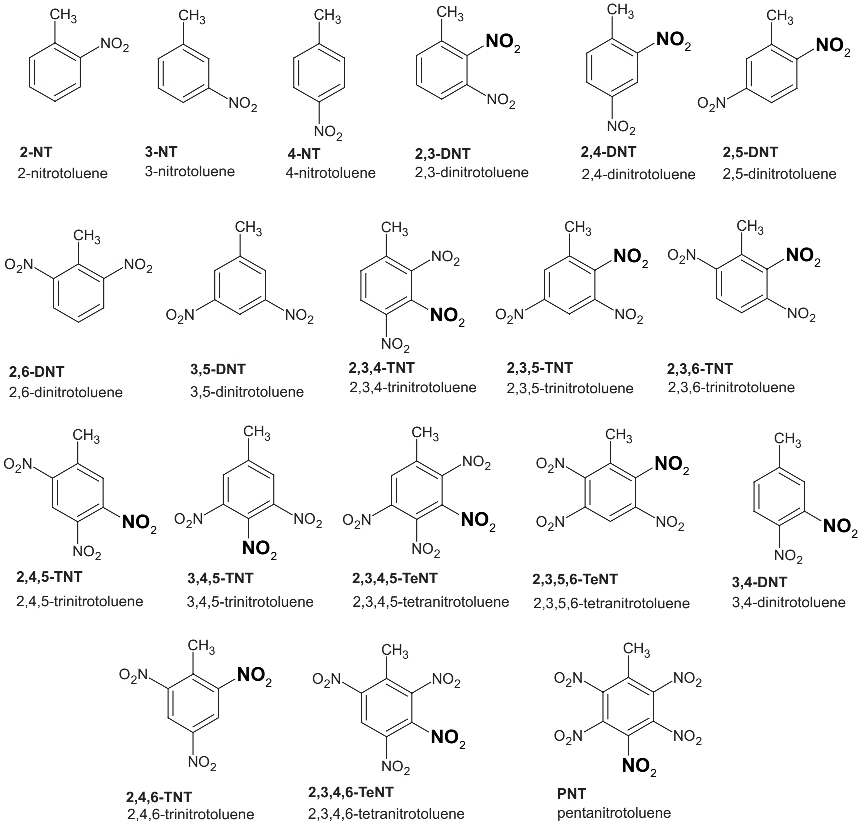

Figure 2. The chemical structures of nitro toluenes with bold emphasized the most reactive nitro group.

Results and discussion

In few recently published papers [19, 20] was proofed that exists logical relationship between low-temperature thermal decomposition characteristics and initiation of detonation. The Evans-Polanyi-Semanov (E-P-S) equation (6) was formulated in Ref. [21]. In this relationship the homolytic character of primary fission was the motive factor to study micro-mechanism of energetic materials initiations.

$$E = \alpha Q_{\mathrm{det}} + \beta \tag{6}$$

Application of relationship Eq. (7), between Heat of explosion Q_{det} and detonation velocity D:

$$Q_{\mathrm{det}} = \frac{D^2}{2(\gamma^2 - 1)} \tag{7}$$

where γ is the polytropy coefficient, leads to Eq. (8). This equation was called modified E-P-S [21].

$$E = aD^2 + b \tag{8}$$

The original E-P-S describes a relationship between activation energy of free radical substitution reactions and corresponding heats of reactions DH. Eq. (8) indicates that strength of the bond being split is critical factor in given reaction.

The energy, E, in both equations (6) and (8) can be the activation energy of thermal decomposition, E_a, or any other energy value which characterizes the reaction, e.g. the energy of electric spark − E_{ES}, drop energy – E_p or charge of the most reactive nitro group in given molecule. If the energy, E, in Eq. (8) is substituted by *BDE* energy of nitro benzenes the relationship is displayed on Figure 3. Analogically for nitro toluenes, the dependence of BDE to square of detonation velocity, D^2, is on Figure 4. Similarly, the energy E in Eqs. (6) and (8) can be substituted by bond disproportionation energy, *DISP*(C-NO_2). Than the Figures 3 and 4 transform to Figures 5 and 6.

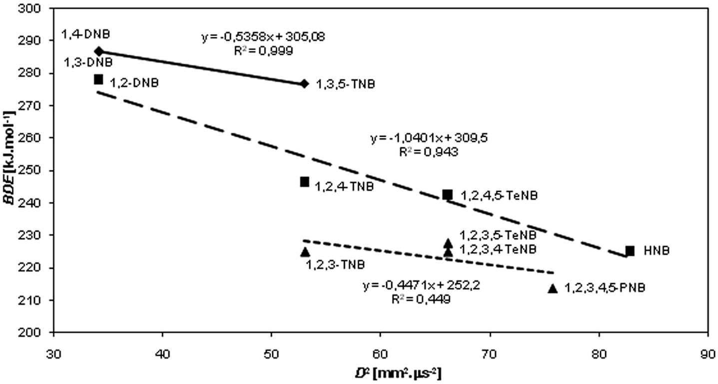

Figure 3. Dependence of *BDE* of nitro benzenes to square of detonation velocity.

