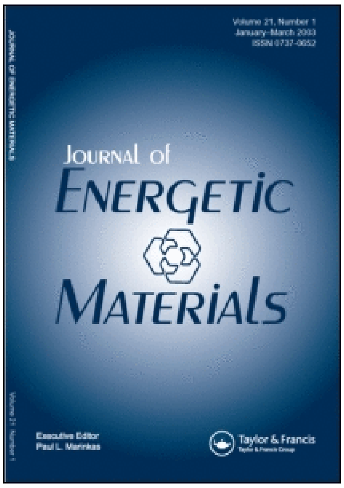

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The study of chemical micromechanism governing detonation initiation of some *m*-dinitrobenzopolyazaarenes

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THE STUDY OF CHEMICAL MICROMECHANISM GOVERNING DETONATION INITIATION OF SOME *m*-DINITROBENZOPOLYAZAARENES

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ABSTRACT

Electronic charges, *q*, at nitrogen atoms of twelve *m*-dinitrobezopolyazaarenes were calculated by means of *ab initio* HF/6-31G** and semi-empirical AM1 methods. The relationships have been confirmed between squares of the detonation velocities or, as the case may be, the detonation heats of the azaarenes and *q*-values for primarily split off nitro groups. These relationships were considered as an analogue of modified Evans-Polanyi-Semenov equation and so they directly specify the most reactive nitro groups of *m*-dinitrobenzopolyazaarene molecules in the detonation.

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INTRODUCTION

It is well known that nitro groups are centres of reactivity in organic polynitro compounds. Therefore, it is logical that there exist relationships between the ^{15}N NMR chemical shifts δ_N of nitrogen atoms in nitro groups of nitramines and the Arrhenius parameters of their thermolysis [1-3], impact sensitivity [1,4], electric spark sensitivity [5] and their detonation characteristics [6]. The last relationship mentioned is expressed by a general equation [6]

$$X = a.\ \delta_N + b \qquad (1)$$

where X can be the heat of detonation, Q, or square of detonation velocity, D^2, and the δ_N values correspond to the primarily leaving nitro groups in the process of initiation of the detonation.

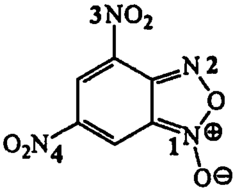
It is also known that the chemical shifts δ_N are connected with electron configurations at the respective nitrogen atoms. From what has been said it follows, for instance, that the detonation characteristics of polynitro compounds should correlate with electronic charges at nitrogen atoms of nitro groups primarily reacting in the initiation of detonation. It is problem that we focus our attention on in the present paper. For this purpose we have chosen a group of *m*-dinitrobenzopolyazaarenes and their derivatives as model of polynitro compounds.

DATA SOURCES

Electronic charges at nitrogen atoms

The calculation of electronic charges at nitrogen atoms of nitro groups of the *m*-dinitrobenzopolyazaarenes investigated was carried out by means of the Mulliken population analysis of electron densities obtained both at a semi-empirical level by the AM1 method and at the *ab initio* level using the HF/6-31G** method [7]. A survey of the compounds studied, their codes and the results obtained are presented in the following tables:

4,6-Dinitro-2,1,3-benzoxadiazol-1-ium-1-olate **(DNBF)**

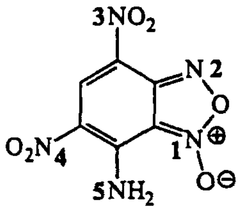


D = 7863 m.s^{-1}

Q_{max} = 6337 kJ.kg^{-1}

Nitrogen No.	HF/6-31G** charges at nitrogen atoms (in electrons)	AM1
1	0.420313	0.422566
2	0.098341	-0.021982
3	0.556700	0.581475
4	0.541763	0.580614

7-Amino-4,6-dinitro-2,1,3-benzoxadiazol-1-ium-1-olate (MADNBF)

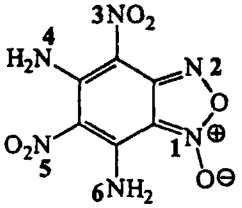


D = 8185 m.s^{-1}

Q_{max} = 5888 kJ.kg^{-1}

Nitrogen No.	HF/6-31G** charges at nitrogen atoms (in electrons)	AM1
1	0.410195	0.418056
2	-0.113868	-0.010994
3	0.519888	0.592023
4	0.543622	0.597019
5	-0.705078	-0.310781

