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Contemplation on spark sensitivity of certain nitramine type explosives

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ABSTRACT

Spark sensitivity of explosives is an important subject. Presently, some correlations are sought between the spark sensitivity and certain molecular orbital characteristics of some nitramine type explosives. For that purpose certain semi-empirical and DFT calculations have been carried out. Investigations have revealed that the nitramines considered undergo decomposition in the electric field mainly via their anionic states.

1. Introduction

Spark discharges occur between conductors with different electrical potentials. A spark is a discrete discharge that leaks through a gap between two conductors in the form of a ionization path in which the stored energy is transferred swiftly. The spark is triggered when the breakthrough field strength is reached at a certain point in the gap. Also, sufficiently high field strength is required in the whole space between the electrodes so that the discharge can travel through that space. A homogeneous electrical field between the electrodes is an important requirement.

In contrast to spark discharges, corona discharges are typical one-electrode discharges which occur in an inhomogeneous electrical field at conductive and earthed sharp end points.

A solid material in an electric field acts as a dielectric material and when the field strength is sufficient, electric and/or electrothermal breakdown occurs. An electric breakdown develops as a result of interaction of free charged particles (electrons and ions) accelerated by an electric field with the particles of a dielectric, or as a result of inelastic displacement of bound charges in a dielectric under the action of an external electric field [1].

Whatever the discharge type is, organic molecules exposed to an electric field should be affected due to polarization depending on the field strength. It is known that the polarizability increases with the size of the atom and with the number of electrons it possesses [2–4]; this can be understood in terms of it being easier for a field to distort the electronic distribution when the electrons are far from the nucleus or well shielded from its charge. Similar generalizations also hold for molecules.

A polar molecule has a permanent dipole moment and most of the explosives molecules fall into this class. Nitro groups and some other explorophores on an explosive molecule make that one to have a permanent dipole moment as long as the geometry and symmetry considerations allow.

The spark sensitivity of various explosive molecules has been the subject of very many articles in the literature [5–15]. In the present study, certain correlations have been sought between the computational data obtained from ionic forms of some nitramines and their spark sensitivity values excerpted from the literature [12].

2. Method

The initial geometry optimizations of all the structures leading to energy minima were achieved by using MM2 method followed by semi-empirical PM3 self-consistent fields molecular orbital (SCF MO) method [16,17] at the unrestricted level (UHF/PM3) [18]. Then, further geometry optimizations were achieved using STO and UHF levels of theory and then within the framework of density functional theory (DFT, UB3LYP) [19] at the levels of 6-31G(d,p) and 6-31+G(d) (unrestricted open shell, note that open shell structures are in doublet state) [18]. The exchange consists of hybrid Hartree–Fock and local spin density (LSD) exchange functions term of B3LYP with Becke's gradient correlation to LSD exchange [20]. The correlation term of B3LYP consists of the Vosko, Wilk, Nusair (VWN3) local correlation functional [21] and Lee, Yang, Parr (LYP) correlation correction functional [22]. The normal mode analysis for each structure resulted in no imaginary frequencies for