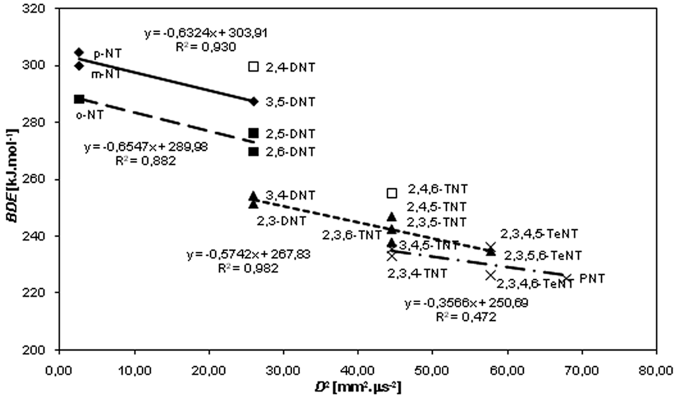

Figure 4. Dependence of *BDE* of nitro toluenes to square of detonation velocity.

There are few different lines in both kinds of dependences, *DISP* and *BDE* to D^2. They are strictly influenced by structure of given molecules. In case of nitro benzenes, the first line (the continuous one) contains just co-planar structures (1,3-DNB; 1,4-DNB and 1,3,5-TNB). This series is primarily influenced by structural fragment $CHC(NO_2)CH$.

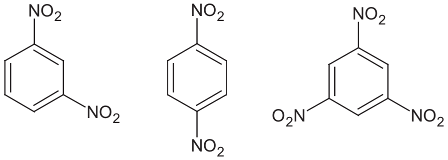

Figure 5. Nitro benzenes containing $CHC(NO_2)CH$ structural fragment.

The second line (dashed one) contains molecules, which has in structure 2 nitro groups in neighborhood (1,2-DNB; 1,2,4-TNB; 1,2,4,5-TeNB and HNB). The important part of structure is fragment $C(NO_2)C(NO_2)$.

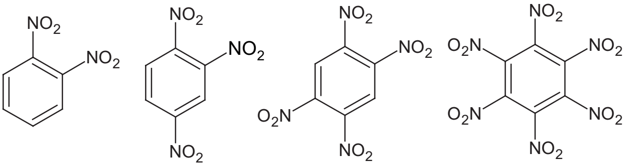

Figure 6. Nitro benzenes containing $C(NO_2)C(NO_2)$ structural fragment.

Finally, the third line (dotted one) contains three consecutive nitro groups (1,2,3-TNB; 1,2,3,5-TeNB; 1,2,3,4-TeNB and PNB).

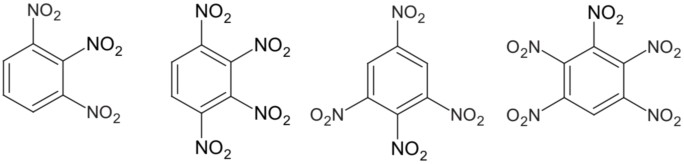

Figure 7. Nitro benzenes containing $C(NO_2)C(NO_2)C(NO_2)$ structural fragment.

Analogously for nitro toluenes, there are again few different lines which describe different structure. There are co-planar structures (*m*-NT; *p*-NT; 3,5-DNT),

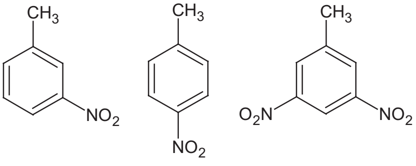

Figure 8. Nitro toluenes containing $CHC(NO_2)CH$ structural fragment.

further molecules with two adjacent nitro groups anywhere on aromatic ring (2,3-DNT; 3,4-DNT; 2,4,5-TNT; 2,3,5-TNT; 2,3,6-TNT; 2,3,5,6-TeNT)

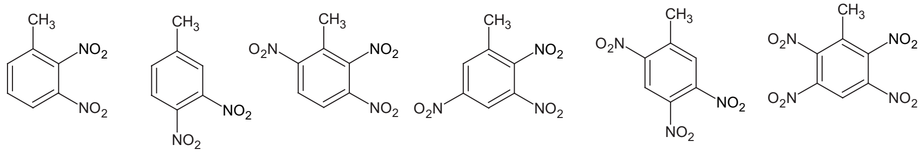

Figure 9. Nitro toluenes containing $C(NO_2)C(NO_2)$ structural fragment.

and molecules with three consecutive nitro groups (2,3,4-TNT; 3,4,5-TNT; 2,3,4,5-TeNT; 2,3,4,6-TeNT; PNT).