5,7-Diamino-4,6-dinitro-2,1,3-benzoxadiazol-1-ium-1-olate (DADNBF)

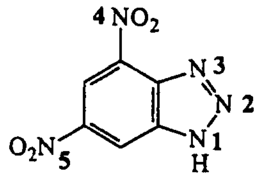


D = 8191 m.s^{-1}

Q_{max} = 5378 kJ.kg^{-1}

Nitrogen No.	HF/6-31G** charges at nitrogen atoms (in electrons)	AM1
1	0.409682	0.423245
2	-0.146552	-0.024150
3	0.532097	0.603703
4	-0.732016	-0.316274
5	0.552022	0.591585
6	-0.715594	-0.320866

4,6-Dinitro-1H-1,2,3-benzotriazole **(4,6-DNBT)**

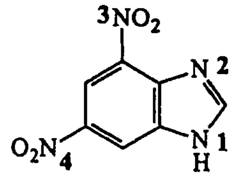


D = 5945 $m.s^{-1}$

Q_{max} = 5637 $kJ.kg^{-1}$

Nitrogen No.	HF/6-31G** charges at nitrogen atoms (in electrons)	AM1
1	-0.538413	-0.216791
2	0.065112	0.083281
3	-0.280743	-0.040927
4	0.541666	0.575093
5	0.540368	0.571311

4, 4,6-Dinitro-1H-benzimidazole **(4,6-DNBIM)**

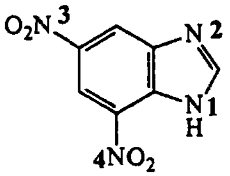


D =6413 $m.s^{-1}$

Q_{max} =5224 $kJ.kg^{-1}$

Nitrogen No.	HF/6-31G** charges at nitrogen atoms (in electrons)	AM1
1	-0.730059	-0.229910
2	-0.495454	-0.112066
3	0.529655	0.576641
4	0.530904	0.573452

5,7-Dinitro-1H-benzimidazole **(5,7-DNBIM)**

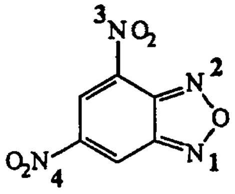


$D = 6413\ m.s^{-1}$

$Q_{max} = 5224\ kJ.kg^{-1}$

Nitrogen No.	HF/6-31G** charges at nitrogen atoms (in electrons)	AM1
1	-0.675928	-0.214679
2	-0.529040	-0.107596
3	0.543582	0.575930
4	0.484854	0.582711

4,6-Dinitro-2,1,3-benzoxadiazole **(4,6-DNBFA)**

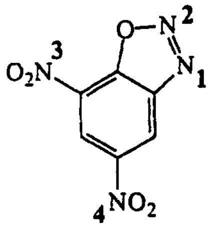


$D = 7189\ m.s^{-1}$

$Q_{max} = 5982\ kJ.kg^{-1}$

Nitrogen No.	HF/6-31G** charges at nitrogen atoms (in electrons)	AM1
1	-0.100657	-0.061889
2	-0.049287	-0.065868
3	0.555847	0.576556
4	0.546299	0.571984

5,7-Dinitro-1,2,3-benzoxadiazole **(DINOL)**

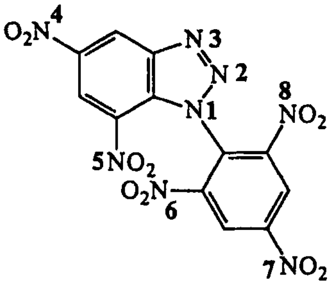


$D = 7115\ m.s^{-1}$

$Q_{max} = 5939\ kJ.kg^{-1}$

Nitrogen No.	HF/6-31G** charges at nitrogen atoms (in electrons)	AM1
1	-0.252523	-0.026196
2	0.195567	0.117745
3	0.551929	0.584769
4	0.547244	0.575827

5,7-Dinitro-1-(2,4,6-trinitrophenyl)-1H-1,2,3-benzotriazole **(BTX)**

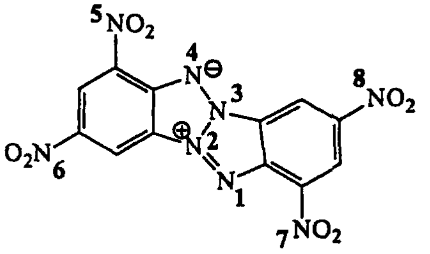


$D = 7359\ m.s^{-1}$

$Q_{max} = 5675\ kJ.kg^{-1}$

Nitrogen No.	HF/6-31G** charges at nitrogen atoms (in electrons)	AM1
1	-0.554367	-0.185190
2	0.074847	0.097146
3	-0.299622	-0.003022
4	0.547695	0.578407
5	0.506449	0.589029
6	0.520598	0.577151
7	0.543159	0.576899
8	0.534585	0.578405