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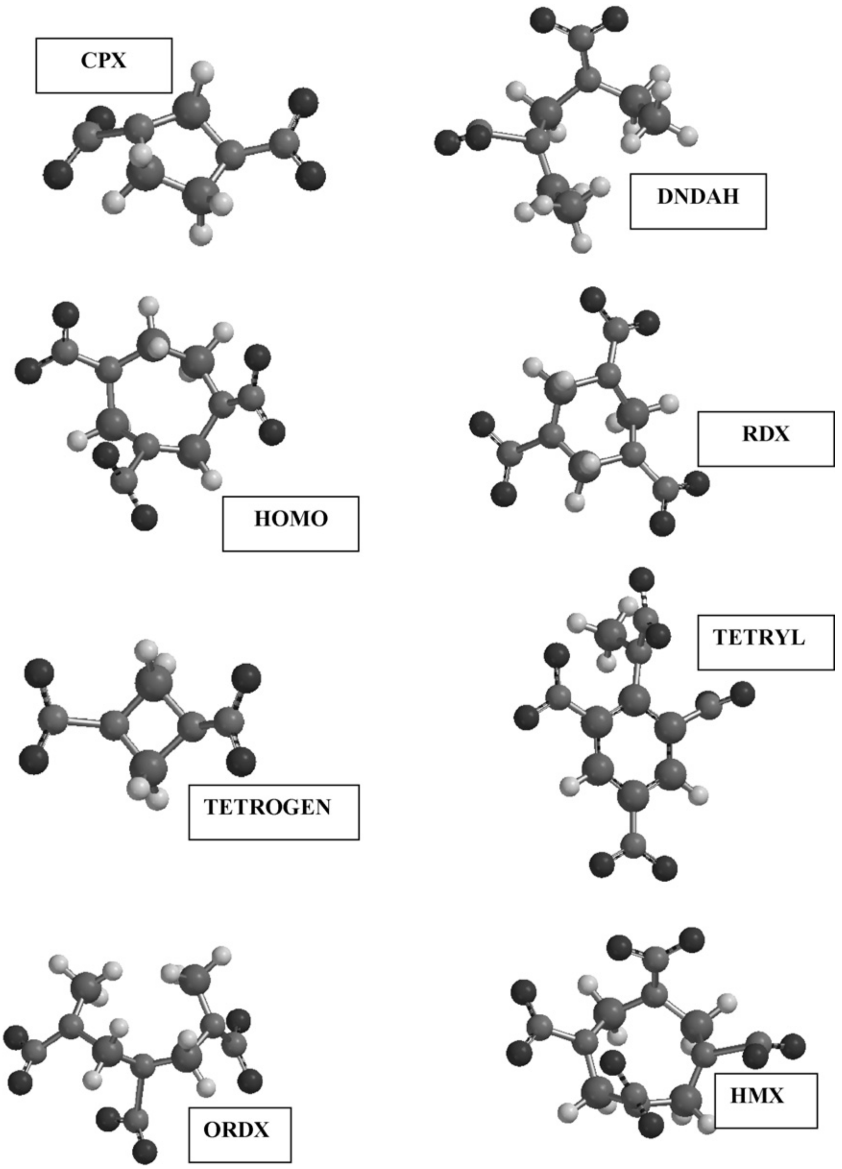


Fig. 1. Geometry optimized (UHF/PM3) anionic structures.

all the three methods of calculations and the spin contamination for open shell systems is acceptable (0.75 ± 0.02). All these computations were performed by using Spartan 06 package program [23].

3. Results and discussion

Initiation of explosives by electric spark has not attracted much attention in the past. Nevertheless, the electric spark sensitivity is an important characteristic of explosives, especially primers and propellants.

When an electric field is applied to an individual molecule, the electron distribution and the molecular geometry are distorted. The polarizability is a measure of the ease with which this occurs. In the electric field, as a result of distortion of the electron distribution, the bond dipoles and consequently the resultant dipole moment of molecules change. As the field strength increases, ionizations of the molecules occur. Depending on the structure and some other factors, especially the field strength, various forms of anionic and cationic species are generated which undergo decomposition starting from the weakest bond(s). To shed some light on to decomposition mechanism of nitramine type explosives in an electrical field, a group of test compounds having various acyclic and cyclic skeletons have been constituted. Of these 20 compounds a subgroup of 8 compounds have been found to exhibit consonance in character in many respects as explained below (see Fig. 1). This subgroup has been used as a test probe for the large group.

3.1. Frontier molecular orbital energy considerations

When a substance is placed in an electric field, it might be polarized and then ionized before undergoing any decomposition possible to occur under the applied conditions. Presently, at the beginning it is assumed that when sparkling occurs over an organic molecule, the structure gains or loses electron(s) prior to disintegration of the molecule to fragments. In other words, decomposition of the molecule in an electric field should occur via its anionic or cationic form(s). So, the following simplified possibilities could be the fates of the structures which are either neutral but polarized or singly or doubly charged structures, undergoing single electron transfer process involving the HOMO and/or LUMO levels.

Table 1
The names of the structures considered and their spark energy values.

