



Important aspects of behaviour of organic energetic compounds: a review

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Abstract

The importance of a prediction tool increases with greater relevance for synthesis, performance and vulnerability predictions. Some important aspects of performance behaviour and their theoretical calculations, which are indispensable in recognising energetic molecules of interest, are described here. This review also discusses on factors influencing sensitivity and overall stabilities of organic energetic compounds especially on nitroaromatics and nitramines, and exceptions to this relationship suggest other factors playing roles in specific instances. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The search for new explosives with a given performance, sensitivity and physical properties is one of the major challenges to the chemical industry. In practice, new energetic compounds are often designed by modifying known substances with higher densities such as by addition and/or modification of explosophoric groups in the molecule. Efforts have been expanded in several laboratories world wide to synthesise new generations of more powerful energetic compounds with improved properties. Such properties include high detonation velocity, reduced vulnerability, low shock and impact sensitivities over those in current use.

Further, the expenditure connected with the development and synthesis of new high energy materials also necessitates the development of theoretical methods. These help the chemists to develop systematic and scientific formulations of appropriate futuristic target molecules having complementary properties of good thermal stability, impact and friction

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Nomenclature

At	an arbitrary atom
C_0	concentration of molecule
D	mean molecular diameter
E	energy released (cal)
ΔH_v	heat of vaporisation
ΔH_s	heat of sublimation
K_{BB}	coefficient of composition of compound
$\log h_{50}$	impact drop height at which there is 50% probability (cm)
N_{at}	number of atoms in the molecules
OB	oxygen balance
P_{c-j}	detonation pressure (kbar)
Q	chemical energy of detonation reaction (cal/g)
Q_{max}	maximum possible heat of formation (kcal/kg)
VOD	velocity of detonation (m/s)
<i>Greek letters</i>	
α	oxygen coefficient
δ	increase in energy
Δ_{in}	sum of interaction between some specific groups
ρ	density (g/cm ³)
ρ_{TM}	theoretical maximum density

sensitivity and enhanced explosive performance. The major goal of these methods, apart from being developed as predictive tools, is to provide insight to understanding the molecules which are responsible for higher performance and which are not.

Various empirical methods complemented the computer output for desk calculations of factors related to detonation velocity, Chapman–Jouget detonation pressure, crystal density, oxygen balance and heat of formation along with structure–sensitivity relationships of C–H–N–O energetic compounds are discussed in the following sections.

2. Velocity of detonation

The basic performance property is the velocity of detonation (VOD), which is a function of the energy produced by explosive decomposition. The standard hydrodynamic theory used for computing VOD of an explosive is concerned only with the amount of energy liberated and the nature of end products, and is independent of chemical reactions.

The density, heat of formation and atomic composition can be integrated into an empirical formula for predicting performance of a proposed explosive. According to Stine [1], the detonation velocity of a pure compound and that of a mixture are identical if the densities, heat of formation and atomic compositions are the same. Therefore, a relation is expected between the detonation properties of an explosives and its chemical constitution. A simple empirical linear relationship between detonation velocity at theoretical maximum density

(TMD) and a factor F that is dependent solely upon chemical composition and structure is postulated for a ideal C–H–N–O explosive [2] as

$$D' = D_0 + (\rho_{TM} - \rho_0) \times 3.0 \quad (1)$$

where D' , D_0 , ρ_{TM} and ρ_0 are the detonation velocities and densities at their respective theoretical maximum and experimentally measured values.

The relationship's principal feature is that F -values are derived solely from molecular formulae and structures as shown in Eq. (1). This requires no prior knowledge of any measured, estimated or calculated physical, chemical or thermochemical properties other than to know or to predict whether an explosive is solid or liquid.

$$F = 100 \times \left[\frac{n(O) + n(H) - (n(H)/2n(O)) + (A/3) - (n(B)/1.75) - (n(C)/2.5) - (n(D)/4) - (n(E)/5)}{M_W} \right] - G \quad (2)$$

where $G = 0.4$ for liquid explosives, whereas $G = 0$ for solid explosives. $A = 1$, if the compound is aromatic, otherwise $A = 0$, for 1 mol of the composition. Here $n(O)$ is the number of oxygen atoms, $n(H)$ the number of hydrogen atoms, $n(B)$ the number of oxygen atoms in excess of those already available to form CO_2 and H_2O , $n(C)$ the number of oxygen atoms doubly bonded directly to carbon as in carbonyl $>C=O$, $n(D)$ the number of oxygen atom singly bonded directly to carbon as in a $>C-O-R$ linkage where 'R' is $-H$, $-NH_4$, etc. and $n(E)$ is the number of nitrate groups existing either in a nitrate ester configuration or as a nitric acid salt such as hydrazine mononitrate.