2,4,8,10-Tetranitrobenzotriazolo[2,1-a]benzotriazol-6-ium inner salt
(TACOT - Z)

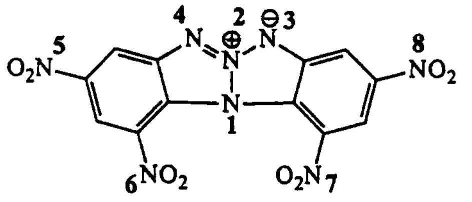


$D = 7461\ m.s^{-1}$

$Q_{max} = 5539\ kJ.kg^{-1}$

Nitrogen No.	HF/6-31G** charges at nitrogen atoms (in electrons)	AM1
1	-0.281632	-0.002441
2	-0.174822	-0.039321
3	-0.175490	-0.039747
4	-0.281546	-0.003693
5	0.517267	0.580525
6	0.547785	0.578090
7	0.514399	0.580671
8	0.547997	0.578144

2,4,8,10-Tetranitrobenzotriazolo[2,1-b]benzotriazol-6-ium inner salt
(TACOT - T)

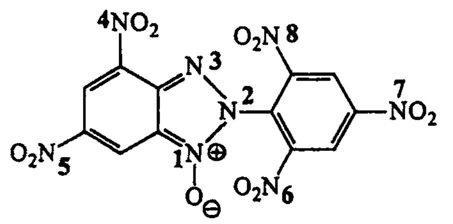


D = 7346 m.s^{-1}

Q_{max} = 5539 kJ.kg^{-1}

Nitrogen No.	HF/6-31G**	AM1
	charges at nitrogen atoms (in electrons)	
1	-0.459395	-0.109596
2	0.169716	0.182392
3	-0.348770	-0.045712
4	-0.348956	-0.045717
5	0.539582	0.574561
6	0.537357	0.586716
7	0.537025	0.586710
8	0.533449	0.574495

4,6-Dinitro-2-(2,4,6-trinitrophenyl)-2H-1,2,3-benzotriazol-1-ium-1-olate
(PDNBTO)



D = 7414 m.s^{-1}

Q_{max} = 5592 kJ.kg^{-1}

Nitrogen No.	HF/6-31G** charges at nitrogen atoms (in electrons)	AM1
1	0.244848	0.059933
2	-0.302465	-0.032339
3	-0.303889	-0.132817
4	0.504308	0.586387
5	0.549123	0.583713
6	0.540466	0.416030
7	0.469070	0.581445
8	0.575260	0.594676

Detonation characteristics

The detonation velocities D and the maximum heats of explosion Q_{max} were calculated according to the well-known Kamlet–Jacobs relationships [8] for the maximum theoretical densities of crystals of the energetic materials studied. The results obtained for the individual materials are shown in the previous Tables.

DISCUSSION

It is a generally known fact that chemical changes in thermolysis or in initiation of polynitro arenes primarily affect nitro groups sterically hindered and/or those adjacent to hydrogen-containing substituents — amino groups in this case (for discussion see Refs [9,10]). In the sense of what has been told, for instance, it was proved that the sterically hindered 5-nitro group of BTX primarily reacted during its initiation with electric spark [5]. The results of AM1 method clearly show that nitrogen atoms of all those nitro groups affected by primary reaction exhibit the highest positive values of the electronic charge, *q*. The inter-correlation between these *q* values and the detonation characteristics of the corresponding *m*-dinitrobenzopolyazaarenes are presented in Figs 1 and 2. The relationships represented in these figures closely resemble those typified by Eq. (1). The reason of differences in the classification of materials in the groups according to Figs 1 and 2 probably lies in the definition relationship between *Q* and *D* values [11,12]:

$$Q = D^2 * \{2*(\gamma^2 + 1)\}^{-1} \qquad (2)$$

where the values of coefficient of polytrope, *γ*, for high explosives vary within the limits from 2.79 to 3.48 [11].