No	Compound	Abbreviation	Spark energy[a] (J)
1	1,3-Dinitroimidazolidine	CPX	9.68
2	3,5-Dinitro-3,5-diazaheptane	DNDAH	12.49
3	1,4-Dinitropiperazine	DNDC	15.97
4	1,3,5,7-Tetranitro-1,3,5,7-tetrazocane (octogen)	HMX	2.89
5	1,3,5-Trinitro-1,3,5-triazepane	HOMO	3.70
6	1,3,5-Trinitro-1,3,5-triazinane (hexogen)	RDX	2.49
7	1,3-Dinitro-1,3-diazetidine	TETROGEN	6.25
8	2,4,6-Trinitrophenylmethylnitramine	TETRYL	5.49
9	4,10-Dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane	TEX	13.10
10	1,3,3-Trinitroazetidine	TNAZ	8.76
11	*trans*-1,4,5,8-Tetranitrodecahydro-pyrazino[2,3-*b*]pyrazine	TNAD	5.43
12	2,4,6-Trinitro-2,4,6-triazaheptane	ORDX	8.08
13	1,3,5,7,9-Pentanitro-1,3,5,7,9-pentazecane	DECAGEN	2.96
14	2,5-Dinitro-2,5-diazahexane-3,4-dione	DMNO	5.49
15	2,4,6,8,10,12-(hexanitro-hexaaza)-tetracyclododecane	CL-20	4.70
16	1,5-Dinitrato-3-nitrazapentane	DINA	5.85
17	2,4,6,8-Tetranitro-2,4,6,8-tetraazononane	OHMX	5.50
18	2,4,6,8-Tetranitro-2,4,6,8-azanonan-1,9-diol diacetate	AcAn	13.93
19	1,4-Dinitrotetrahydroimidazo[4,5-*d*]imidazol-(1H, 3H)-dione	DINGU	15.19
20	2,5-Dinitro-2,5-diazahexane	DMEDNA	8.24

[a] Taken from Ref. [12].

Electron transfer from the HOMO

$$\text{Cations}\quad A^{+}-e^{-}\rightarrow A^{2+}$$

$$\text{Neutrals}\quad A-e^{-}\rightarrow A^{+}$$

$$\text{Anions}\quad A^{-}-e^{-}\rightarrow A$$

Electron transfer to the LUMO

$$\text{Cations}\quad A^{+}+e^{-}\rightarrow A$$

$$\text{Neutrals}\quad A+e^{-}\rightarrow A^{-}$$

$$\text{Anions}\quad A^{-}+e^{-}\rightarrow A^{2-}$$

Usually, spark energy experimental results are hard to interpret in terms of structure–activity relationship concept because very many factors (partly mentioned in Section 1) are operative. Also it is a matter of question what the mechanism of explosion at those conditions is. Usually, no idea can be obtained whether cations or anions are involved in some stage of the explosion mechanism. However, a statistical analysis of the experimental data together with theoretical results based on certain hypothesis may shed some light on to the subject.

The experimental spark energies excerpted from the literature are tabulated in Table 1 [12]. In the list some compounds like ORDX and DNDAH are acyclic nitramine type explosives. TETRYL is unique in the group but can also be classified as acyclic nitramine because the nitramine moiety is not involved in a cycle. The rest of the compounds contain two to four nitramine groups embedded in certain cyclic structures.

Table 2 shows the correlation values for the group of experimental spark energy values with the HOMO and LUMO energy groups (calculated at UHF/PM3 level) for the cationic, neutral and anionic forms. In the table, the first entries are for eight selected compounds (see Table 1) which constitute a subgroup. The subgroup, compared with the large group enables one to observe the effect of charge development as the group population increases arbitrarily. Although, the numerical values standing for the small and large groups are very different in sign and magnitude (the neutral case is exceptional) the general outcome is that the correlation between the LUMO energy and the spark energy is better than the correlation between the HOMO energy and the spark energy (Table 2). However, when the small group is considered, the anionic case gives a better correlation over the others but for the large group, the neutral case is better. This turn over clearly indicates that different electrical states are involved for different sets of explosives while the breakdown of the structures under sparkling conditions occurs. The first eight compounds in Table 1 constitute a consistent set in terms of group character. By trial and error, some suitable structures can be added to an already consistent set without disturbing the group character. From Table 2 it is clear that the electron-accepted states (anions) of the species in the subgroup correlate better with the experiment. Moreover, the anionic case exhibits better correlation than the others which indicates that anions are involved somehow in the decomposition mechanism of these compounds.

Table 2
Correlations between the groups of cationic, neutral and anionic forms of the compounds and the group of spark energy values (UHF/PM3).