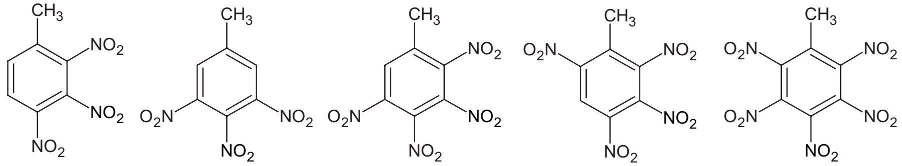

Figure 10. Nitro toluenes containing $C(NO_2)C(NO_2)C(NO_2)$ structural fragment.

Moreover, in structure of nitro toluenes is a methyl group which determines new group (dash-and-dotted one). This group has NO_2 next to methyl and from the other side of NO_2 is hydrogen bonded (*o*-NT; 2,6-DNT; 2,5-DNT; 2,4-DNT; 2,4,6-TNT).

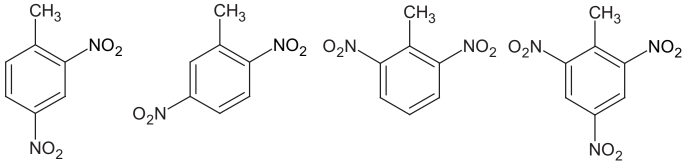

Figure 11. Nitro toluenes containing $C(CH_3)C(NO_2)CH$ structural fragment.

It has to be explained why 2,4-DNT and 2,4,6-TNT are excluded from plots in Figure 4. Both of them have in structure $C(CH_3)C(NO_2)CH$, but they differ by the pathway of decomposition. Many papers were written to describe the decomposition of nitro aromatics [22-24]. From these studies is known that 2,4-DNT has a special way of decomposition [22]. That is why the 2,4-DNT is out of corresponding curve. Instead of $C-NO_2$ fission, the splitting of N-OH bond in aci-form is the first step of disintegration (see Figure 12). 2,4,6-TNT should behave similarly, but Cohen et al. [25] find latter pathway which afterwards leads to water elimination and formation of dinitroanthranil.

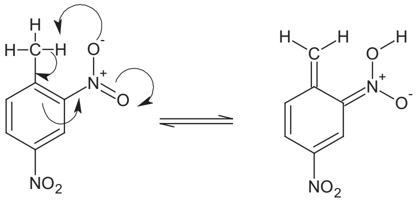

Figure 12. Mechanism of 2,4-DNT rearrangement.

On the next two Figures 13 and 14 are shown dependences of *DISP* energy to square of detonation velocity. In comparison to dependences of *BDE* energy to D^2 the higher regression coefficients are seen. Much better distinguishing of structure also results from this comparison. In case of nitro toluenes, interesting thing is that above mentioned exceptions 2,4-DNT and 2,4,6-TNT fit the corresponding curve significantly closely. It seems to be probable that *DISP* energy is independent of the way of decomposition.

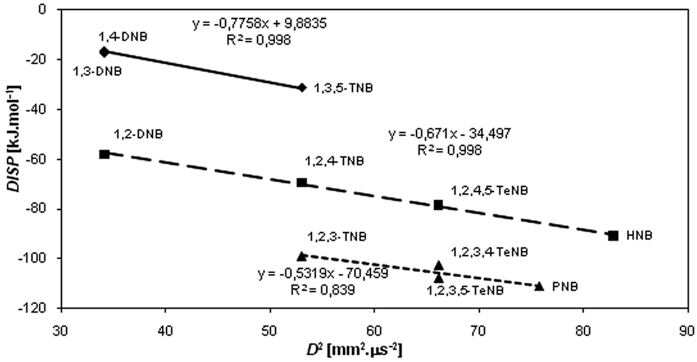

Figure 13. Dependence of *DISP* of nitro benzenes to square of detonation velocity.

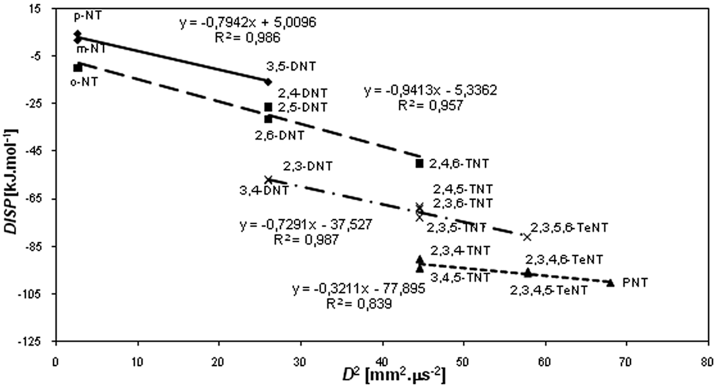

Figure 14. Dependence of *DISP* of nitro toluenes to square of detonation velocity.

