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Sensitivity and Performance of Energetic Materials

Svatopluk Zeman*, Marcela Jungová

Abstract. This paper provides an overview of the main developments over the past nine years in the study of the sensitivity of energetic materials (EM) to impact, shock, friction, electric spark, laser beams and heat. Attention is also paid to performance and to its calculation methods. Summaries are provided of the relationships between sensitivity and performance, the best representations for the calculation methods of performance being the volume heat of explosion or the product of crystal density and the square of detonation velocity. On the basis of current knowledge, it is possible to state that a single universal relationship between molecular structure and initiation reactivity does not yet exist. It is confirmed that increasing the explosive strength is usually accompanied by an increase in the sensitivity. In the case of nitramines this rule is totally valid for friction sensitivity, but for impact sensitivity there are exceptions to the rule, and with 1,3,5-trinitro-1,3,5-triazepane, 1,3,5-trinitro-1,3,5-triazinane, β–1,3,5,7-tetranitro-1,3,5,7-tetrazocane and the α–, β– and ε–polymorphs of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane the relationship works in the opposite direction. With respect to the QSPR approach there might be reasonably good predictions but it provides little insight into the physics and chemistry involved in the process of initiation.

Keywords: Energetic materials; Sensitivities; Performance; Review;

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Content

1. Introduction.

As has been stated in these surveys [1, 2], the sensitivity of high energetic materials (EMs) is primarily due to the chemical character of the materials. This means that it is possible to use the term "initiation reactivity of EMs". This reactivity is connected with the chemical reactions of the materials in their condensed state, in which the Gibbs Free Energy is highly exergonic, entropy is positive and the exothermic heat of reaction is 4,000 – 15,000 times greater than the activation energy of the particular change. These basic conditions, depending on the impulse intensity, charge crystallography and diameter, its density and/or packing, will usually lead to a rapid onset of burning, deflagration or detonation of the given EMs [3]. The main experimental interest in EMs has, until recently, been largely focused on studies of shock and impact sensitivities and, in the past 25 years, quantum chemistry methods (DFT) [4 - 16] have been widely used in a theoretical approach to these two sensitivities and to other properties of EMs [16 - 18] including semi-empirical solving of the electric spark sensitivity [19, 20]. To a lesser extent, the approach using physical organic chemistry has been used not only to study impact and shock reactivity [1, 2, 21 - 24] and also friction sensitivity [25 - 30], but particularly also the thermal reactivity of EMs [1, 2, 21, 31 - 33] with the main objective being to study the chemical mechanism of the primary fission during initiation [1, 2, 19 – 21, 23, 29].

Performance is another important characteristic of energetic materials. This is connected with the above-mentioned exothermicity of their decomposition, together with the velocity of this decomposition and with the suitable chemical composition (preferably the gaseous products of explosion) [3]. This characteristic can be best described by detonation parameters [3, 34 - 36] and by the results of various tests, such as the Trauzl test, or by measurements using ballistic mortars (here one is referring to the strength of explosives, or relative performance) [37]. The relationship between performance and sensitivity characteristics has been studied for a relatively long time, but before 2000 an interest in the relationship with parameters of thermal decomposition was predominant, namely in relation to the study of the chemical micro-mechanism of initiation [1, 2, 21, 38, 39]. Only Licht, in 2000, on the basis of his analysis [40], has shown that a high level of performance is usually accompanied by an enhanced sensitivity and that an insensitive explosive do not exhibit top performance. It has subsequently been shown that this can be considered as a general rule but the author has stated that this result is not documented by theory, so far [40].

The most used and the most studied method of impact sensitivity determination is the Kast fall hammer method, which forms part of the UN recommendations for the transport of dangerous goods [41] and where the Bruceton analysis [42] for evaluation of the results has been widely used. At the present time this analysis can be substituted, for example, by the probit analysis [43]. It would be appropriate also to mention the Russian approach to impact and friction sensitivities [44 - 47] and their interesting results merit special attention.

Some complications exist in the case of electric spark and shock sensitivities, such that it is difficult to justify such results as a form of standardization, as it is in the case of impact sensitivity, even though some international standards do exist [24, 48, 49].

This paper relates to the study [1], which was published in 2007. Attention is now paid not only to individual sensitivities of energetic materials but also to the relationship between them and their performance and to certain facts resulting from it.

2. Sensitivities

Concerning the Physics of Explosion, the development and discussion of the undermentioned sensitivities (with the exception of shock sensitivity) are grouped together in the monograph [50]), covering roughly the period 1960–2007.

2.1. Impact sensitivity (IS)

Impact sensitivity measurements can be obtained either on the basis of the first reaction of decomposition or by sound detection [1, 2, 21, 51]. Not surprisingly, these two different methods lead to different values for impact sensitivity, both of which appear in the literature, frequently without mentioning the origin of the measurements. Irrespective of the method used, these two groups of results show a relationship with molecular-structural parameters [1, 2, 21, 23] and a relationship between both the groups has been described and interpreted [51]. The most serious data based on sound detection measurements (using the Bruceton method) come from the Los Alamos National Laboratory [52] and/or the Naval Surface Weapons Center [53 - 55]. For scientific purposes, in our laboratory, we selected the published impact sensitivity results and those obtained by us on the basis of their correlation with the NMR chemical shifts of those atoms bearing the most reactive nitro group in the molecule [1, 2, 21]. In the case of nitramines we use the ^{15}N shifts of the aza nitrogen atoms [1, 2, 23, 56], as is shown in Fig. 1. Particular lines in this Fig. represent structural similarity (or conformational similarity in the reaction centers) in the corresponding nitramines, and differences in the slopes correspond mainly to differences in intensity of the intermolecular interactions between the individual series [2, 23]. Using this type of relationship it is possible to specify the reaction centers of initiation also in polynitro compounds [1, 2, 21, 23, 29].

Figure 1

As for the development and rationalization of the scientific research, numerous predictive methods for IS have been published in the literature during the last 30 years [1, 57]. A survey concerning development in this area up to 2008 is given in a review by Keshavarz [57], who has also recently developed relatively complicated semi-logarithmic relationships with no less than six restrictions, based on data for some 86 different polynitro compounds [58], but the results do not compare well with experimentally derived values. In another IS prediction [59] the same author, starting from the elemental composition of the EM, has derived positive and negative molecular moieties for increasing and decreasing core function for the IS prediction and constructs a semi-logarithmic relationship, all based on the IS data for 90 different polynitro compounds. In another study [60] Keshavarz et al. present a new computer program for IS prediction and both these papers [59, 60] represent, to a certain extent, a statistical approach. Lai et al. present [61] a similar solution for IS prediction with their correlations starting from the atoms C, H, N, O number in 196 compounds, and other amending factors, which are determined by the effect of the connective positions of groups on impact sensitivity. Lai has divided this group into six sub-groups with corresponding relatively complicated equations and he has stated that his approach gave better results than those provided by the Keshavarz equations (see in review [57]).

For IS prediction, Wang et al. [62] have used the QSPR model with the molecular structure description of 156 nitro compounds by means of combining both the electronic and topological characteristics (ETSI approach) of the molecules analyzed. However, as it was noted in [1], due to the mixed data from very different structures (aromatic and aliphatic with the C-NO_2 and N-NO_2 groupings) their predictions are, at best, just an indication. With the use of 3D descriptors for the entire set of 156 structurally different energetic compounds and by means of multiple linear regression in their QSPR study, Xu et al. [63] have come to the view that their nonlinear model (built by ANN) could be used for an estimation of IS for new EMs. These QSPR approaches, in general, do not allow an evaluation of the chemical physics of initiation.

A relatively large number of publications have dealt with correlations which involve quantum chemically generated values [1, 4, 5, 14, 57, 64, 65]. Thus, the B3P86/6-31G** method was used by Cao [66] for performance and impact sensitivity prediction of hypothetical dinitramino benzenes which included in the calculation both the net charge of nitro groups and the oxygen balance of the compounds studied. The author compares his results with those from the approach according to Politzer et al. [8, 11] and limits himself to stating that the difference here is inexplicable. On the same basis Zhang and Gong [67] have calculated the electron density at the critical points of the N-O bond for 33 specific polynitro compounds and the results correlated with those for impact sensitivity – however, they did not find any relationship but only a trend was intimated there. Atalar et al. [68] have calculated the bond dissociation energies, BDE, of the weakest N–N bonds for 14 cyclic nitramines by means of the UB3LYP/6-31G* and UB3LYP/6-31+G* // PM3 methods. The relationships found between the BDE values and the logarithms of impact sensitivity for these nitramines, expressed as drop energy, E_{dr}, are not unambiguous as there are three individual relationships corresponding to the structurally close sub-groups of the nitramines studied [68]. Recent papers from Politzer et al. [6, 8, 11 – 13, 15 – 17 ,65] represent the most sophisticated solution so far concerning sensitivity, primarily based on surface electrostatic potentials. These potentials can serve as the basic determinant of all molecular properties [13, 16]. Besides these electrostatic potentials, other features are related to sensitivity, such as amino substituents, layered crystal lattice, free space in the crystal lattice, weak trigger bond and the N/C ratio in the molecular framework [13, 16]. Already in the paper [1] it has been stated that the Excitonic model of initiation by Kuklja is in agreement with experimental findings obtained from low-temperature decomposition studies of polynitro compounds. Kuklja has published a comprehensive paper [18]. Using quantum-chemical modeling and simulations of inter- and intra-molecular interaction she has studied their influence on earlier chemical decompositions, their connection with structural and electronic defects and deformations, all these being in the context of initiation of EMs and the experimental data. In connection with the intermolecular interactions it is appropriate to mention the Ma et al. paper [69] from which it appears that the planar conjugated molecular structure and intermolecular hydrogen bonding, supporting the π-π stacking, are necessary for the crystal engineering of low-sensitive high-energy explosives. Besides, they found that the O….O interactions are dominating intermolecular interactions in most of the existing impact sensitive EMs. Zhu and Xiao have reviewed some recent studies in predicting impact sensitivity for different classes of energetic crystals based on first-principles band gap which has been developed to measure impact sensitivity for a series of energetic crystals [70]. The smaller the band gap is, the easier the electron transfers from the valence band to the conduction band, and then the more easily decomposition or explosion will occur. The first-principles band gap criterion is applicable to different series of energetic crystals with similar structure or with a similar thermal decomposition mechanism [70]. These structural and thermo-analytical similarities are very important, but they have not been taken sufficiently into account in the above mentioned approaches, and their meaning will be shown later. Zhang's approach [71], based on the largest Mulliken charges of the nitro groups in the polynitro compound molecules, is relatively well known. However, in Zhang's understanding, these charges have a curvilinear relationship to impact sensitivity showing possibly just a trend, mainly as a result of not taking into account any structural similarity in the compounds studied. On the other hand, using the same approach for the nine "genuine" highly thermostable polynitro arenes leads to two linear relationships [72]. An absence of structural similarities, with the choice of some unsuitable data in the study of the relationship between IS and the crystal lattice compressibility in nitramines [12], leads to different conclusions compared with when the E_{dr} value for pure ε–HNIW (ε–2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane) is included into the group of nitramines analyzed [73]. A relationship between the E_{dr} values and the crystal lattice free volume, ΔV, is thus not uniquely determined [73]. Including the bulk (K) and shear (G) modules of the nitramines studied and their PBXs into this analysis has led to the discovery [73] that a relatively tight linear correlation exists between the $K.G^{-1}$ ratios and impact sensitivity.

An interesting approach to impact sensitivity has been published by Mathieu [74]. He has described approximate relationships between the shock sensitivity index, SI, and impact sensitivity, h_{50}, for 156 different polynitro compounds. The SI index is defined by the equation

$$SI = \frac{ND_{min}}{\Delta_d H_0} \qquad (1)$$

where N is the corresponding number of atoms and $\Delta_d H_o$ is the heat of reaction. This relationship is not unambiguous and can be broken down into four sub-groups (apparently on the basis of the structural similarity of the EMs). In another paper, Mathieu has used the rate constant, k_{pr}, already derived in his paper [74] for the exothermic reaction, which is expressed as a sum of contributions arising from the various explosophores i potentially associated with the initiation [76]:

$$k_{pr} = \frac{1}{N_A} \sum_i Z_i \exp(-\frac{E_i^{\dagger}}{k_B T_e}) \qquad (2)$$

where k_B is the Boltzmann constant, N_A the number of atoms per molecule, T_e the temperature of the process activation, $E_i^{\dagger}$ the activation energy and Z_i is the pre-exponent [75, 76]. Between the k_{pr} values and impact sensitivity, h_{50}, Mathieu has found [75] a relatively respectable logarithmic relationship. Following this paper [75], Mathieu and Alaime have derived [76] for the drop weight impact height h_{50} the expression

$$h_{50} = \left(\frac{k_c}{k_{pr}}\right)^4 \qquad (3)$$

where k_c is an empirical constant. The authors claim [76] that, compared with previous approaches, their process is more complete and exhibits a good predictive value.