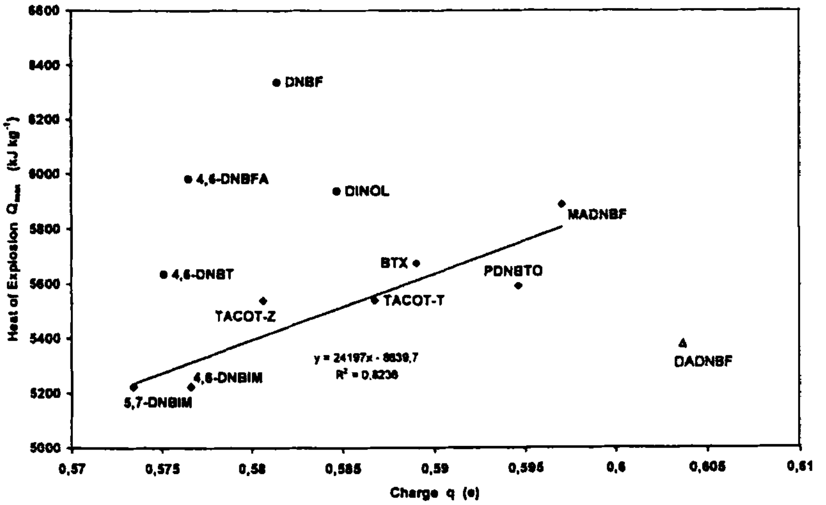


FIGURE 1: Relationship between outputs of AM1 method and heats of explosion

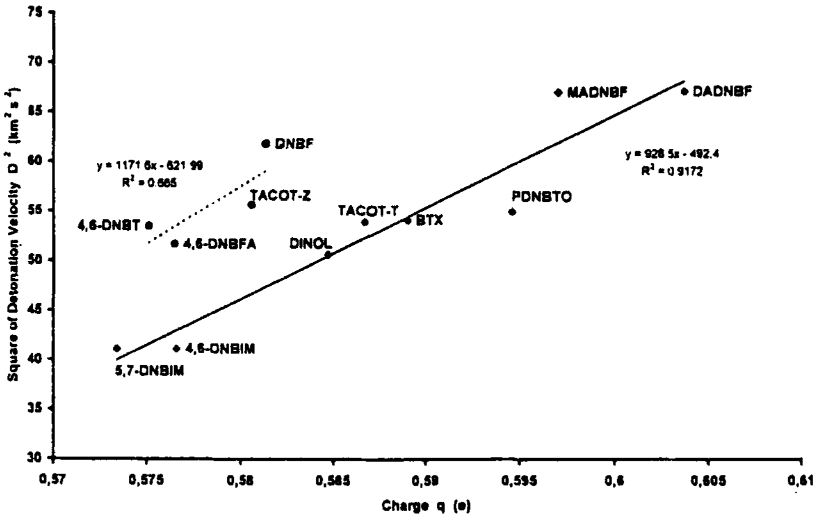


FIGURE 2: Relationship between outputs of AM1 method and squares of detonation velocities.

Figures 3 and 4 represent analogous relationships resulting from the *ab initio* HF/6-31G** method. They were, however, derived with the application of the *q* values of those nitrogen atoms that exhibit the maximum values of this charge according to the AM1 method. The dependences depicted in these figures are more equivocal: a probable reason lying in the fact that the *ab initio* HF/6-31G** method describes the equilibrium geometry of a molecule (even though of an isolated one in gaseous phase) better than the semi-empirical AM1 method does. As it follows from Refs [2,4,13] the geometry of molecule (its conformation) represents one of the factors affecting the detonation initiation by impact, shock or electric spark. However, intermolecular interactions in molecular crystals also exert a large effect in this sense [2,4,14,15]. These interactions have not been involved in the calculation methods adopted, which can be another reason for the division of the compounds investigated into several sub-groups according to Figs 1-4.