Based on the above empirical equation, Rothstein and Petersen [2] calculated D (detonation velocities) using Eq. (3) for a number of explosives:

$$F = 0.55D' + 0.26 \quad (3)$$

The analysis of data shows that 63 of 64 D' -values, 98% lie within 7% of experimental values with the correlation coefficient for the linear regression plot of all is greater than 0.96. Finally, experimental detonation pressures P_{c-j} from detonation velocities D' (Eq. (4)) for explosives with a variety of structures, compositions and physical forms fit well with the relationship made in Eq. (4) with the correlation coefficient 0.99.

$$P'_{c-j} = 93.3D' - 456 \quad (4)$$

This process therefore, appears to offer a simple and quick method for estimating detonation pressures at maximum theoretical densities where a high degree of accuracy is not essential.

Kamlet and Jacobs [3] have shown that detonation pressure and detonation velocity of C–H–N–O explosive can be calculated at their initial densities above 1 g/cm^3 while using the following simple empirical equations:

$$P = 15.58 \rho^2 \varphi \quad (5)$$

$$D = 1.029 \varphi (1 + 1.30 \rho)^2 \quad (6)$$

$$\varphi = NM^{1/2} Q^{1/2} \quad (7)$$

where P is the pressure in kbar, D the detonation velocity in m/s, N the number of moles of gaseous detonation products per gram of the explosive, M the average weight of these gases in g/mol, Q the chemical energy of the detonation reaction in calories per gram and ρ is the initial density in g/cm³.

The Kamlet and Jacobs method is very useful for the rapid calculation of most important constants and characterising high explosives.

Other methods of calculating parameters of detonation have been developed by Pepkin et al. [4] They worked out a method of calculation of heat of detonation when bulk formula of explosive and enthalpy of formation, ΔH_f^0 are known. Thus, for an explosive $C_aH_bO_cN_d$,

$$Q_{\max} = \frac{28.9b + 470(c - b/2) + \Delta H_f^0}{M_W} \quad (8)$$

where Q_{\max} is the maximum possible heat of detonation (kcal/kg), M_W is the molecular weight of the compound, the heat of detonation Q_ρ at density ρ (g/cm³) is

$$Q_\rho = Q_{\max}[1 - (0.528 - 0.165\rho)(1.4 - \alpha)] \quad (9)$$

where α is the oxygen coefficient calculated from the following equation:

$$\alpha = \frac{c}{2a + 2b/2} \quad \text{when } \alpha \geq 1.4, \quad Q_\rho = Q_{\max} \quad (10)$$

Pepkin et al. [4] calculated the rate of detonation, D (m/s) of explosive with the bulk formula $C_aH_bO_cN_dF_e$ at a given density ρ_1 using the following equation:

$$D^2 = 8.0(Q + R) \quad (11)$$

where Q is the heat of detonation (kcal/kg) calculated from Eq. (8) and

$$R = \left(\frac{n}{n_z}\right)^3 \rho_1^2 \quad (12)$$

where n_z is the number of molecules in the products of detonation, and $n = K_{BB}\rho^{1/2}$, where n is the number of molecules in the products of the detonation, ρ_1 the density of the explosive and K_{BB} is the coefficient of the composition of the compound which can be calculated as

$$K_{BB} = \frac{0.135a(a/(a+b)) + 21b(b/(a+b)) + 0.4(c+d+e)}{M_W} \quad (13)$$

Again the detonation pressure is calculated from the following equation:

$$P = \rho_1 D^2 \left(\frac{x_1 - 1}{x_1}\right) \quad (14a)$$

where x_1 is the experimental degree of compression in the front of the detonation wave where density is ρ and is represented as

$$x_1 = \frac{\rho}{\rho_1} \quad (14b)$$

The calculated and experimental data for D and P show mean deviation of ca. 1.4% (Table 1).