Paper [23] points out the well-known fact that the impact sensitivity of energetic materials depends, in general, on the quality and granulometry of the crystals. This was demonstrated for HNIW, for which special conditions for obtaining its RS-grade crystals are required to ensure perfect placing of the molecules into the crystal lattice during crystallization (see for example Ref. 73 and quotations therein). However, most nitramines (for example) when crystallized from a simple “beaker” in the laboratory give products the impact sensitivity of which corresponds to the published data (i.e. the NSWC and LLNL based data [52 – 54]). The paper [23] has tried to find an answer to this observation and has stated that attention should be paid to the dependence of impact sensitivity on the specific surfaces of crystals from a sample of the given individual energetic material obtained by screening.

2.2. Shock sensitivity

It is well-known that the primary physical mechanism with initiation by shock is entirely different from that involved by impact (see review [1]). Another well-known fact is that each EM has its own critical initiation pressure, *P**, and initiation density, $\rho*$ [77, 78]. If the initiation pressure is lower than *P*,* decomposition of EM will start and develop using a "hot spots" mechanism (or it might be extinguished), while at greater pressure and density the decomposition proceeds through a homogenous mechanism (depending on the chemical structure of the EM) [77, 78]. This fact is one of the reasons for results from shock sensitivity measurements being frequently non-reproducible . Small scale and large scale gap tests are being used for experimental determination of this sensitivity [79]. We have used a small water gap test [24], standardized by STANAG [48], and we discovered that it only requires a very small change in its arrangement for measurement results to be different. Such sensitivity to minor, insignificant, changes in the arrangement is another problem here.

On the basis of results from the Los Alamos Natl. Lab. large scale gap test Keshavarz et al. have derived a method for shock sensitivity prediction for pure and mixed explosives by using their modified statistical method [57, 80]. Their approach includes density, oxidation and porosity coefficients of the explosive charge and the number of nitraminic groupings in the molecule or explosive mixture. In this connection, the influence of porosity in this kind of gap test is experimentally well described [81]. These authors have used a similar approach in the case of the small scale gap test [57, 82]. Numerical modeling of shock-to-detonation transition in the same gap test of a PBX based on HMX (β–1,3,5,7-tetranitro-1,3,5,7-tetrazocane) has been published by Ju Zhang et al. [83]. Using an Euler program, they insert hot spots during the passage of a shock wave through both the pure HMX and the PBX based on it, and have described a new strategy without generating spurious spikes, demonstrating that numerical convergence can be achieved [83].

Using the ReaxFF program to study the shock induced decomposition of RDX (1,3,5-trinitro-1,3,5-triazinane) is the subject of paper [84]. Concerning the intermediate products of the RDX decomposition here [84], they are, in principle, the same as those in the low-temperature thermal decomposition of this nitramine carried out in a vacuum [85]. Tan et al. [86] have employed DFT/BLYP/DNP to calculate the bond dissociation energy (BDE) of X-NO_2 (X = C. N, O) and the largest Mulliken charges (Q_{NO2}) of the nitro group in 14 kinds of nitro compounds. They have found that these values are in good agreement with the logarithm of the experimental shock initiation pressures. The authors reflect that these BDE and Q_{NO2} values may be important factors influencing the shock sensitivity of nitro compounds. On the basis of their model, the authors have predicted the BDE of C-NO_2 and Q_{NO2} of another 14 kinds of heterocyclic nitro compounds which are used for predicting shock sensitivity [86]. Taking into account the findings of Tan et al. [86], Mathieu proposes the ratio of the weakest bond dissociation energy of nitro compounds to their decomposition enthalpy per covalent bond as a practical shock sensitivity index [87]. Without any empirical fitting, this correlates remarkably well (R >= 0.95) with shock sensitivity data reported for 16 molecules spanning the most significant families of explosive compounds. It demonstrates that sensitivity structure relationships should take the energy content of the material into account [87]. The results of shock sensitivity measurements by means of a little water gap test on plastic bonded explosives (PBXs) with polyisobutylene binder (C4 matrix) [24] showed a good linear relationship with impact sensitivity with crystalline fillers of the following PBXs: 1,3,5-trinitro-1,3,5-triazinane (RDX), β–1,3,4,7-tetranitro-1,3,5,7-tetraazocane (β–HMX) and cis-1,3,4,6-tetranitro-octahydroimidazo-[4,5-d]imidazole (bicyclo-HMX, BCHMX). The PBX with the ε–2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) filler did not belong to this group [24] because this particular polymorphic modification possesses a globular and crowded molecule with morphological instability.

2.3. Friction sensitivity

A study of the friction fundamentals of explosives [50] was undertaken by Brown [88] in 1970. Unlike the case of impact and shock sensitivities for EMs, no further attention seems to have been paid to the characteristics of friction sensitivity (FS) of such materials in the past 40 years. At the moment, two methods are the most commonly used here - ABL friction [37, 89] tests and BAM friction [37, 90] tests - with the second one being the one most encountered in Europe. This particular sensitivity depends [91] on the crystals' hardness, their thermal conductivity, the shape and size of their rubbing surfaces, but also on whether the given material melts before decomposition or not. Hardness appears to be the most important physical characteristic for friction [91]. As data concerning crystal hardness is relatively lacking in the literature, Harris has substituted crystal density and for several primers has found a good relationship with FS [91]. Our experience shows that the results of FS determination can also be heavily influenced by "human variability". This finding, coupled with different approaches to the FS measurements [37, 89, 90], is probably the reason why this type of sensitivity does not attract the attention of theoretical chemists/physicists. Nevertheless, taking the BAM friction test, careful measurements by a single researcher provide results showing relationships which also correlate with the results of other stability and physico-chemical tests [2, 25 – 27, 29] and also with the output of DFT calculations [28].

The investigation of β–HMX fractions with different granulometric distributions showed that the lowest impact sensitivity is connected with the highest FS and *vice versa.* There exists a relatively wide range of β–HMX grain sizes in which the FS is practically the same. Inclusion of a wider assortment of nitramines into the above-mentioned relationship results in their being split into a number of partial groups, which are relatively closely connected with the molecular-structural characteristics of the nitramines under study [25]. Comparison of FS with heats of fusion, $\Delta H_{m,tr}$, leads to a finding that the increase in $\Delta H_{m,tr}$ values is—more or less—connected with a decrease in friction sensitivity [25]. Considering the Arrhenius parameters of non auto-catalyzed thermal decomposition of these nitramines, and subsequently comparing them with the corresponding FS, leads to the general finding that increasing values of activation energies of the said decomposition are connected with decreasing FS values [26]. A similar trend was found in the relationship between FS and the hypothetical initiation temperature for 5% conversion of the nitramines after 50 μs of their thermolysis. However, the trend in the relationship between FS and the hypothetical initiation temperature might be reversed if, for a given series of nitramines, their initiation reactivity is predominantly determined by the energy content of their molecules and a closer similarity in their molecular structures [26]. Results from the DFT B3LYP/6-31-G(d,p) // 6-311+G(d,p) calculations of the positive ($V_{S,max}$) and negative ($V_{S,min}$) extremes of molecular surface electrostatic potentials $V_S(\mathbf{r})$ [65] of such nitramines show relationships with their FS - while there is an ambiguous relationship between the $V_{S,max}$ and FS values, the increase in

$V_{S,min}$ values is related (more or less) with decreasing FS [28]. As in the case of other nitramine sensitivities, their FS also exhibits a relationship with the ^{15}N NMR chemical shift of the nitrogen atoms in the nitramine groupings [2, 29]. Using ^{15}N shifts of the nitrogen atoms in the nitro groups results in more sophisticated relationships than those resulting from the use of the shifts of aza atoms. In this sense, the initiation by friction differs from initiation by impact and seems to be similar to initiation by shock, electric spark, and initiation in low temperature thermolysis [2, 29]. Correlation with the nitro nitrogen atom shifts is logical because the oxygen atoms of these nitro groups, by their dipole-dipole interactions, are in contact with the oxygen and nitrogen atoms of nitro groups in neighboring nitramine molecules in the crystal (see references in paper [25]), which is the decisive factor governing the crystal structure of nitramines. This type of interaction will act against the shear slide during friction.

Mostly on the basis of the Jungova's paper [25, 26], Iranian authors Keshavarz et al. [92] have derived their new method of predicting the friction sensitivity of nitramines with a general formula $C_aH_bN_cO_d$ as a function of the optimized elemental composition and the contributions of specific molecular structural parameters. For formulation of this program, 20 nitramines with different molecular structures were used, and for the program testing, another 11 nitramines with complex molecular structures were used [92].

2.4. Electric spark sensitivity

There are several different approaches and types of apparatus reported in the literature for measuring and solving electric spark sensitivity (E_{ES}) [37, 48, 50, 93 - 96]. The E_{ES} values corresponding to these various options are to be found here [19, 20, 93] (in decreasing order of magnitude [19, 21 93]). It seems that in Europe the Czech Defense Standard (a part of STANAG [48]) gains ground.

At the University of Pardubice two kinds of instrument were constructed over time in the 1994 – 2002 period for studying electric spark sensitivity [1, 2, 19, 20, 95]. They differed in the electrode configuration and the circuit structure [20, 95], but mainly in the construction of their spark gaps. Originally, the discharge in the spark gap has gone through an air gap (model RDAD [20, 95]) while in the recent model of the instrument (ESZ KTTV [20] in its latest version ESD 2008A [97]) the electrode is in direct contact with the sample. The construction difference leads to a difference by an order of magnitude in sensitivity values [1, 2, 19, 20, 95]. The considerable electrical energy losses in the air gap between the upper electrode and the sample surface in the older system (RDAD) of measurement contribute to this difference – a large part of the discharge is converted into the expressive thermal component here [1, 2, 20]. Nevertheless, the values from the measurements carried out with the RDAD instrument were comparable with those of the Los Alamos Natl. Lab. [95]. Even though results from the RDAD instrument also correlate very well with the molecular structure of polynitro compounds [1, 19, 21, 98, 99] they cannot be taken as values of a "pure" (real) electric spark sensitivity. It is important that the semi-logarithmic relationship between the E_{ES} values and dissociation energies $DH(N\text{-}N)$ in nitramines is directly proportional [19]. The relationship of the results from both these instruments (i.e. RDAD and ESZ KTTV) is represented by a broken-line [19] for nitramines and full lines for polynitro arenes [20]. The majority of published papers about prediction of the electric spark sensitivity (see for example [98 - 106]) are based on our results using the RDAD apparatus [21, 95, 107 - 111].

In practice, the standard [48] is based on the real electric spark sensitivity which is obtainable by the ESZ KTTV type of instrument, i.e. the current version ESD 2008A [97]. Results from this kind of instrument have a close relationship with the molecular structure of the polynitro compounds measured [1, 19, 112]. Detailed analysis has shown [112] that the correlation of the E_{ES} values with the largest net charges of the nitro groups (Q_{NO2}) in polynitro arenes is linear but not uniform. It divides the compounds studied into a group of "genuine" polynitro arenes and a group of derivatives with a hydrogen atom in the γ-position towards the nitro group. In each from these groups there are respectively four and three individual linear relationships [112], consistent with the already mentioned structural similarity [71]: electric spark sensitivity mostly increases with rising Q_{NO2} values [112]. However, the generally accepted assumption that the most positive Q_{NO2} value in the molecule represents its sensitivity [71] cannot be regarded as universally valid - it would be useful to study the findings from crystallographic studies of the respective compounds to enable further understanding [2, 112]. In keeping with the knowledge about initiation reactivity of polynitro compounds [1, 2, 19, 21, 23, 29, 38, 39], the E_{ES} values correlate with those characteristics of the molecular structure which correspond to the primarily leaving nitro group in the polynitro compound molecules. Thus, these E_{ES} values for nitramines logically correlate with ^{15}N NMR chemical shifts of nitrogen atoms of the primarily reacting nitro group and with the charges on these atoms [19]. In an attempt at classifying the reaction center in molecules of polynitro arenes by means of ^{13}C NMR chemical shifts of the "bearers" of primarily leaving nitro groups (see Fig. 2), logical dependencies were observed, especially in the case of derivatives whose primarily reacting nitro group is conjugated with the rest of the molecule [1, 21, 113]. An analogous relationship with ^{15}N NMR chemical shifts of nitrogen atoms of the primarily reacting nitro group in a larger group of polynitro arenes is presented in Fig. 3. The reverse semi-logarithmic relationship between the E_{ES} values and dissociation energies *DH(N-N)* in nitramines [19] has been interpreted by Turker [105]. This trend is the opposite of the analogous relationship for the RDAD results [19]. The E_{ES} values also correlate with heats of fusion for the nitramines studied, probably due to the influence of dislocations in their crystals on electric spark sensitization. This assumption could be relevant to the significant influence of the shapes and sizes of the crystals on electric spark sensitivity for energetic compounds in general [19].