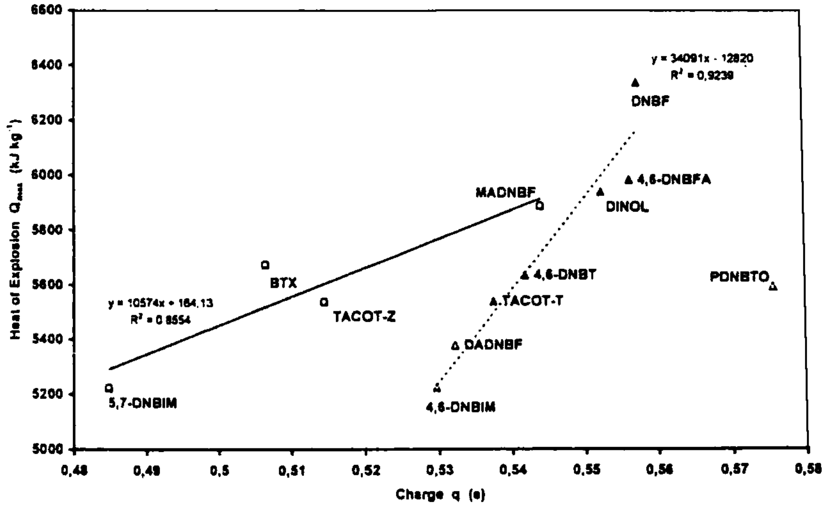


FIGURE 3: Relationship between *ab initio* HF/6-31G** charges and heats of explosion

As it was already mentioned, a relationship between the activation energies, E_a, of non-autocatalyzed thermolysis of nitramines and chemical shifts δ_N values it was also found in the general form [1-3]:

$$E_a = a_1 * \delta_N + b_1 \qquad (3)$$

A combination of equations (1) and (3), together with introducing Q for X in equation (1), gives [6]:

$$E_a = C \pm \alpha * Q \qquad (4)$$

The equation (4) – generally – is a form of Evans-Polanyi-Semenov relationship (there is heat of reaction ΔH instead of Q in the original relationships), which was originally derived for radical substitution reactions [16,17]. This relationship is valid for narrow sets of compound structures and it documents that the strength of bond being split is a decisive factor in the given reaction. It was proved that Eq. (4) also holds for the detonation transformation of energetic materials [2,18-20].

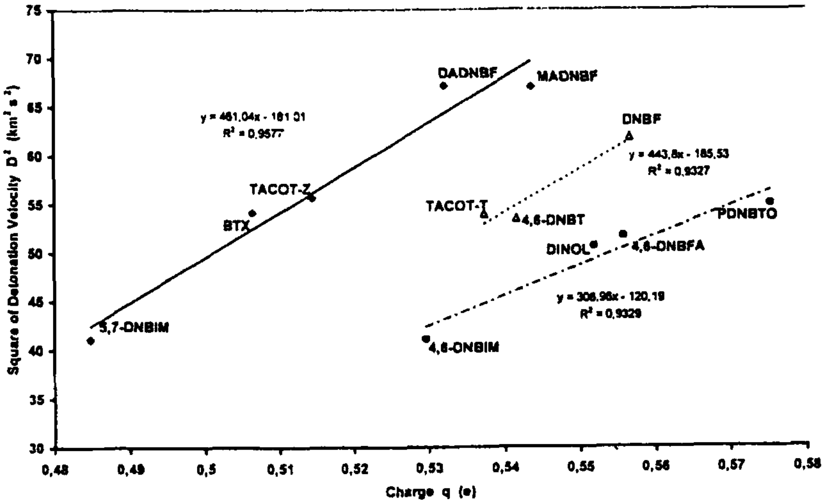


FIGURE 4: Relationship between *ab initio* HF/6-31G** charges and squares of detonation velocities

The relationship (4) does not only document the importance of the bond primarily splitting in detonation of individual energetic materials, but also signals the identity of chemical mechanism of primary splitting in low-temperature thermolysis and detonation reactions [2,6,18]. The above-mentioned statements allow a similar conclusion to be drawn in the case of the relationships given in Figs 1-4.

As it was the case with nitramines and Eq. (1) [6] also the relationships depicted in Figs 1-4 directly specify the most reactive nitro groups of *m*-dinitrobenzopolyazaarene molecules in their detonation.

CONCLUSION

The relationships between the square of the detonation velocities or heats of explosion and electron charge on nitrogen atoms of nitro groups in *m*-dinitrobenzopolyazaarenes molecules can be considered as an analogue of Evans-Polanyi-Semenov equation [16,17] in its modified form (i.e., as a relationship between activation energies of low-temperature thermolysis and explosion heats of energetic materials [2,18-20]). These relationships show that the strength of bond primarily homolyzed is a decisive factor in detonation of energetic materials in general. The relationships directly specify the most reactive nitro group of *m*-dinitrobenzopolyazaarene molecule in the detonation. These statements agree with theoretical findings [21-26] concerning shock and impact reactivity of polynitro compounds.

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