	Cation	Neutral	Anion
HOMO energy correlation with the experiment	−0.17228	0.34665	0.59209
	0.00986	0.32245	−0.06213
LUMO energy correlation with the experiment	0.25972	0.39797	0.61502
	−0.05305	0.41982	0.17166

Based on orbital energies in eV and spark energies in joules. The first numerical entries are for the subgroup of the first eight compounds listed in Table 1.

Table 3
Some statistical data for the HOMO energy group of the anionic structures considered.

	UHF/PM3	UB3LYP/6-31G(d,p)	UB3LYP/6-31+G(d)
Correlation with the experiment	0.592096	0.523468	0.617161
Skewness	0.895151	0.110552	0.105712
SDV	0.681612	0.449126	0.512914

HOMO energies in eV and spark energies in joules are employed. The data stand for the subgroup considered. SDV: standard deviation.

Table 4
Some statistical data for the LUMO energy group of the anionic structures considered.

	UHF/PM3	UB3LYP/6-31G(d,p)	UB3LYP/6-31+G(d)
Correlation with the experiment	0.615021	0.419549	0.385748
Skewness	−0.812880	−0.97672	−1.160951
SDV	0.571689	0.851776	0.731782

LUMO energies in eV and spark energies in joules are employed. The data stand for the subgroup considered. SDV: standard deviation.

Table 5
Correlation between the groups of HOMO and LUMO energies (eV).

UHF/PM3	UB3LYP/6-31G(d,p)	UB3LYP/6-31+G(d)
0.55136	0.44772	0.35096

The data stand for the subgroup considered.

Tables 3 and 4 show some statistical data for the HOMO and LUMO energy groups of the anionic species and their correlations with the experimental spark energy data group. As seen in those tables, the correlations are better with the HOMO energy group of the anions. In the case of PM3 treatment, the correlation with the LUMO energy group and the experimental group is better than the correlation of the later group with the HOMO energy group. However, as seen in Table 5 correlation with the HOMO and LUMO energy groups for the PM3 case is not negligible. Due to that fact the spark energies seem to be correlative with the HOMO energies as well. However, when the correlation between the HOMO and LUMO energy groups is low, as the case of UB3LYP/6-31+G(d), it becomes evident that the spark energy does not correlate appreciably with the LUMO energies.

3.2. *Electrostatic considerations*

In the case of explosives, explosion occurs also triggered by the cleavage of the bond where the bond strength is the lowest [24]. A bond between a NO_2 group and an atom in an organic nitro compound is usually heteropolar, due to the inductively and mesomerically electron attracting nature of the NO_2 group.

The presence of electrostatic charges on atoms of a heteropolar bond cause emergence of Coulombic force of attraction which contribute the overall bond strength of the bond of particular interest. When that bond is to be broken down heterolytically, some extra energy has to be pumped in to the system to overcome ionic force of attraction due to those opposite charges. The energy required to break that bond is the sum of homolytic covalent bond dissociation energy and the ionic charge separation energy. In the case of ionized molecules, the above-mentioned ionic term of energy requirement might be quite or more important than the covalent bond dissociation energy.

Assume that in the ionic form of an explosive molecule, Q_1 and Q_2 stand for opposite charges accumulated on atoms of a particular bond having length of r. The ionic attraction energy then simply is

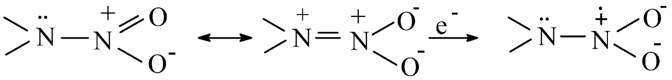
$$E = \frac{Q_1 Q_2}{r} \tag{1}$$

In the present treatment also the neutral forms have been considered besides the mono ionic structures for the comparison purposes. Although, at first sight the mono cations and anions have been the focus of interest presently, in the experimental conditions higher ionic forms may be generated which could blur success of the present approach. However from Table 6, it is seen that the correlation of anionic case is greater than the others in absolute value. The formation of either cation or anion of any molecule generally results appearance of highly elongated nitramine bond which at first sight seems to be the indication of ease of bond cleavage.

Table 7 shows the correlation of the attraction energy group with the spark energy group for the anions. Whereas various attraction energy values at different level of calculations and the spark energy for the anionic compounds considered are shown in Table 8 (based on electrostatic charges). Note that in all types of calculations presently performed on every anion considered, $Q1$, the charge of nitrogen of NO_2 moiety is positive whereas Q_2, the charge on amine nitrogen, is negative, thus all E values defined by Eq. (1) are negative.