Figure 2

Figure 3

In polynitro compounds possessing more than one potential reaction center in their molecule it has been again shown [1, 21] that there can be selective initiation reactivity depending on the kind of impulse [110]. A decrease in electric spark sensitivity (i. e. an increase in the E_{ES} values), when the grain size of the nitramines' crystals increases, confirms the French idea (see in [114, 115]) about the mechanism of spark energy transfer into the powdered reactive solid, i. e. in this case to decrease the number of intergrain points per unit volume [115]. However, dislocations in the crystals should also have some effect on this type of energetic material initiation [19]. Artificially introducing fine and hard particles (nano-diamond, crushed glass) into the crystalline nitramines decreases the electric spark sensitivity of the resulting mixtures, i. e. the particles behave as a flegmatizing additive, where the number of intergrain contact points of the nitramine grains is decreased by introducing the foreign particles [115]. In 2005 Berger et al. [118] presented information about their innovative method and instrument for electric spark sensitivity determination which gives E_{ES} values similar to those using the ESZ KTTV method. In the absence of sufficient results, it has been impossible to make any sensible comparison of the two methods.

2.5. Sensitivity to laser beams

Even though publications in this area have appeared in the literature since 1960 [119], the number of publications is somewhat lower in comparison with the other kinds of energetic material sensitivity. However the findings have been variously summarized in older papers [1, 119, 120], in a very good report [121], in an already mentioned monograph [50], in a part of another monograph [122] and in an excellent overview with quantum chemical analysis of the EMs' sensitivity, including initiation by laser, which was published [18] by Kuklja. Therefore, in what follows, only certain papers not included in these overviews are mentioned [18, 50].

A frequently cited paper [123] deals with determination of the ignition time of nanoscale particle diameter composites of aluminum (Al) and molybdenum trioxide (MoO3). A 50-W CO2 laser provided the ignition source and high-speed digital images were used to determine the ignition time and burn rates. The Al particle composites showed significantly reduced ignition times that varied from 12 ms up to 6 s respectively for nanometer scale particle size compared with the micrometer scale Al particle composites. Lee et al. have rigged up a model for simulating high energy laser heating and ignition of confined EMs [124]. The model considers the effect of irradiating a steel plate with long laser pulses and continuous lasers of several kilowatts and also the thermal response of well-characterized EMs for ignition; the final model was verified on RDX, HMX and TATB [124]. Bhattacharya et al. [125] used ultraviolet lasers at different wavelengths, such as 226, 236, and 193 nm, to prepare the excited states of nitromethane (NM), dimethylnitramine (DMNA), and isopropyl nitrate (IPN) which are used as model molecules for C-NO2, N-NO2, and O-NO_2 active moieties, respectively. The major decomposition pathway of electronic excitation at 193 nm of NM and IPN involves fission of the X-NO_2 bond to form an electronically excited NO_2 product, which further dissociates to generate NO. The production of NO molecules from electronically excited DMNA is proposed to go through a nitro-nitrite isomerization pathway. Abdulazeem et al. [126] have dealt theoretically with the behavior of β–lead azide when heated by continuous and pulsed laser; it has been argued that this azide initiation with low energy laser is thermal in origin. Civiš et al. [127] have studied 2,2-dinitroethylene-1,1-diamine (FOX-7) under the influence of a combination of laser-induced breakdown spectroscopy (LIBS) and selected ion flow tube mass spectrometry (SIFT-MS) and they tried to formulate the chemical mechanism of the FOX-7 molecule fission. Brown et al. [128] dealt with observations of the hot-spot formation in energetic RDX-PCTFE-aggregates subjected to dynamic pressure loading and laser irradiation by means of adiabatic heating, laser heating and thermal decomposition. The effects of the electromagnetic absorption coefficient coupled with void distribution and spacing, grain morphology, crystal-binder interactions and dislocation densities were analyzed to determine their influence on the time, location and mechanisms of hot-spot formation. Four different mechanisms for hot-spot initiation under dynamic laser and pressure loads were identified, which depend on the localization of plastic shear strain and laser heat absorption within the aggregate. The authors of this paper [128] have found that the hot-spot formation is accelerated by higher absorption coefficients and by localized plastic deformations that occur in areas of significant laser heating. In the paper [129] the authors consider the interplay between optical and thermal energies, analyze the applicability of the thermal mechanism of initiation, and estimate the limits of its efficiency in the process of laser initiation of energetic materials. They propose a simple demonstration of a feasibility of non-thermal selective photo-initiation while challenging the widely popular perception of the thermal nature of laser initiation. Paper [130] deals with a microcenter heat explosion model: on the basis of the aluminum nanoparticles' absorptivity in the PETN-matrix and the dependencies of the absorptivity on the particles' sizes and wave length of irradiation, the authors have shown that the particle's radius, which corresponds to the absorption maximum, and the peak values, depend on the irradiation wave length. The authors also calculated the dependencies of the critical initiation energy densities on the metal inclusions' radii for the energetic materials. They concluded that the RDX aluminum composite is the recommended material to use in optic detonators, especially for the second harmonic of the ND:YAG laser [130]. A micro-hotspots model for the laser initiation is described in study [131]. The authors take into account the melting of the matrix of the energetic material and the nano-metallic component contained in the mixture. Melting leads to a reduction in the maximum heating temperature and a slight change in the radius of the most heated nanoparticle. The dependencies of the critical initiation energy density of explosive decomposition of PETN with aluminum nanoparticles on the inclusion radius with and without melting are calculated. With melting taken into account, the model gives a higher critical initiation energy density for explosive decomposition. In the case of inclusions of large radius, the formation of the reaction site of explosive decomposition occurs before complete melting of the metal inclusion, which results in solidification of the melt during the induction period. Kalenskii et al. [132] have dealt with the influence of laser wavelength on the critical energy density for initiation on PETN containing nanoscale aluminum inclusions at radiation wavelengths of 1064 and 532 nm. The critical initiation-energy density that corresponds to a 50% probability of explosion was 1.15 J cm^{-2} for the first harmonic of a neodymium laser and 0.7 J cm^{-2} for the second. It was shown that the particle diameter corresponding to the absorption efficiency maximum and the amplitude of the maximum depend on the radiation wavelength. The authors calculated dependencies of the critical initiation energy density for energetic materials on the radius of metallic nanoparticles. The qualitative agreement between theoretical and experimental results is shown [132].

While papers dealing with elaboration of the theories, models, predictions etc. concerning initiation by laser, are working with a maximum of four compounds (very often on RDX, HMX, PETN or FOX-7) as a model compound, the authors, who develop new high nitrogen primers, are addressing this problem from the perspective of their practical needs. For all of them it is possible to mention studies carried out by Klapoetke et al. [133, 134]. The paper [133] treats 1,2-bis[5-(1-methylhydrazinyl)tetrazol-1-yl]ethane and its corresponding metal [$Cu^{2+}{}_2$, $Co^{2+}{}_3$, $Ni^{2+}{}_4$] complexes and paper [134] addresses tris(carbohydrazide)metal(II) perchlorates [M(CHZ)(3)](ClO4)(2) (MMg^{2+}), ($Mn^{2+}{}_2$), ($Co^{2+}{}_3$), $Ni^{2+}{}_4$, and ($Zn^{2+}{}_5$) and the bis(carbohydrazide)diperchloratocopper(II)$_6$; both these groups of metal(II) complexes were investigated by means of the single-pulsed laser irradiation and it was shown that all these complexes detonated after initiation by monopulsed laser light. The initiation mechanism seems to be of a thermal nature.

2.6. Sensitivity to heat (thermal reactivity)

Basically, there are two main method groups presented in the literature for dealing with sensitivity to heat [50, 135 – 139]:

a) Thermoanalytical methods, such as Differential Thermal Analysis (DTA), Differential Scanning Calorimetry (DSC) and Thermogravimetry (TGA), the results of which can be used to determine Arrhenius parameters [136, 137]. These parameters are usually associated with a given chemical reaction or may describe the global process and can be used to calculate the critical temperature and self-heating properties associated with a particular explosive of a given size and geometry [135, 137]. The vacuum stability test would also best be placed in this group [32, 33, 44, 138 – 141].

b) Determination of the experimental critical temperatures for explosives of a given size and geometry by carrying out a variety of tests where the explosive may be confined or unconfined. These tests include [50, 135, 136] an isothermal cook-off, slow cook-off, one-liter cook-off and the isothermal Time-To-Explosion (Henkin test), where the first two mentioned are large-scale and confined, the one-liter cook-off is large-scale and unconfined and the Henkin test is very small-scale and moderately confined [135, 136].

2.6.1. Thermal kinetics and stability

The well-known problem of defining the kinetics and mechanism of the thermal decomposition of energetic materials is the strong dependence of the corresponding kinetic parameters on temperature, pressure, and the construction materials in contact with the decomposed sample [1, 21, 142, 143]. Hence the correlation of results obtained from thermal analyses of energetic materials using different methods and/or different types of apparatus of different origin is relatively rare [1, 21, 142 - 144] even though in the last few years it is possible to observe a certain consolidation [137, 145]. So far the most reliable results in this area are the theoretical and practical findings obtained by Russian scientists on the basis of their manometric method (see Refs. [44, 142, 146] and quotations therein). The data obtained by this method are known to correspond to the non-autocatalyzed stage of thermal decomposition of the given material (i. e. to molecular structure [1, 21, 144]).

The literature contains an almost inexhaustible amount of thermal analysis data of EMs from different thermoanalytical equipment, methods and authors which are mostly simply a part of other papers about syntheses of new substances or development of new explosives; findings of this kind could usefully be grouped together in a separate monograph.

For a comparison with each of the Arrhenius parameters from the different resources and from the Russian manometric method it is possible to use their relationship with the ^{15}N NMR chemical shifts [1, 21, 144] (similar to the case of impact sensitivity shown in Fig. 1). For this purpose we have used also our new approach to molecular surface electrostatic potentials (EPS) [147]: as a criterion of the imbalance between the $V_{S,max}$ and $V_{S,min}$ EPS extremes, we have derived their sum and used as a new simple characteristic for ESPs - $V_{S,\Sigma}$ (eqn. 4), whose values have close relationships to the Arrhenius parameters of thermal decomposition of the nitramines studied [147] – see Fig. 4 for activation energies of thermolysis.

$$V_{S,\Sigma} = V_{S,max} + V_{S,min} \tag{4}$$

Figure 4

Scheme 1

These summed ESPs also correlate well with the rate constants of the monomolecular thermal decomposition of nitramines and with their heats of fusion; increasing the $V_{S,\Sigma}$ values leads logically to decreasing values for the rate constants mentioned and to increasing physical stability in nitramines discussed in paper [147].