The substitution of the energy *E* in Eq. (8) by the *DISP* energy and simultaneously the square of detonation velocity D^2 by nitro group charge $Q(NO_2)$ leads to the relationship between *DISP* energies and charges $Q(NO_2)$ and shown for series of nitro benzenes in Figure 15 and for nitro toluenes in Figure 16, respectively. Both plots are characterized by single regression lines with high correlation coefficients (r = 0.93 and 0.95) which describe the expected indirect rule of proportion between ease of bond fission (decrease of DISP value) and nitro group charge (increase of positive charge). Nevertheless, the structural selectivity of *DISP* vs. D^2 relationships was lost. But changes in charges are too small ($\Delta Q(NO_2) \sim 0.14$ e) in comparison with changes of energy ($\Delta E \sim 100$ kJ.mol^{-1}) and it could be note that both quantities are structure oriented parameters with high covariance and their use should be done separately. Recently, the alternative approach based on electrostatic potentials was developed [26, 27] and a comparison with results obtained would be needed in future.

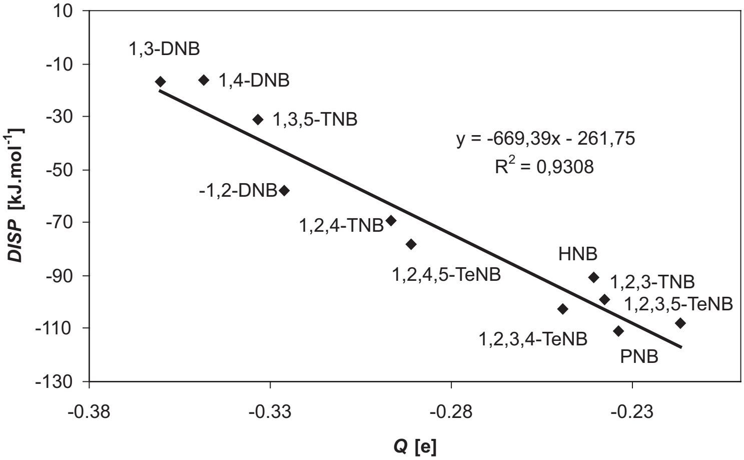

Figure 15. Dependence of *DISP* of nitro benzenes to the charges of the most reactive nitro group.

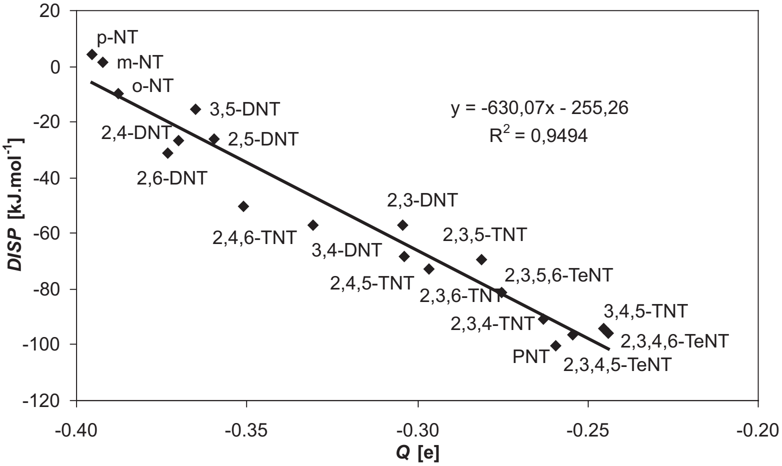

Figure 16. Dependence of *DISP* of nitro toluenes on the charges of the most reactive nitro group.

Conclusion

In this study the disproportionation energies of an isodesmic reaction RC-NO_2 + SC-H → SC-NO_2 + RC-H proved to be an alternative measure of initiation mechanisms of nitro aromatic energetic materials. Comparison of relationships between *DISP* energies and square of detonation velocity D^2 for series of nitro benzenes and toluenes reveals the higher selectivity to molecular structure for *DISP* than *BDE* energies. The property of *DISP* energies to describe structure-property relationships is similar to findings also in other CHNO energetic materials as nitramines and nitramides. Regarding the detonation as a "zero-order reaction" the findings given above lead to the construction of SPRS model where *DISP* energies could be considered as structural Hammett-like constants.

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