Note that PM3 method predicts the molecular geometries very close to real ones [18,25]. The results of UHF/PM3 treatment reveals that although bond length elongation in the anionic case results in less negative attraction energy values, in the group there exist some odd members. For instance, the nitramine bond length of TETRYL in the anion form is somewhat shorter as compared to the neutral form. It might arise from the localization of the excess electron on the aromatic moiety. Because in that case, the increased electron population over the aromatic ring causes shift of some electron population of amine nitrogen towards the adjacent nitro group. Consequently, the nitramine bond acquires some (or more) double bond character and gets shorter. Indeed, charges on the nitrogens of the nitramine bond of TETRYL decrease in the anion as compared to the neutral form.

Another odd compound in the anionic group is DNDAH for which the attraction energy in the anion form is more negative than its neutral form but the bond length is longer than the neutral one. First of all, one should note that in the case of anionic group, with the exception of TETRYL, all the structures have less positive charge on NO_2 nitrogen of the longest nitramine bond but more negative charge on the amine nitrogen (with the exception of HOMO case) which indicates that the excess electron is accumulated on the nitro group and consequently the contribution of the mesomeric structure II decreases.



(I) (II) (III)

Thus, the nitramine bond elongates in the anionic form due to repulsion between the unpaired electron (on the radical cation) and the electron pair (see structure III). Note that the negative charge on the amine nitrogen of DNDAH is the greatest within the group. A similar behavior is exhibited by TETROGEN but its attraction energy in the anionic case is less negative than its neutral form.

As seen in Table 6 computational data for the group has very low correlation value with the experimental group data in the case of any explosion mechanism based on cation formation during the spark-induced explosion experiments for the presently considered explosives. The neutral case should be the out of consideration for

Table 6
Correlation of the group of attraction energy data with the group of experimental spark energy data for the sets of structures.

Neutral set	Cation set	Anion set
0.12944	−0.04177	−0.71772

Based on UHF/PM3 electrostatic charges. The data stand for the subgroup considered.

Table 7
Correlation of the attraction energy group with the spark energy group for the anions. The data stand for the subgroup considered.

	UHF/PM3	UB3LYP/6-31G(d,p)	UB3LYP/6-31+G(d)
Based on Mulliken charges	0.299018	0.433878	−0.121151
Based on electrostatic charges	−0.717721	0.295616	0.157173

Table 8
The attraction energy values at different level of calculations and the spark energies for the anionic compounds considered. Based on electrostatic charges. The data stand for the subgroup considered.

Molecule	UHF/PM3	UB3LYP/6-31G(d,p)//UHF/PM3	UB3LYP/6-31G(d,p)	UB3LYP/6-31+G(d)	Spark energy (J)
CPX	−0.62277	−0.21304	−0.12027	−0.12069	9.68
DNDAH	−1.05657	−0.15148	−0.05585	−0.06594	12.49
HOMO	−0.30325	−0.03407	−0.12182	−0.16494	3.70
RDX	−0.43525	−0.09960	−0.10939	−0.14153	2.49
TETROGEN	−0.73564	−0.24043	−0.00079	−0.00361	6.25
TETRYL	−0.72231	−0.22244	−0.02662	0.08862	5.49
ORDX	−0.37155	−0.08823	−0.04412	−0.01557	8.08
HMX	−0.41427	−0.08576	−0.10877	−0.06703	2.89
Correlation with the experiment	−0.71772	−0.40851	0.29562	0.15717	

Attraction energy is in (unit electron)^2/Å.

such kind of experimental conditions and the consequent rejection of such a hypothesis has been supported by the low correlation value with the experimental group data. However, group data of the anionic set correlates pretty well with the experiment, although the correlation is negative which means inherently that more negative attraction energy having explosive requires more spark energy to explode. It is logical because the attraction energy presently considered is the Coulombic attraction energy to be overcome. In the light of above considerations for the set of compounds, it is very probable that explosion by sparking occurs via anionic states as predicted above section based on orbital energies (the HOMO energies) above.