A comprehensive analysis of the kinetic parameters of thermolysis of EMs using predictive methods has been documented in [148, 149]. The first of these [148] assumes that the activation energy of some 86 energetic compounds with different molecular structures and with the general formula $C_aH_bN_cO_d$ can be expressed as a function of an optimized elemental composition as well as the contribution of specific molecular structural parameters. The second method [149] uses a new computer program, named EDPHT 2.0, which also embraces the prediction of the crystal density and enthalpy of formation and, in the case of activation energies of thermolysis, reflects the work reported in Zeman's papers [143, 144, 149 – 153]; for predicting activation energies this program needs no experimental data and the conformity of its results with data from the Russian manometric method is good. The experimental investigation of the relation of the molecular structure of 10 nitric esters and their thermal reactivity is addressed in the papers by Yan et al. [154, 155]. For this purpose TGA and DSC were used. With the exception of the evaporable members of this series, the activation energies of decomposition correspond to those from using the Russian manometric method [154]. The results of an investigation, using thermogravimetry (TGA) techniques and quantum chemical calculations, into the decomposition kinetics and mechanisms of 2-amino-4,6,-diazido-s-triazine and its five derivatives have been reported in paper [156]. The rate-limiting steps for the materials involved are the scission of the azido group for which the kinetic compensation effect was found and compared with some other groups of EMs. Authors Yan et al. have studied the influence of variously-based polymeric binders on the cyclic nitramines RDX, HMX, BCHMX and ε–HNIW: polyisobutylene (C4 matrix), acrylonitrile-butadiene rubber (Semtex 10 matrix), styrene-butadiene rubber (Formex matrix), vinylidene fluoride and hexafluoropropene copolymer (Viton A200) and the ter-polymer of vinylidene fluoride, hexafluoropropylene and tetrafluoroethylene (Fluorel), and the results are presented in an interesting series of papers [157 – 163]. It was found that the Formex binder has a significant effect on the activation energy distribution of nitramines [163], that hydrocarbon polymers have little effect on the thermal stability of BCHMX [157], and in the case of HNIW, that the binders C4, Semtex and Formex could greatly mitigate the decomposition process of this nitramine from a single step to a multistep, resulting in lower impact sensitivity, whereas fluoropolymers have only a slight effect [158]. It has also been proved that Semtex and Viton A are better binders than C4 and Formex for HNIW and RDX based PBXs in terms of their greater thermal stability, and Formex is a poor binder for BCHMX [160]. A vacuum stability test with these PBXs has shown [32, 33] that the C4 matrix does not fully eliminate the specific influence of the nitramine filler's molecular structure (crowding in their molecules – in HNIW and BCHMX) on the initiation reactivity of the corresponding PBXs. This represents a difference from the study of PBXs with the Formex P1 binder [33] where their matrices increase the reactivity of the nitramine fillers to such an extent that the above mentioned specific influence of molecular structure is practically eliminated.

2.6.2. Thermal criticality

The theory of thermal criticality, as well as that of the cook-off, is well presented in a monograph [50]. Critical temperatures are very important when considering the risks of any given EM [50]. These temperatures are obtainable by means of the well-known Frank-Kamenetskii theory [50, 79, 137] using kinetic data from thermoanalytical methods. This has been done, for example, for PBXs [141, 159, 164], nitric esters [154, 155], a group of new high nitrogen EMs [165, 166] or several trinitromethyl explosives [167]. Simple methods of critical temperature estimation using non-isothermal DSC have also been published [168, 169], one of them on the basis of Harcourt-Esson's equation [169]. The isothermal Time-To-Explosion or Explosion Delay [79, 137, 170], i.e. the Henkin test [170 – 174], in which a relationship between the logarithm of the induction period and reciprocal induction temperature (in K) is specified, is often mentioned along with critical temperature [137, 170, 171]. The cook-off tests [50, 173 - 182] in both their small and larger versions are, in principle, similar to explosion delay; numerical simulations of these tests have appeared relatively frequently in the literature [177 – 179, 181, 182].

3. Performance

3.1. The most frequent methods of determination

Detonation velocity (*D*), detonation pressure (*P*) and heat of explosion (*Q*) are the basic characteristics of any explosive's performance. According to the Chapman-Jouget solution the relationships between these characteristics can be expressed as [183]:

$$D_{CJ}^2 = 2Q(\gamma^2 - 1) \tag{5}$$

$$P_{CJ} = \frac{\rho_0 D_{CJ}^2}{(\gamma+1)} \tag{6}$$

where *Q* is the chemical heat stored in the material per unit mass (heat of explosion), γ is the polytropic coefficient (a ratio of c_p/c_v, where c_p and c_v are the middle specific thermal capacities) and ρ_0 is the starting charge density. These characteristics can be obtained experimentally, above all detonation velocity [37, 184], but also detonation pressure [37, 185] and heat of explosion [186]; recently a laboratory-scale method for estimation of performance was published, which is based on milligram quantities of EMs and on schlieren imaging of the shock wave generated in air by the formation of a laser-induced plasma on the surface of the given energetic material residue [187] (a strong linear correlation exists between the laser-induced shock velocity and the performance characteristics of the EM). However, there are a number of different methods for prediction. One of the more frequently used is the Kamlet and Jacobs method for CHNO explosives [188], and also Stine's approach [189] might be mentioned. For CHNOF explosives there exist the method developed by Short et al. [190], the CHEETAH computer program [191], available only for authorized US government contractors, and the very popular EXPLO5 program [192] developed by Suceska. The last two programs are usable also for EMs with a metal content; Wang et al. have modified the Kamlet and Jacobs method for metal-containing explosives [193]. The data required for all these calculations are the formula, the heat of formation and the density of the given compounds. Formula and molecular weight are sufficient for calculating detonation velocity for CHNO [194] and CHNOF [195] explosives according to Rothstein and Petersen. Formula, density and heat of formation of EMs are the data for the BKW program [196] for calculating detonation characteristics. In practice, for research and technical purposes, the results from the lead block test (Trauzl test), ballistic mortar measurements and the change of the parameters of air shock waves are often used as characteristics of an EM's performance [37].

3.2. The most frequent uses of computer-based methods

In our research on PBXs based on the interesting cyclic nitramines RDX, HMX, BCHMX and HNIW, we have used the Kamlet and Jacobs, Short et al., CHEETAH and EXPLO5 methods of calculation [197 – 200], and have found that, for fluorinated binders [200], the *D* values of the PBXs studied, according to the Short et al. method, are systematically lower in comparison with experimental measurements, while the EXPLO5 and CHEETAH programs gave values close to the experimental ones; all three methods used gave very similar values for detonation pressure in the explosives studied. In the case of non-fluorinated binders [197 – 199], the *D* values calculated using the Kamlet and Jacobs method were again systematically lower compared with experimental values while the results from both the computer programs were closer to the experimental ones, with CHEETAH giving values 'better' than those from EXPLO5. All three methods provided comparable results for detonation pressures for the explosives studied [197 – 201]. For PBXs bonded by a polyurethane binder, it was shown that, by using certain modifications of the Kamlet and

Jacobs equations for detonation velocity, it is possible to obtain very good correspondence with the experimental *D* values [202].

The performance predictions using a quantum chemical approach (B3LYP/6-31G*) often depend on predictions of the heats of formation and densities of the given EMs with subsequent use of the Kamlet & Jacobs method for calculating the performance characteristics [13, 203 – 207]. A combination of this approach with the QSPR method and subsequent performance calculation using the CHEETAH program has been described for explosive performance and the sensitivity of new high-energy molecules by Cho [10]. Similarly, by optimizing of molecular structure using B3LYP/6-31G*, with subsequent use of the QSPR approach with several nitrogen-rich EMs, detonation velocities have been predicted [208]. On the basis of heats of formation, predicted by the Born-Haber energy cycles, experimental crystal densities and by means of the EXPLO5 program, Liu et al. [209] have predicted the performance of a series of nitro-1,2,3-triazolate salts.

A series of papers has been published in this area during the past eight years by Keshavarz et al. [210 - 217]. Zamani and Keshavarz have used a combination of the M06-2X/6-311++G** method (for heats of formation prediction) and the BKW program for evaluating the thermochemical and performance properties of nitro-substituted borazines [210]. Using loading density, atomic composition and some structural parameters of the CHNO explosives, Keshavarz has derived an empirical formula for predicting the detonation pressure (with estimation of results using the BKWS and BKWR programs], without considering heat of formation [211]; the author has used a similar approach in another of his papers concerning CHNO and CHNOAl explosives [212]. Again, without the need for the heat of formation, Keshavarz derived a method for the specific impulse prediction [213] for CHNO explosives. Using a simple computer program named EDPHT, complemented by the results from other computer programs, Keshavarz et al. [214] have introduced a way of predicting the following: velocity of detonation, detonation pressure, heat of detonation, detonation temperature, the Gurney velocity, the adiabatic exponent and specific impulse of high explosives; the method can also predict detonation performance for aluminized explosives that can have non-ideal behaviors. Prediction methods by this author for non-ideal explosives are summarized and discussed in the review [215]. On the basis of previous studies for decomposition paths of CHNOClFAl explosives, Keshavarz has introduced a new "hand-calculation" method for prediction of the detonation pressure of explosives and their mixtures [216]. Also the strength of the CHNO explosives prediction using the Trauzl test has been described [217], based on elemental composition, gas phase heats of formation of EMs and which uses the group additivity method.

Türker has dealt with the estimation of detonation velocity using mathematical models [218, 219]. According to the first of these [218] he has derived a mathematical expression between the square of detonation velocity and the total energy and molecular weight of the given explosive, whereby the total energy was obtained using the UB3LYP/6-31G(d) method. The second model [219] is a linear one with the same variables.

Zeman and Atalar [220] have calculated the values of bond dissociation energies, *BDE*, of the weakest N–N bonds and total energies, E_{total}, of molecules of 14 cyclic nitramines by means of the UB3LYP/6-31G* and UB3LYP/6-31+G*//PM3 methods. The authors found no totally unambiguous relationships between the logarithms of detonation velocities and BDE/E_{total} ratios due to the influence on sensitivity of a real conformation and intermolecular force in a real molecular crystal. However, partial relationships of this type can be used for evaluation of effectiveness of the method of designing molecular structures of energetic cyclic nitramines for obtaining products with the maximum possible performance [220]. In a similar manner to that used in the thermal analysis study [147] Zeman and Friedl have found that the summed electrostatic surface potentials, $V_{S,\Sigma}$ (see eqn. 4), have close relationships with the *D* values [221]; this new criterion is shown to be the best SEP characteristic for the study of detonation initiation. The increase in the $V_{S,\Sigma}$ values corresponds with an increase in the *D* values (energy content of molecules).

The authors of paper [222] predict heats of explosion on the basis of the relationship of such heats with both the NBO charges (Q_{NO2}) and the ^{15}N NMR chemical shifts of polynitro arenes, respectively; these characteristics were obtained by means of B3LYP/6-311+G(d,p) and B3LYP/6-311+G(2d,p), respectively. The uniform relationship with Q_{NO2} is interesting, whereas the second approach is not new (see Ref. 116) and the calculated ^{15}N NMR chemical shifts differ from measured values.

4. Mutual relationships between sensitivity and performance

The homolytic fragmentations or reactions of the C–NO_2, N–NO_2, N–NO, and O–NO_2 groupings, or other bearers of explosibility (i.e. explosophores), are common primary fission processes of energetic materials under thermal [1, 2, 21, 22, 31, 38, 39, 113, 142, 143, 146, 147, 151, 154], impact [1, 2, 21, 23, 56, 68, 74], friction [25 – 29], shock [1, 2, 21, 154, 221] and electric spark stimuli [1, 2, 19, 20, 112, 115]. Therefore, it is natural that relationships should exist between the characteristics of low-temperature thermal decomposition and other kinds of sensitivities, including the detonation parameters [1, 2, 21, 38, 56, 143].

4.1. Relationships based on the heat of explosion

Heat of explosion here comprises not only own heat, Q, but also its representatives in the sense of eqns. 3 and 4, including ratio $P.\rho^{-1}$. In 1980, one of the first relationships of the $P.\rho^{-1}$ values with Piloyan activation energies of thermal decomposition of polynitro arenes and its subsequent analysis [39, 223] led to the discovery that the chemical micro-mechanism of the primary fission in low-temperature thermolysis should be identical with those of detonation initiation. This finding was later supported by analysis of the findings from other authors (see in papers [2, 21, 39]) and activity in this area is continuing. In the latter period, Fried et al. [224] and, recently, Mathieu [75] (see eqn. 1) have included “heat of decomposition” of EMs into their relationships between the bonding energies of the first splitting bonds and impact sensitivity of EMs.

In further work [39] a relatively wide spectrum of relationships between heat of explosion and/or its representatives, and the results of impact, friction, electric spark and thermal sensitivity measurements have been described [1, 2, 21, 22, 27, 31, 39, 56, 74, 154]. All these relationships have their origin in the earlier-mentioned identity of the homolytic primary fission in both the detonation and low-temperature thermal decompositions of energetic materials (for relevant quotations, see Refs. [1, 2, 143]); this was one of the reasons to use the Evans–Polanyi–Semenov equation (E–P–S) in a modified form [225] to study the chemical micro-mechanism governing initiation of energetic materials [1, 30, 31, 143, 226]:

$$E_a = \alpha \cdot Q + \beta \qquad (7)$$

where E_a can be the activation energy of thermal decomposition, drop energy (impact sensitivity), energy of electric spark, friction sensitivity, half-wave polarographic potential (see Refs. 1, 2, 21, 226 and references therein) but also the slope of the Kissinger relationship (i. e. the ratio $E_a.T^{-1}$ – original relationship see Ref. 227), Q can be the heat of explosion or its representative, D^2 [1, 2, 21, 31, 226] or the relative explosive strength [201, 228], and latterly also the product $\rho.D^2$ (representative of P and/or explosive strength) [30, 31, 201]; the last product correlates well with explosive strength [201, 228]. As well as the original E-P-S equation [225], eqn. 7 is also valid for groups of molecules with closely related structures and underlines the importance of the bond that is the first to split in the molecule during the detonation of any given material [1, 2, 21, 226].