Table 1
Calculated and experimental data for D and P

Compound	ρ_1	Q	K_{BB}	x_1	D_{calc} (m/s)	D_{exp} (m/s)	P_{calc} (kbar)	P_{exp} (kbar)
TNT	1.64	1010	0.0202	1.38	6900	6940	215	220
Tetryl	1.80	1173	0.0207	1.37	7600	7700	297	
Cyclonite (RDX)	1.802	1300	0.0260	1.34	8740	8800	349	347
Octogen (HMX)	1.903	1320	0.0260	1.33	9100	9150	390	393
PETN	1.77	1375	0.0260	1.36	8500	8370	338	350

Bernard [5,6] worked out different formulae for determining the rate of detonation based on kinetic theory of detonation, and the same can be correlated with the densities ρ in the shock wave front by the following equation:

$$D_{max} = \frac{P_1}{P_{max}} \frac{KT_0 d}{h} \quad (15)$$

where D_{max} is the experimental rate of detonation at an infinite diameter and at maximum density and a plot of D_{max} against $\log \rho_1$ gives a straight line. In the above equation, K is the Boltzmann constant, h the Planck's constant, D the mean molecular diameter and T_0 is the initial temperature of the explosive.

Bernard and co-workers [7] further extended this calculation to the rate of detonation of C–NO₂, O–NO₂ and N–NO₂ compounds by using the following two equations:

$$D_{\infty}^{\rho_{max}} = \frac{\rho_1}{\rho_{max}} \frac{\kappa T_0}{h} \left(\frac{6M}{\pi N \rho_{max}} \right)^{1/3} \quad (16)$$

and

$$D^2 = C_0 \left(\frac{M}{n} \right) \quad (17)$$

where h is the Planck's constant, M the mean molecular mass of the products, N the Avagadro number, C_0 the concentration of molecules on the surface of explosives, n the number of nitro groups in the molecule and is a exponent varying from 1.5 to 2.

A characteristic feature of the calculation by Bernard is that he does not use the enthalpy of detonation but assumed that the density, ρ_1 in the shock front, that is, the compression by the shock wave is decisive for the rate of detonation. The explosophoric groups such as NO₂, N₃ etc. are particularly strongly compressed. Thus, ρ_1/ρ_{max} for dinitrobenzene is 1.40, for picric acid 1.88 and for azides it is ~ 1.7 .

Major emphasis was focused on the development of TIGER hydrodynamic code for energy performance calculations of some potential explosives molecules. Using this hydrodynamic theory Jayasurya [8] calculated the performance of strained caged nitramines, reveals that octanitrocubane and tetranitrotetraazacubane are more powerful than HMX by 39 and 49%, respectively. The current development in real world of explosives are 1,3,3-trinitriazetidine (TNAZ) and CL-20 afford about 0.7 and 16% more power than HMX.

3. Velocity of detonation as a function of oxygen balance

Another parameter related to the molecular formula of a compound is oxygen balance [9]. This parameter is used in all predictive schemes related to detonation velocity and sensitivity. Oxygen balance represents lack or excess of oxygen needed to produce the most stable products in a compound and is given by

$$\frac{16(Z - 2X + Y/2)}{M_w} \times 100 \quad (18)$$

where X , Y , and Z represent number of atoms of carbon, hydrogen and oxygen in the molecule. If the numerator is not equal to zero, there is a deficiency of either oxygen or fuel and maximum efficiency will not be reached in the production of energy. Oxygen balance (OB) of explosive is connected with both the energy available and with potential end products, it is expected that detonation velocity is a function of OB.

Fig. 1 shows a plot of detonation velocity against oxygen balance for some mixtures adjusted to a common loading density of 1.7 g/cm^3 . For any given OB, it is seen that the PETN mixture has a lower VOD than the corresponding ones containing RDX. It is evident from Fig. 1 that as the oxygen balance approaches zero, the detonation velocity increases.