On the other hand, either UB3LYP/6-31G(d,p)//UHF/PM3, UB3LYP/6-31G(d,p) or UB3LYP/6-31+G(d) treatment based on above-mentioned attraction energy definition for the anions considered failed to give a good correlation. However, the set of UB3LYP/6-31G(d,p)//UHF/PM3 treatment which is based on PM3 geometry optimizations seem to be better than the sets of other DFT calculations (also, correlation of dipole moments with the spark energy is better in the case of PM3 treatment than the others, e.g., 0.30 and 0.002 units for UHF/PM3 and UB3LYP/6-31+G(d), respectively). Hence, the PM3 geometries, at least in the present case, lead to much better correlations. This success of PM3 method could not be attributed to mere coincidence but due to its semi-empirical nature. Table 8 shows the bond energies of the anions at different level of calculations. As seen there, the correlation of the anionic set of compounds with the experimental values is the highest in absolute value in the case of UHF/PM3 type calculations.

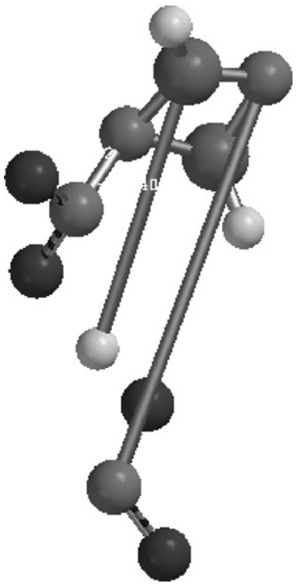


Fig. 2. Geometry optimized structure of TETROGEN anion (UB3LYP/6-31+G(d)).

In the present work, two different approaches quite independent from each other have been followed. The first one correlates the HOMO and LUMO energies with the spark energies and the second is based on electrostatic attraction energies of the atoms flanking the broken nitramine bond. Both of these approaches yield various degree of correlations. In the light of the present results the simplified picture of fate of any nitramine (A) considered could be represented as,

$$A + e^- \rightarrow A^- \rightarrow \text{fragments}$$

Since, NO_2 group is a good electron acceptor, formation of an anion is very probable. In the case of nitramines, the acceptance of extra electron located on NO_2 moiety causes charge-lone pair repulsion with the adjacent amine nitrogen atom. Thus; the nitramine bond elongates. Meanwhile, electron distribution seems to occur in such a way that the NO_2 nitrogen acquires positive but the amine nitrogen gets negative charges. This outcome has been observed in all the present treatments irrespective of the method applied and basis set used. However, the net charge of the NO_2 group after fission of the anion is some small negative value. This mechanism should be further complicated in the case of nitramines like TETRYL because it contains not only N–NO_2 but also C–NO_2 linkages. Another interesting compound considered is TETROGEN. All the DFT geometry optimizations of TETROGEN indicate that C–H bond of it also elongates and should contribute the fission process in the electric field (see Fig. 2).

Some of the nitramines considered possess more than one nitramine bond, hence some complications arising from the presence of extra nitramine bonds may lower the correlation with the experimental results in absolute value. Especially, at high voltages selectivity of nitramine NO_2 may be decreased or completely lost. The dispersion of the data points could be partially attributed to the experimentation. Because, the electrodes not in tight contact with the explosive material (which acts as a dielectric in a parallel plate capacitor) should require higher extra spark potential than the actually required. The air gap between the electrodes complicates the picture because breakdown potential of air depends on the atmospheric pressure as well as dampness.

4. Conclusions

As conclusions the followings can be asserted.

- The nitramine compounds considered preferentially decompose via anionic states in an electric field (valid for all the compounds listed in Table 1).
- When the successes of calculation methods used are compared, correlation of the spark energy with the HOMO energy group of anions is better for UHF/PM3 and UB3LYP/6-31G(d,p)//UHF/PM3 treatments than the UB3LYP/6-31G(d,p) but the UB3LYP/6-31+G(d,p) treatment is the best. Whereas, when the LUMO energy

group is considered the success order is UHF/PM3 > UB3LYP/6-31G(d,p) > UB3LYP/6-31+G(d,p) (only the compounds in the subgroup listed in Table 1 are considered).

- The correlation between the experimental data group and the attraction energy group is better for UHF/PM3 and UB3LYP/6-31G(d,p)//UHF/PM3 than the others.

In the light of the present results, it seems that in the electric field, nitramines exhibit some common features at least for the subgroup considered, but their behavior is complicated by certain factors arising from individual identity of the structures.

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