A relationship, in the sense of eqn. 7, between impact sensitivity and heat of explosion, Q (in kJ.g^{-1}) or square of detonation velocity [2, 31], respectively, shows in PBXs increasing this sensitivity with increasing performance characteristics. However, using these variables in pure nitramines gave ambiguous results as shown in Fig. 5 [56]:

Figure 5

Other situations will occur if we take detonation as a reaction of the zero order (which in reality it is); the heat of reaction, i.e. heat of explosion, will have a dimension in Joules per unit volume [30, 56, 201]. Fig. 6 corresponds to this approach, where the heat of explosion is in MJ.m^{-3} (i.e. product of ρQ_{real}) and the nitramine group is again divided into several logical groups according to the conformational similarity of their molecules and/or reaction centers. Here the relationship of the logarithm of sensitivity to performance already corresponds to the general rule about reciprocal relationships between impact sensitivity and performance of energetic materials, with the exception of line E; this line is analogous to the D and E lines in Fig. 5 [56].

Figure 6

By incorporating the “exceptional” cyclic nitramines mentioned earlier around line E into the polymeric matrixes, the resulting PBXs have impact sensitivities which already follow the general rule (see Fig. 7).

Figure 7

Because a semi-logarithmic relationship exists between impact and friction sensitivities [25], a linear relationship has been found between friction sensitivity and volume heat of explosion (ρQ_{det}) [30, 201]. Maximum volume heat of explosion very good correlates with the critical pressure of explosion initiation, P^*, as it was shown by Pepekin et al. [230].

In line with eqn. 7, Nesterenko et al. have described [231] the relationships of impact sensitivity and heat of explosion for some 67 nitro-, nitroxy- and nitramino-compounds. The authors have used impact sensitivity data from Russian sources (see quotations in Ref. 231) and the heats of explosion calculated according to Pepekin et al. [229]. In this way they obtained partial relationships which comply with their structural similarity, and follow the general rule of impact sensitivity dependence, but the correlation coefficients are lower compared with those for impact sensitivity determined according to the BAM method [231]. Using the Russian laboratory methodology of sensitivity specification, Smirnov et al. [47] derived relationships (multinominals) for impact and friction sensitivities into which they included the heats of explosion and the melting points of some 28 polynitro compounds studied. Smirnov et al. have developed also a very interesting method of predicting energetic material parameters, including the critical pressure of detonation initiation (shock sensitivity) [232]; they have also inserted heat of explosion into the corresponding multinominals. The authors have stated that the sensitivity of substances possessing extreme parameters is considered to be unacceptably high [232]. As already mentioned, their Russian colleagues deserve greater publicity for their general approach to sensitivity of EMs.

Recently Politzer and Murray have dealt with the relationship between the impact sensitivity and heat of explosion of some 30 polynitro compounds with different molecular structures [233], but without taking in account of molecular similarity. Because of this, their conclusions are somewhat different from those which have so far been presented here.

Relationships between activation energies of thermal decomposition of polynitro compounds, obtained by the Russian manometric method, and heat of detonation or the square of detonation velocities were the first published versions of eqn. 7 [1, 2, 21, 22, 143, 226]; besides the study of the primary fission of their molecules, using the Arrhenius parameters for newly synthesized cyclic nitramines has extended the application possibilities of this equation. The equation then differentiates these parameters not only according to the molecular structure and the physical state of the energetic materials during their thermal decomposition, but it also allows certain hypotheses to be put forward concerning the formation of reactive micro-regions (pre-decomposition states) in the heated nitramine crystals [22]. We have also a very good experience with using the slope of the Kissinger relation, E_aT^{-1} [227] as a characteristic of thermal decomposition of energetic materials [1, 2, 31, 39, 73, 141, 226, 234, 235] obtained by means of a simple DTA, not only for pure substances but also for mixtures of industrial explosives [1, 226, 234], PBXs [31] or triacetone triperoxide mixtures [235]. All these relationships show [1, 21, 39, 226] that the effect of temperature in the classical sense has no influence on the process of detonation initiation by shock, impact or electric spark, that the primary fragmentation of polynitro compounds in their detonation transformation proceeds under milder conditions than those present at the front of the detonation wave or in its reaction zone, and that the detonation transformation itself of the given substance should be preceded by an induction period whose necessity was also postulated from the point of view of physics of explosion [77, 78]. For interpretation of the specific behavior of HNIW in the detonation of the corresponding PBXs detonation [31], the relationship "E_aT^{-1} - ρD^2" has shown to be better compared with simply using D^2.

4.2. Relationships based on detonation velocity

In Cho's paper [10] mentioned earlier, the author tries to present graphically a relationship between impact sensitivity and detonation velocity of 7 explosives with different structures, but the resultant plot can, at best, be considered only as a trend. In papers [32, 33] a linear relationship between the logarithm of the specific rate constants (zero order reaction rate) and detonation velocities of three PBXs is suggested, the constants coming from the vacuum stability test. Recently, a recently discovered logarithmic relationship between the rate constants, *k*, of the unimolecular thermal decomposition at a given temperature and detonation velocities of some 17 nitramines generally shows decreasing *k* values with increasing velocities [22]. A key part of this relationship rests in the equivalence of the primary fission processes in the low-temperature thermal decomposition and in the initiation and growth of detonation in the nitramines studied. The influence of the molecular structure on the division of these nitramines into sub-groups is here slightly lower, the influence of the physical state in thermal decomposition is clear and, in addition, the influence of thermochemistry of detonation is observed [22].

By dividing the detonation velocity by 2.97 the Guerney velocity coefficient can be obtained [236] whose linear relationship with the energy of detonation (from the EXPLO5 program) divides the group of nitramines and PBXs based on them into both the brisant and high brisant explosives groups [197].

5. Mutual relationships between different sensitivity data

The homolytic fragmentations or reactions of the C–NO_2, N–NO_2, N–NO, and O–NO_2 groupings, or other bearers of explosibility (i.e. explosophores), are common primary fission processes of energetic materials under thermal [1, 2, 21, 22, 146], mechanical and electric spark stimuli [1, 2, 21, 23, 25, 23]. Therefore, it is natural that mutual relationships exist between characteristics of the individual sensitivities [1, 2]. By that way, the already mentioned relationship between friction (shear slide with fixed volume) and impact sensitivity (uniaxial compression) can be described as a semilogarithmic equation [25, 237]. Between impact sensitivity and specific rate constants (derived from outputs of the vacuum stability tests with PBXs [32, 33]) was found logarithmic relationship [32, 33] as well as between these constants and electric spark sensitivity of the said explosives [32]. Approximate linear dependence between the logarithm of electric spark sensitivity and thermal stability threshold of polynitroarenes shows, that increasing thermal stability here is connected with increase in the electric spark sensitivity [238]. A ratio of numbers hydrogen and oxygen atoms in molecule and the contribution of specific molecular structural parameters are base for a link derivation between the impact sensitivity of energetic compounds and their activation energies from thermal decomposition, carried out by Keshavarz at al. [239] (of more less it is a statistical approach). Interrelations of the above-mentioned type are not very widened, yet.

6. Remarks concerning the study of the initiation reactivity of energetic materials

Different approaches to the problem of initiation reactivity of EMS are reviewed in several publications (see for example [1, 2, 13, 15, 16, 18, 21, 39, 64, 240]) but they mostly concern impact and shock sensitivities. Some of them are very sophisticated and deal with the influence of molecular structure, defects and other characteristics of the corresponding crystals upon such sensitivities, but they mostly only concern a few energetic materials as being representative (most often RDX, but also HMX, Fox-7 and TATB – see in Ref. 18 and citations therein). Other, also sophisticated studies, include a larger assortment of energetic materials, but with different molecular structure and without taking account of molecular structural similarity [10, 13, 15, 16, 71]. The earlier mentioned first-principles band gap criterion [70] should be applied here. The importance of the molecular similarity in a study of the molecular structural dependence of the EMs' shock reactivity is also perceptible when we take in account the Accumulation mechanism of detonation initiation (see in Refs. 1 and 241 and references therein). This theory (or rather a compendium of several theories [1, 241]) basically deals with the transformation of low-frequency vibrations of the crystal lattice (acoustic phonons) into high-frequency vibrations (vibrons), with subsequent spontaneous localization of vibrational energy in the explosophore groupings of the EM's molecule. Here also molecular skeletal vibrations should play an important role. It is clear that only similar skeletal structures will have comparable skeletal vibrations (comparable force constants of the concerned bonds in molecules). Acceptance of this requirement leads to obtaining Figs. 1 - 6. On the basis of current knowledge, it is possible to state that a single universal relationship between molecular structure and initiation reactivity does not yet exist.

The QSPR approach, which depends on the quality and number of the descriptors chosen, might produce reasonably good predictions. However, this approach provides little insight into the physics and chemistry involved in the process of initiation.

7. Conclusions

As has already been mentioned in paper [1] there is a dramatic rise in the use of theoretical methods for studying energetic systems. This study has provided an insight into the understanding of some factors affecting their behavior, but, on the other hand, it has also highlighted the presence of a great deal of opacity and guesswork. One of the two main problems is in the area of standardizing testing methods and in the credibility of the published sensitivity data, especially concerning electric spark and shock sensitivities. The second problem concerns the quantum chemical calculations and simulations which are based on certain opinions held by their authors - and the results reflect this observation [1].

For studying impact sensitivity, the data bases of the Lawrence Livermore Natl. Lab. (LLNL) and Naval Surface Weapons Center (NSWC) [52 – 55] can generally be taken as providing standard values. A comparison for individual EMs using this data is possible by means of the relationships between the results from impact sensitivity measurements and the NMR chemical shifts of key atoms in the reaction centers of the EM molecule or the performance characteristics of the given EM [1, 2, 21, 51]. Computational solving of this sensitivity continues to involve different versions of the DFT approaches [66 – 69], but also the use of surface electrostatic potentials [6, 8, 11 – 13, 15 – 17, 65], and the excitonic model of initiation (see Ref. 18 and citations therein). The first-principles band gap criterion which is applicable to different series of energetic crystals with similar structure, or similar thermal decomposition mechanism, is an important finding [70]. This structural and thermoanalytical similarity is not treated by many authors, other than by the use of sophisticated solutions. Taking account of the significance of the structural similarity in nitramines, and eliminating the inappropriate impact sensitivity data (namely of HNIW), a new correlation has been found [73] between the impact data and the ratio of bulk and shear modules. It is interesting to note the impact sensitivity prediction based on the rate constants of the exothermic reaction [74 – 76] which can be expressed as the sum of contributions arising from the various explosophores potentially associated with initiation. Certain more or less statistically-based prediction methods [59 – 61] are valid for impact sensitivity only for a relatively small group of polynitro compounds. There is a fairly high level of confusion in the literature concerning the impact sensitivity of the HNIW polymorphic modifications [23, 73], and a question that remains largely unanswered is why does a simple crystallization of nitramines in “a beaker” give products whose impact sensitivity is in compliance with data in the NSWC and LLNL bases [23] whereas, by sieving such products, fractions are obtained the impact sensitivity of which shows a certain dependence on the specific surfaces of the grains in such fractions [23].

The start, and subsequent evolution, of the decomposition of any particular EM depends heavily on the manner in which it was initiated. This would be different if initiated by the "hot spots" or by a homogenous mechanism (depending on the initiation intensity) [77, 78], and this is one of the reasons for frequent occurrence of non-reproducible results from shock sensitivity measurements. Modelling of this sensitivity is not as widespread as is modelling of impact sensitivity. Modified statistical methods have been derived for predicting the results of the large scale [57, 80] and small scale [57, 82] gap tests, and modelling for the small-scale one using the Euler program has been published [83]. It has also been shown that the X-NO_2 bond dissociation energies, *BDE*, and the largest Mulliken charges, Q_{NO2}, of nitro groups can be in good agreement with the logarithm of the experimental shock initiation pressures [86].~~].~~ However, the generally accepted assumption that the most positive Q_{NO2} value in the molecule represents its sensitivity [71] cannot be regarded as universally valid [72, 112]. It has also been demonstrated that sensitivity - structure relationships should take account of the EM's energy content [87]. An important finding is that the ReaxFF computer program used on shock initiation of RDX [84] gave intermediate decomposition products, which are in principle the same as those from low-temperature thermolysis of this particular nitramine.