Martin and Yallop [10] found that the linearity of the relationship between oxygen balance and detonation velocity can be improved by using the following modified formula:

$$\frac{(Z - 2X + Y/2) \times 100}{n} + \frac{100W}{n} \quad (19)$$

where n is the number of atoms in molecule, and W is computed by summing the oxygen atoms according to their linkages.

An empirical equation was derived from the use of best available experimental values for the detonation velocities of common organic high explosives:

$$D = 2509 + 13.25\Omega + 3793\rho + 12.81\Omega\rho \quad (20)$$

where Ω and ρ are oxygen balance and loading density, respectively.

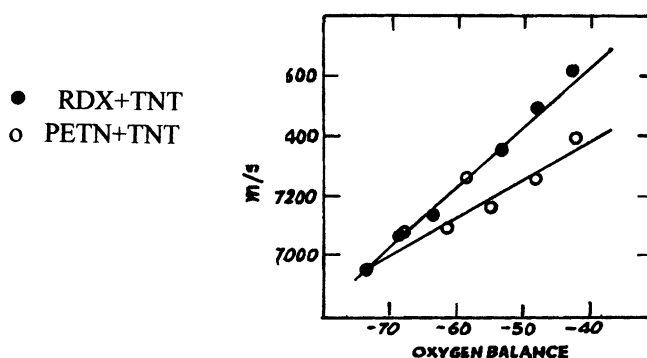


Fig. 1. Detonation velocity of mixture of RDX and PETN with TNT as a function of OB.

Table 2
Experimental and calculated values of D , the rate of detonation

Explosive	D_{exp} (m/s)	D_{calc} (m/s)
TNT	6980	6345
Tetryl	7450	7505
EDNA	7920	7900
Cyclonite (RDX)	8200	8185
PETN	7820	7880

By means of Eq. (20) the detonation velocity of a pressed or cast organic high explosive can be calculated with a standard error of about 2% and only data required are the structures of explosives and the loading densities.

The detonation velocity may be expected as a linear function of oxygen balance and it is further improved by taking into consideration the exact nature of oxygen linkages in an explosive molecule. When there is exactly enough oxygen in the explosive to fully oxidise the carbon and hydrogen to carbon dioxide and water (i.e. $OB = 0$), the heat of explosion will be optimum, which in turn improves the performance (detonation velocity increases). Any deviation from perfect oxygen balance, either positive or negative will lead to a lower heat of explosion. Roth [11] pointed out that modified OB is successful only for a restricted class of explosives and correlation breaks down for explosives with positive OB. He concluded that OB is a concept that provides useful qualitative information and it should not be used for quantitative correlation except for chemically similar explosives.

A number of authors tried to extend the method of Martin and Yallop [9] and in particular, Pagowski's work [12,13] merits attention. In this connection, he attempted to correct equation of Martin and Yallop suggesting the effective oxygen balance (B):

$$B = \left(z - 2x - \frac{y}{2} + P \right) \left(\frac{100}{n} \right) \quad (21)$$

where P is the correction accounting for energy gain or loss, from the actual chemical structures of the compounds while taking into account different oxygen atoms, i.e. those which are bonded with carbon (C=O, C–O–N) and those NO_2 which are free to develop the exothermic reaction of oxidation.

Pagowski gave a semi-empirical equation for the rate of detonation, D which fits well to experimental values (Table 2).

$$D = 8600 + 32.7B \text{ at } \rho = 1.6 \text{ g/cm}^3 \quad (22)$$

Martin and Yallop [10] introduced a further term in the detonation velocity against oxygen balance (Ω) relationship, in order to explicit account for heat of formation. In general, variation in heat of formation is associated mainly with presence of oxygen in molecule. The modified empirical equation which includes heat of formation is

$$D = 2590 + 11.97\Omega - 0.706H + 3764\rho + 13.67\Omega\rho + 0.108\rho H \quad (23)$$

where D is in m/s, H in cal/g and ρ is in g/cm^3 .