Some of the reasons why measuring friction sensitivity seems unattractive to many theoretical chemists/physicists are the apparent "human variability" of the results obtained and the very different approaches used. Nevertheless, when based on carefully carried out BAM friction tests, the results show a good correlation with the molecular-structural [25, 29] and detonation characteristics [27] of nitramines. Using the DFT approach it was found that increasing the negative extreme of molecular surface electrostatic potential is connected with decreasing friction sensitivity in nitramines [28]. The same trend in friction sensitivity is observed in the case of rising activation energies of thermal decomposition for these EMs [26]. Taking friction data from papers [25, 26] other authors have derived a statistical method for predicting friction sensitivity [92].

Overall, the summary mentioned here concerns the method for measuring the impact and friction sensitivities that is most widely used in Europe - the BAM method. The same level of attention should be paid to the Russian methodologies used to measure impact, friction [47], and also shock sensitivities.

Electric spark sensitivity determination presents a complicated situation both in the published values and in any standardization. The literature contains partly measurement data, heavily influenced by thermal effects (discharge through an air gap [20, 95] with large energy losses), partly data without this effect (electrode is in direct contact with the sample [20]). The second case is of interest from the point of view of including in any standards. This method gives results which correlate with the molecular structure of the EMs [1, 2, 19, 113], including bond dissociation energies [19] and the largest net charges of the nitro groups [19]. Concerning the study of the initiation mechanism, the correlations are significant between this sensitivity data and the NMR chemical shifts of key atoms in the reaction center of the molecules (i.e. atoms bearing the most reactive nitro groups – see this paper and Refs. [1, 2, 19]). If the structural similarity of polynitro compounds is accepted here, then relationships are obtained which are typical for those of the type "molecular structure - reactivity" in physical organic chemistry.

Studies of sensitivity to laser beams using a sufficiently large selection of EMs is lacking, and there appears to be no real agreement in the opinions concerning the initiation mechanism by a laser beam [18]. The main topic of interest concentrates on PETN, RDX, and then on HMX, TATB and FOX-7. A difference has been documented concerning the fission of nitromethane (NM), and isopropyl nitrate (IPN) on the one hand, and dimethylnitramine (DMNA) on the other [125]. A demonstration of the likelihood of non-thermal selective photoinitiation, which also challenges the widely popular perception concerning the thermal nature of laser initiation, is discussed in paper [129]. On the other hand, a study of the micro-spots model for laser initiation [131] of an aluminum nano-particles mixture with PETN tends to support the thermal nature and also refers to the melting of PETN.

Methods for thermal reactivity specification for EMs are to be found in relative abundance in the literature. Problems with the mutual compatibility of results from thermoanalytical methods are discussed in several papers [1, 2, 21, 142, 143]; so far the most reliable results in this area are both the theoretical and practical findings obtained by the Russian manometric method [1, 2, 21, 44, 142, 146]. The kinetic parameters for EM decomposition, comparable with the Russian methods (for the example of nitric esters see Refs. 154 and 155) can be obtained without serious difficulty using the TGA and DSC techniques. These techniques have been used for thermal reactivity specification of quite a number of PBXs [157 – 163] on the basis of which the sensitivity of the given PBX [158] and cook-off time [159] were predicted and interpreted. A linear relationship between the activation energies of this thermolysis and the sum of the negative and positive extremes of molecular surface electrostatic potentials, $V_{S,\Sigma}$, of the nitramines studied has been successfully used for analysis of the kinetic data obtained from thermolysis of nitramines [147]; these summed potentials also correlate well with the rate constants for the monomolecular thermal decomposition of the nitramines mentioned [147]. A statistical method of predicting the activation energies of the thermolysis of some 86 polynitro compounds [148] was the precursor of the new program, named EDPHT 2.0, which is usable also for prediction of the crystal density and enthalpy of formation [149]. Very important critical temperatures can be obtained from the kinetic data of thermoanalytical measurements with EMs [50, 79, 141, 154, 155, 159, 164 – 169]. The important small and larger cook-off tests [50, 173 - 182] are frequently numerically simulated [177 – 179, 181, 182].

Besides the experimental determination of the main performance characteristics (the detonation velocity, *D*, pressure, *P*, and heat, *Q*), different methods for their prediction are also relatively popular. The best would seem to be the CHEETAH program [191], available only for authorized US government contractors. The EXPLO5 program [192] is also widely popular and easily available, and there is wide-spread use of the Kamlet & Jacob method for CHNO explosives [188] and for CHNOF [190]. The Stine method is little used but produces good results [189]. Metal-containing EMs can be treated by the CHEETAH and/or EXPLO5 programs, or by the Wang et al. modification of the Kamlet & Jacob method [193].

Other prediction methods for performance mostly concern a limited selection of EMs. Thus, using molecular structure and weight of individual EMs, Rothstein and Petersen have developed programs for CHNO [194] and CHNOF [195] explosives detonation velocity calculation. Prediction using DFT approaches usually concentrates on the quantum-chemistry calculation of density and heat of formation of the individual EMs with subsequent completion by using the Kamlet & Jacobs calculation [13, 203 – 207], but the EXPLO5 program is also used here [209]. Another six prediction methods involve DFT calculation of the heat of formation with subsequent use of the BKW program [210], and a statistical approach for CHNO explosives with estimation of results by the BKWS and BKWR programs [211] and for CHNOAl EMs [212]. Both these methods do not take into account heat of formation, similar to the situation with specific impulse prediction [213]. A subsequent step for all methods is the "hand-calculated" procedure for detonation pressure of CHNOClFAl explosives and of their mixtures [216]. From the point of view of the DFT calculations it is worthwhile remembering the relationship between the logarithm of detonation velocity, D, and a ratio of the BDE of the weakest N-N bond with total energies of nitramine molecules [220] and the relationship between the D values and the summed electrostatic surface potentials, $V_{s,\Sigma}$ [221] of these nitro compounds.

The initiation reactivity of EMs from the standpoint of physical organic chemistry [1, 21] has shown that the primary fragmentation processes of molecules of energetic materials in low-temperature thermal decomposition should be identical with those in the impact, electric spark and shock initiations. The existence of a relationship between the sensitivity and performance characteristics (the best with heat of explosion, Q) correlates well with this. In the literature one also finds reference to a modified Evans-Polanyi-Semenov equation (E-P-S), valid for polynitro compounds but also for explosive condensed mixtures [1, 21, 30, 31, 143, 226]. Recently it has been shown that this equation is valid also for the results of the Russian methodology for determining impact sensitivity [231]. An essential part of evaluating using this equation is taking account of the structural similarity of the EMs studied, otherwise the result is represented by a meaningless set of points. The equation mentioned here mostly corresponds to the general finding that high performance is usually accompanied by an enhanced sensitivity, although, in the case of impact sensitivities for the individual nitramines and using their Q values in units of $kJ.g^{-1}$, it was actually valid in less than 50% of cases [56]. However, taking the detonation process as the zero order reaction then the Q values result in $MJ.m^{-3}$ and the originally modified E-P-S equation is changed into a semi-logarithmic one [56]. The semi-logarithmic correlations show relatively tight relationships and they correspond to a logical set of nitramine groups, even if, in some cases, these groups might be generated by a lower number of nitramines. Exceptions to this rule are 1,3,5-trinitro-1,3,5-triazepane, 1,3,5-trinitro-1,3,5-triazinane, β–1,3,5,7-tetranitro-1,3,5,7-tetrazocane and the α–, β– and ε–polymorphs of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane in which the relationship works in the opposite direction. The α–1,3,5,7-tetranitro-1,3,5,7-tetrazocane and γ–2,4,6,8,10,12-hexanitro-

2,4,6,8,10,12-hexaazaisowurtzitane crystal modifications, however, comply with this rule [56]. Traditional problems with the "high" impact sensitivity of the ordinary (*technical*) quality of ε–2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (*i.e. of 2 – 4.5 J*) [24] should reflect the disorderliness of its molecules in the crystal lattice. The RS-quality of this nitramine [74] already belongs among the exceptions [30], too, and may be a candidate for being solved using quantum chemistry. For friction sensitivity of nitramines and PBXs based on them, the relation to the volume heat of explosion is linear and without exceptions [30]. Using the simple DTA and Kissinger method [227] for evaluating the results produced slopes for the Kissinger equation, $E_a T^{-1}$, in relation to the square of detonation velocity (representative of Q) enabled studying mixtures such as PBXs [31], industrial explosives [226, 234], triacetone triperoxide mixtures [235] etc. The specific behavior of HNIW in the detonation of the corresponding PBXs has been interpreted based on the "$E_a T^{-1}$- ρD^2" relationship [31] (the product ρD^2 corresponds well with results from the ballistic mortar experiments [30, 31, 201]). Regarding the detonation velocity, a new logarithmic relationship between it and the rate constant of the unimolecular reaction at the given temperature for 17 nitramines has been described [22] and which reflects the structural similarities.

It is clear from all that has been mentioned earlier, that the indirectly proportional relationship between performance and sensitivity of energetic materials has the characteristic of a general rule (it is concordance with Refs. 40 and 131). For nitramines, exceptions to this rule exist and need explaining. At the present time, it is not really possible to describe the relationship between sensitivity and performance and also the relationships between sensitivity and molecular structure of the individual EMs just using a single equation. QSPR methods, in certain measurements, do enable getting close to such a simplification, but with minimal inclusion the chemistry and physics into the corresponding relationships, they often give results which deviate significantly from reality. It is therefore clear that the theories advanced here are insufficient, and that both the general rule and the exceptions mentioned still require more research to find a serious scientific explanation for all types of sensitivity for EMs.

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Legends to Figures and to Scheme:

Figure 1: Relationship between the ^{15}N NMR chemical shifts of the key aza atoms in molecules (the position is given by the number in parentheses for non-isochronous molecules) and drop energies of the nitramines studied - taken from paper [56].

Figure 2: Relationship between electric spark sensitivity (*EZ KTTV*) and ^{13}C NMR chemical shifts of carbon atoms – bearers of the most reactive nitro groups in molecules of genuine polynitro arenes (*the numbers in brackets denote the positions in molecule*) - constructed here from the ^{13}C NMR shifts [21, 113] and the E_{ES} values [112, 113] of the studied compounds.

Figure 3: Relationship between electric spark sensitivity (*EZ KTTV*) and ^{15}N NMR chemical shifts, δ_N, of nitrogen atoms in the most reactive nitro groups of polynitro arenes (*the numbers in brackets denote the positions in the molecule*) - constructed here from the ^{15}N NMR shifts [116, 117] and the E_{ES} values [112, 113] of the compounds studied.

Figure 4: Relationship between the activation energies of thermal decomposition from different authors and the $V_{S,\Sigma}$ values [147]: line I corresponds to decomposition in the solid state, line II to decomposition in the liquid state, line III to decomposition during the “solid-liquid” transition state and line IV corresponds to crowded molecules decomposed in the liquid state [147].

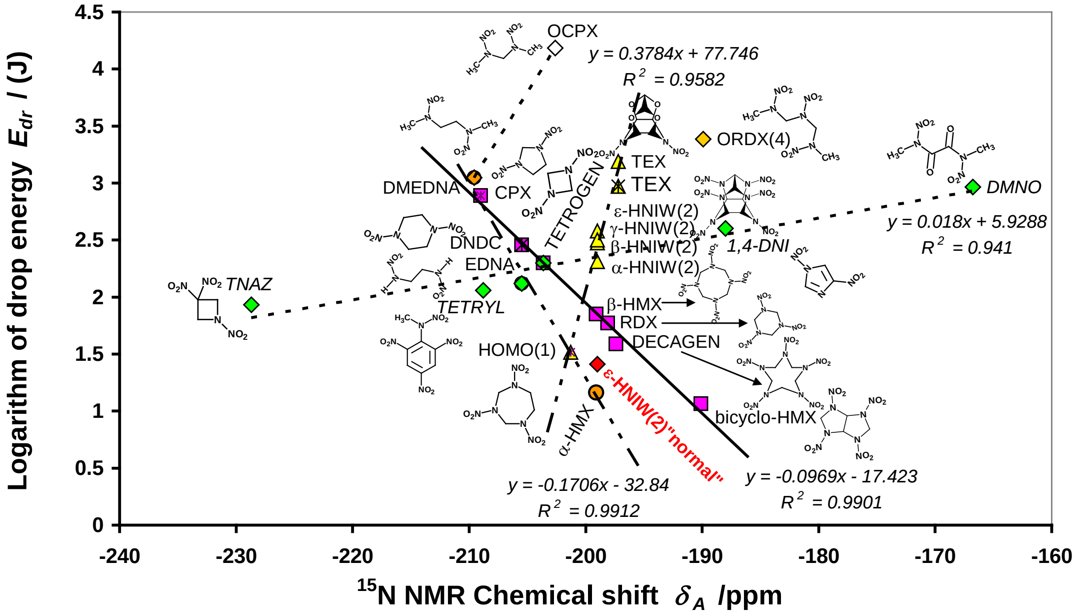
Figure 5: Relationship between the drop energies, $E_{dr,}$, and heat of explosion, Q_{real}, for the nitramines studied [56]; the heat of explosion, Q_{real}, corresponds to the calorimetrically determined one and was calculated according to the semi-empirical relationships by Pepekin et al. [229].

Figure 6: Redrawn Fig. 5 - relationship between the logarithm of the drop energies, $E_{dr,}$, and volume heats of explosion, ρQ_{real}, for the nitramines studied [56].

Figure 7: Redrawn semi-logarithmic relationship, originally between impact sensitivity and the product of $\rho.D^2$, from paper [30] into the present form with accentuated line E for exceptional nitramines (this Fig. is the extended one from Ref. 201). Energy of detonation was obtained by the EXPLO5 program. Here suffix –Si means 12% by wt. of polydimethylsiloxane binder, -sem means 15% by wt. of acrylonitrile-butadiene binder, -PA means 9% by wt. of polymethylmethacrylate binder, -V9 means 9% by wt. of Viton A 200, -C4 means of 9% by wt. of polyisobutylene binder. RS-ε–HNIW is a product with decreased sensitivity [73].

Scheme 1: Structural formulas of the nitramines to Figs. 4, 5 and 6

Figure 1



Logarithm of drop energy E_{dr} / (J)
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
-240
-230
-220
-210
-200
-190
-180
-170
-160
^{15}N NMR Chemical shift δ_A /ppm
OCPX
y = 0.3784x + 77.746
R^2 = 0.9582
ORDX(4)
DMNO
y = 0.018x + 5.9288
R^2 = 0.941
TEX
TEX
ε-HNIW(2)
γ-HNIW(2)
β-HNIW(2)
α-HNIW(2)
1,4-DNI
DMEDNA
CPX
TETROGEN
DNDC
EDNA
TNAZ
TETRYL
β-HMX
RDX
DECAGEN
HOMO(1)
ε-HNIW(2)"normal"
α-HMX
bicyclo-HMX
y = -0.1706x - 32.84
R^2 = 0.9912
y = -0.0969x - 17.423
R^2 = 0.9901

Figure 2

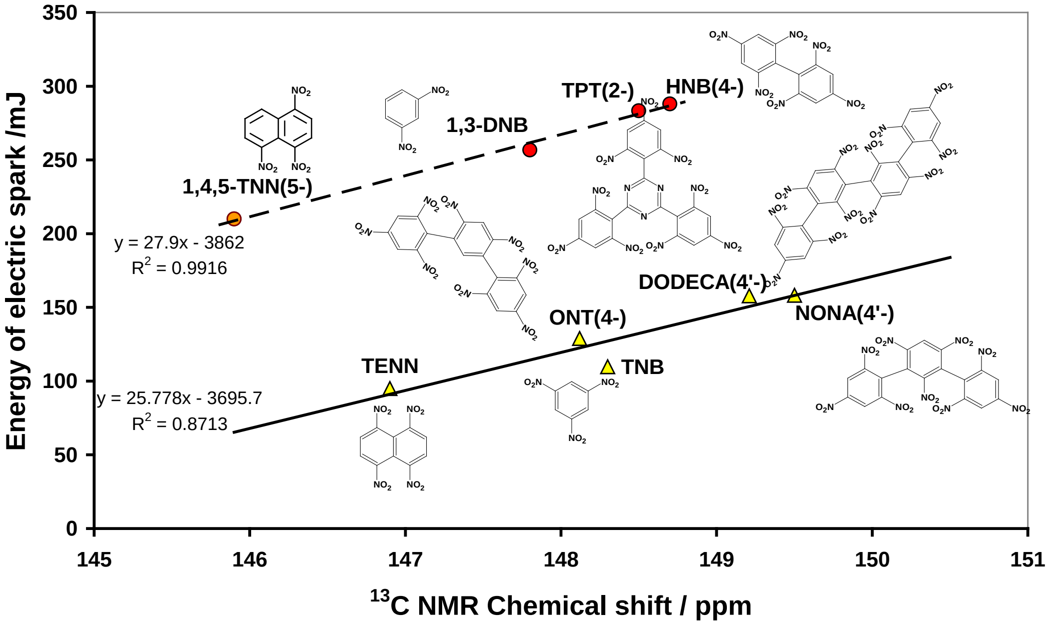

Energy of electric spark /mJ
0
50
100
150
200
250
300
350
145
146
147
148
149
150
151
^{13}C NMR Chemical shift / ppm
1,4,5-TNN(5-)
1,3-DNB
TPT(2-)
HNB(4-)
DODECA(4'-)
NONA(4'-)
ONT(4-)
TENN
TNB
y = 27.9x - 3862
R^2 = 0.9916
y = 25.778x - 3695.7
R^2 = 0.8713
NO_2
O_2N
N

Figure 3

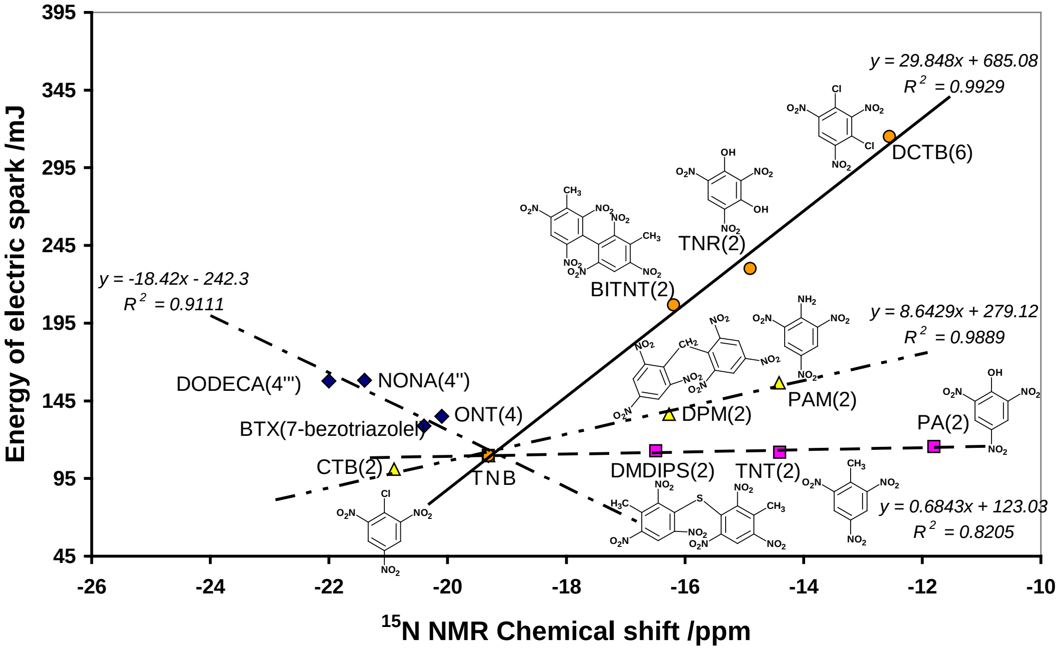
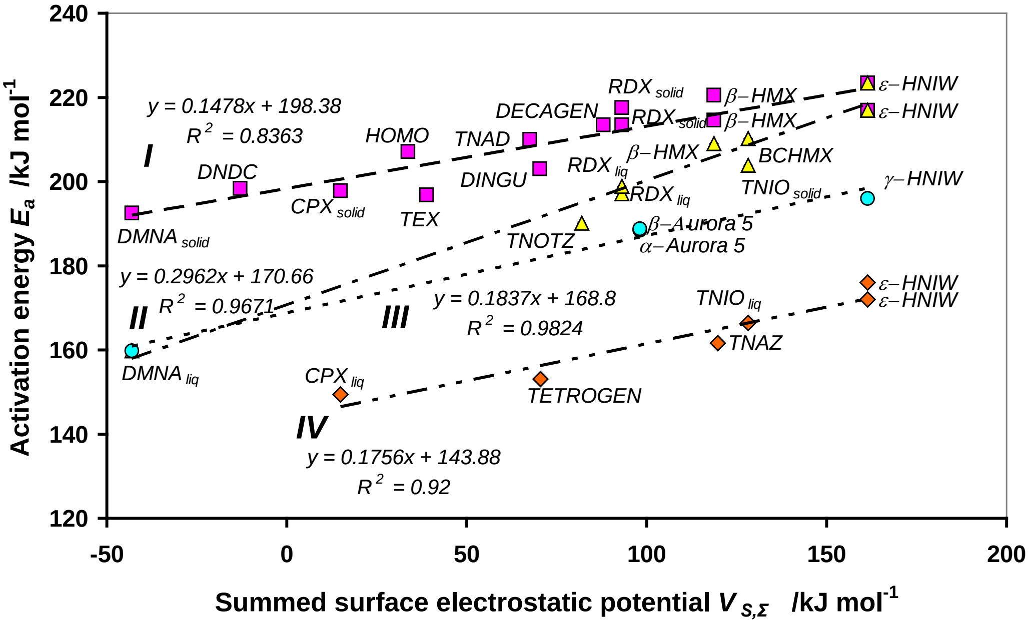

Energy of electric spark /mJ
395
345
295
245
195
145
95
45
-26
-24
-22
-20
-18
-16
-14
-12
-10
^{15}N NMR Chemical shift /ppm
y = 29.848x + 685.08
R^2 = 0.9929
DCTB(6)
TNR(2)
BITNT(2)
y = -18.42x - 242.3
R^2 = 0.9111
y = 8.6429x + 279.12
R^2 = 0.9889
DODECA(4''')
NONA(4'')
ONT(4)
BTX(7-bezotriazolel)
PAM(2)
DPM(2)
PA(2)
CTB(2)
TNB
DMDIPS(2)
TNT(2)
y = 0.6843x + 123.03
R^2 = 0.8205

Figure 4



y = 0.1478x + 198.38
R² = 0.8363
I
DNDC
HOMO
TNAD
DECAGEN
RDX solid
RDX solid
β−HMX
β−HMX
ε−HNIW
ε−HNIW
β−HMX
BCHMX
RDX liq
RDX liq
DINGU
CPX solid
TEX
DMNA solid
TNIO solid
γ−HNIW
TNOTZ
β−Aurora 5
α−Aurora 5
y = 0.2962x + 170.66
R² = 0.9671
II
III
y = 0.1837x + 168.8
R² = 0.9824
TNIO liq
ε−HNIW
ε−HNIW
TNAZ
DMNA liq
CPX liq
TETROGEN
IV
y = 0.1756x + 143.88
R² = 0.92
Activation energy Ea /kJ mol-1
240
220
200
180
160
140
120
-50
0
50
100
150
200
Summed surface electrostatic potential VS,Σ /kJ mol-1

Figure 5

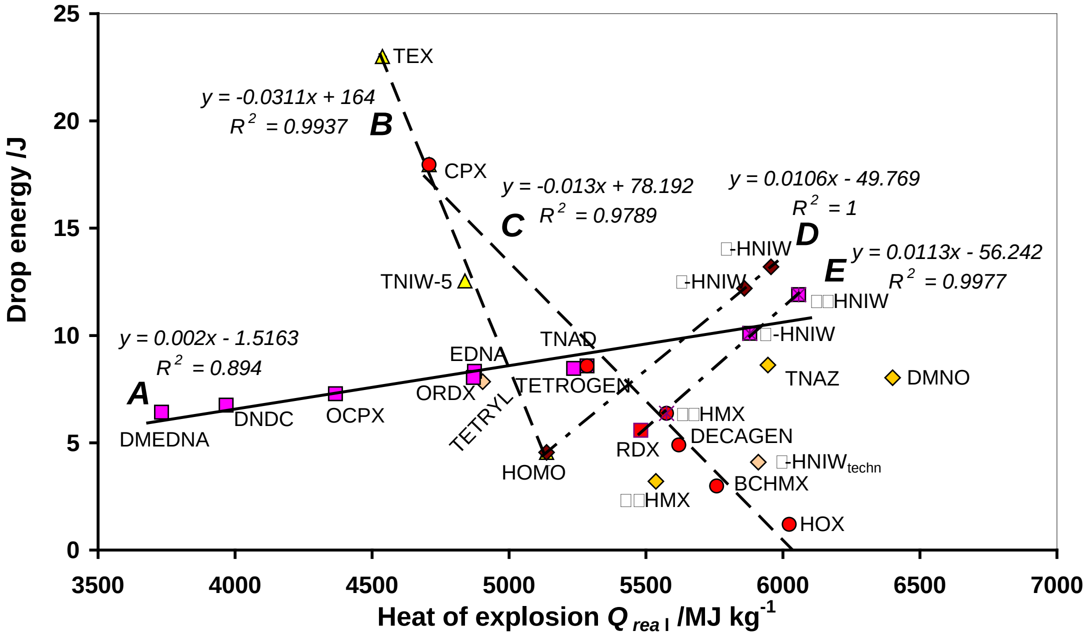

25
20
15
10
5
0
Drop energy /J
3500
4000
4500
5000
5500
6000
6500
7000
Heat of explosion Q_{real} /MJ kg^{-1}
A
y = 0.002x - 1.5163
R^2 = 0.894
B
y = -0.0311x + 164
R^2 = 0.9937
C
y = -0.013x + 78.192
R^2 = 0.9789
D
y = 0.0106x - 49.769
R^2 = 1
E
y = 0.0113x - 56.242
R^2 = 0.9977
TEX
CPX
TNIW-5
EDNA
ORDX
TETRYL
TNAD
TETROGEN
HOMO
DMEDNA
DNDC
OCPX
RDX
□□HMX
DECAGEN
□-HNIW
□-HNIW
□□HNIW
□□-HNIW
TNAZ
DMNO
□-HNIW$_{techn}$
BCHMX
□□HMX
HOX

Figure 6

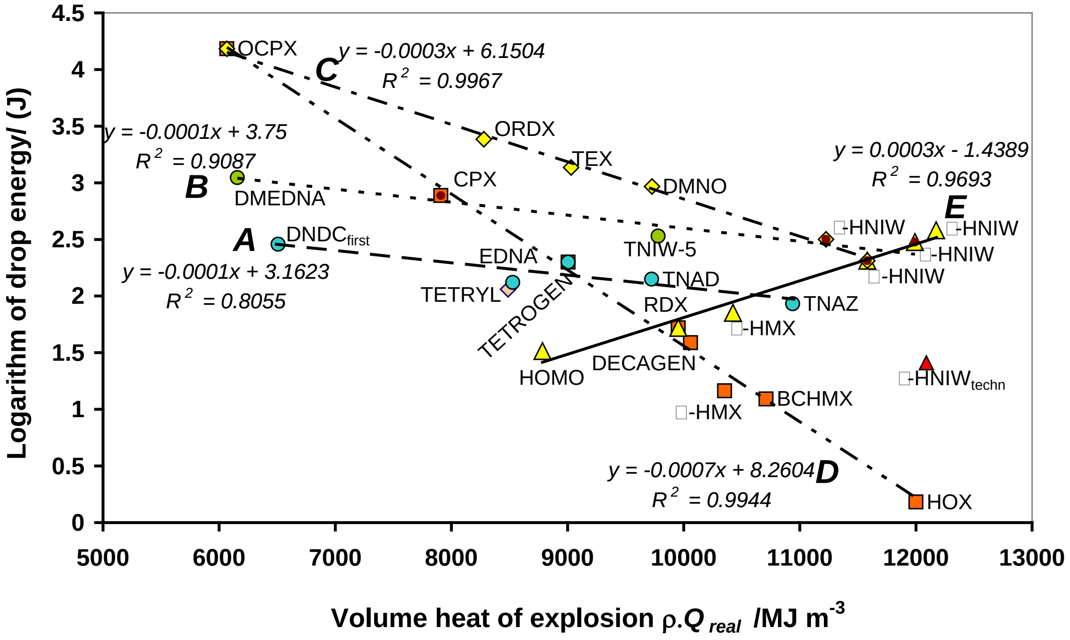
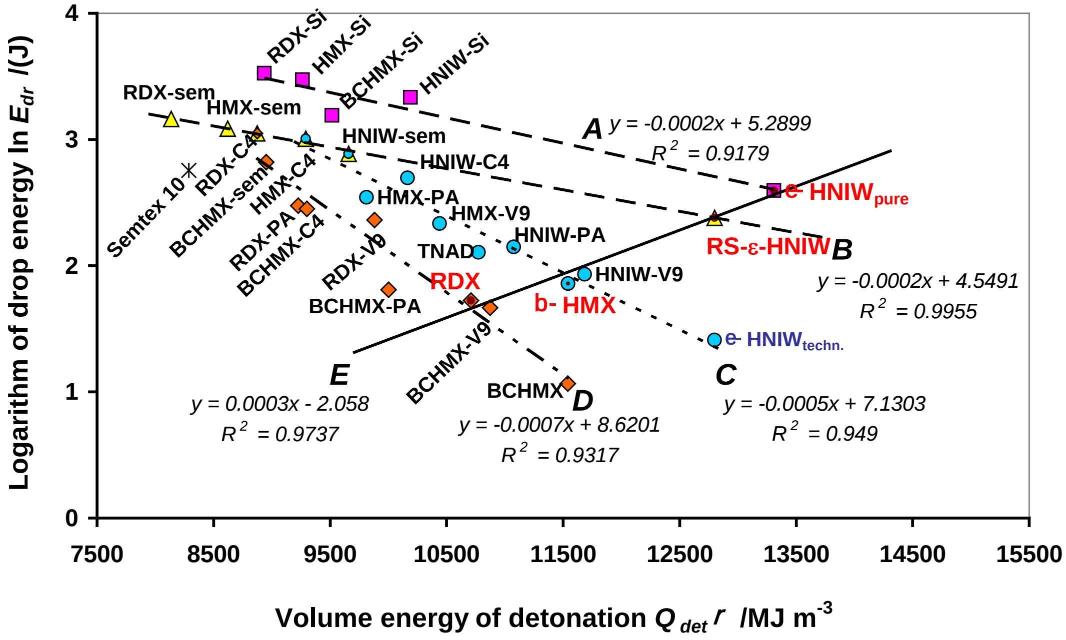
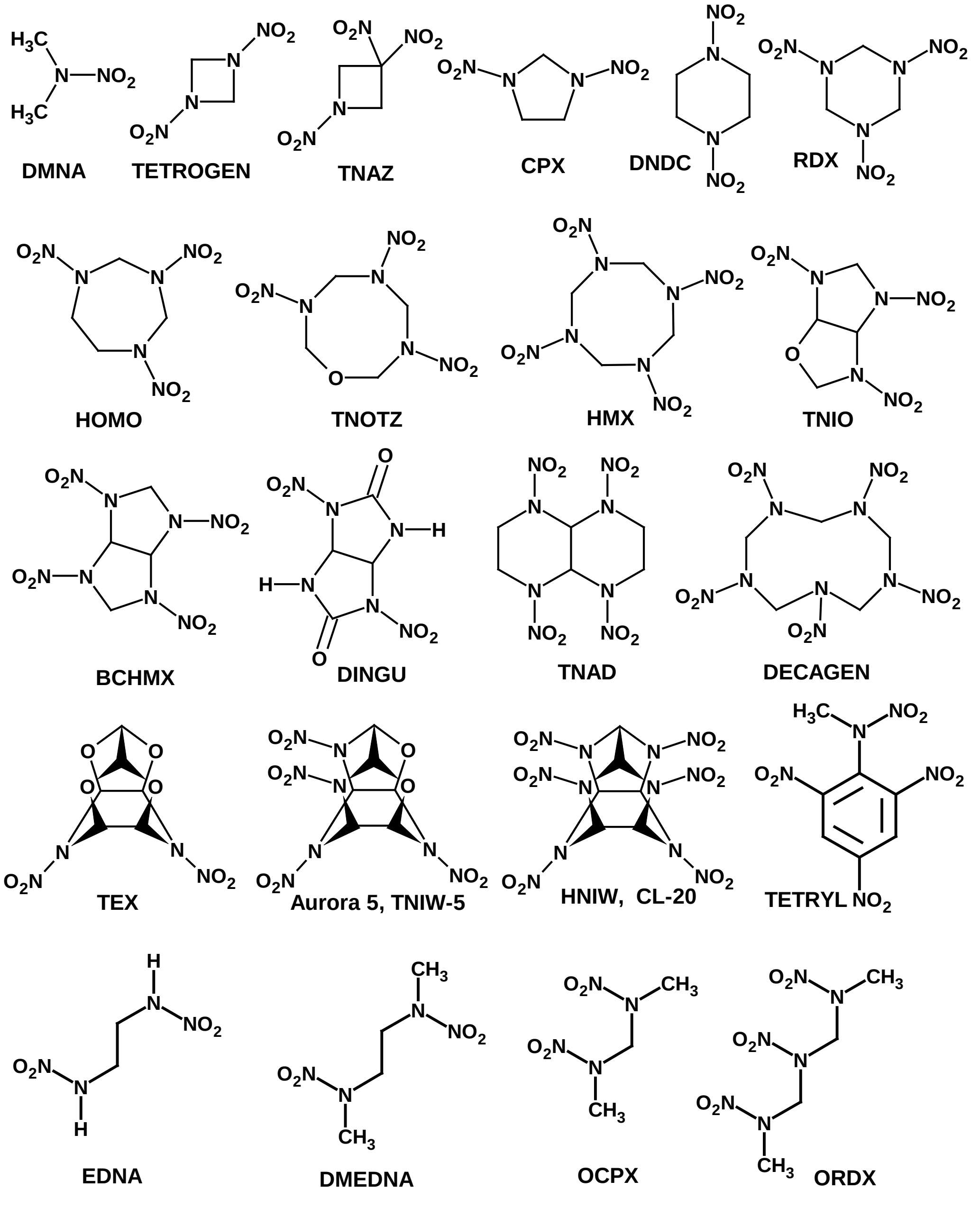

Logarithm of drop energy/ (J)
Volume heat of explosion ρ.Q real /MJ m-3
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
5000
6000
7000
8000
9000
10000
11000
12000
13000
OCPX
C
y = -0.0003x + 6.1504
R2 = 0.9967
ORDX
TEX
DMNO
y = -0.0001x + 3.75
R2 = 0.9087
B
DMEDNA
CPX
y = 0.0003x - 1.4389
R2 = 0.9693
E
□-HNIW
□-HNIW
□-HNIW
□-HNIW
A
DNDCfirst
y = -0.0001x + 3.1623
R2 = 0.8055
EDNA
TNIW-5
TNAD
TETRYL
TETROGEN
RDX
TNAZ
□-HMX
HOMO
DECAGEN
□-HMX
BCHMX
□-HNIWtechn
y = -0.0007x + 8.2604
R2 = 0.9944
D
HOX

Figure 7



Logarithm of drop energy ln E_{dr} /(J)
Volume energy of detonation Q_{det} r /MJ m^{-3}
0
1
2
3
4
7500
8500
9500
10500
11500
12500
13500
14500
15500
RDX-Si
HMX-Si
BCHMX-Si
HNIW-Si
RDX-sem
HMX-sem
HNIW-sem
HNIW-C4
Semtex 10
RDX-C4
BCHMX-sem
HMX-C4
RDX-PA
BCHMX-C4
HMX-PA
HMX-V9
HNIW-PA
TNAD
RDX-V9
RDX
BCHMX-PA
b- HMX
HNIW-V9
BCHMX-V9
BCHMX
ε- HNIW$_{pure}$
RS-ε-HNIW
ε- HNIW$_{techn.}$
A
B
C
D
E
y = -0.0002x + 5.2899
R^2 = 0.9179
y = -0.0002x + 4.5491
R^2 = 0.9955
y = -0.0005x + 7.1303
R^2 = 0.949
y = -0.0007x + 8.6201
R^2 = 0.9317
y = 0.0003x - 2.058
R^2 = 0.9737

Scheme 1


DMNA
TETROGEN
TNAZ
CPX
DNDC
RDX
HOMO
TNOTZ
HMX
TNIO
BCHMX
DINGU
TNAD
DECAGEN
TEX
Aurora 5, TNIW-5
HNIW, CL-20
TETRYL
EDNA
DMEDNA
OCPX
ORDX