4. Heat of formation

Energetic materials decompose, ignite, and explode by heat and impact. Therefore, the ‘heat of formation’ is a measure of energy content of a compound. It is an important factor to consider in designing new energetic materials or evaluating existing ones and to investigate characteristics of energetic materials, as it enters into the calculation of explosive and propellant properties such as detonation velocity, detonation pressure and specific impulse.

However, no direct experimental value for heat of formation is available. It is normally possible to calculate a value indirectly from the details of molecular structures. Broadly heat of formation is calculated by the following:

- group additivity method;
- quantitative structure–property relationship;
- quantum mechanics.

4.1. Group additivity method

Group additivity method has been successfully applied to the estimation of heats of formation of solid entropies, heat capacities of ideal gases and liquids. Benson and Buss [14] showed that thermodynamic properties are additive and the heat of formation can be estimated to approximately ± 3 kcal/mol. Using group additivity method, Shaw [15] suggested that the heat of formation of solid can be calculated better directly from the group values. The “heat of formation” for solid nitroaromatic compounds has been estimated by group additivity method, using both ideal gas group values with measured heat of sublimation and solid group values. The heat of formation of nitrobenzene can be calculated using the following formula with known value of benzene molecule:

$$\Delta H_f(\text{PhNO}_2) = 1(\text{C}_B\text{-NO}_2) + 5(\text{C}_B\text{-H}) = 16.9 \text{ kcal/mol}$$

where $\text{C}_B\text{-H} = 3.3$ kcal/mol and $\text{C}_B\text{-NO}_2 = 0.4$ kcal/mol.

From the heats of formation of each compound in the ideal gas state, the value for the group $\text{C}_B\text{-NO}_2$ (ideal gas) has been derived. An average value of $\text{C}_B\text{-NO}_2$ (ideal gas), 3.1 kcal/mol was used, and heat of formation was estimated for each compound. An additive method for predicting the standard heats of formation at 298 K of aliphatic and alicyclic polynitro compounds, was given by Bourasseau [16]. It consists of the following three steps:

1. Evaluation of the enthalpy of formation in the gaseous state.
2. Estimation of the enthalpy of vaporisation for a liquid or enthalpy of sublimation for a solid.
3. Calculation of interaction terms, mainly within NO_2 groups.

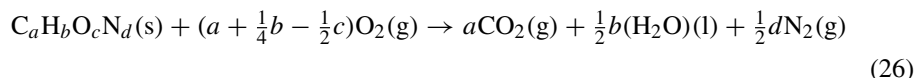
For aliphatic and alicyclic polynitro compounds, heat of formation at 298 K can be predicted by the following relations:

$$\Delta H_{fc} = \Delta H_{fg} - \Delta H_v + \Delta_{in} \quad (\text{liquid}) \quad (24)$$

$$\Delta H_{fc} = \Delta H_{fg} - \Delta H_s + \Delta_{in} \quad (\text{solid}) \quad (25)$$

where ΔH_{fc} is the heat of formation in condensed state, ΔH_{fg} the heat of formation in gaseous state, ΔH_v the heat of vaporisation, ΔH_s the heat of sublimation and Δ_{in} represents the sum of the interaction between some specific groups.

Rouse [17] calculated the ‘heat of formation’ experimentally from heat of combustion of the explosive with the stationary bomb calorimeter, using idealised equation of the bomb reaction:



The standard internal energy (cal/mol) of idealised combustion reaction at 298 K is given by

$$-\frac{\Delta E_c^0}{M} = \frac{A + (B + \delta) \Delta t - \Delta E_a - \Delta E_w + \Delta E_c + \Delta E_{co} - W}{m} \quad (27)$$

where A, B are constants and are determined during the calibration of calorimeter with samples of NBS standard benzoic acid and of *para*-benzoic acid (3404, 4313 and 3414). The values found for A and B are approximately -8.8 cal and 2624.6 cal/K, respectively, δ is the increase in energy equivalent of bomb contents during calibration experiment, ΔE_{co} the energy that would have been released by combustion of residual carbon monoxide, W the sum of the terms in the correction of the internal energy of combustion to standard state that are essentially constant of all experiments as one explosive, m the molecular weight of sample of explosive (g/mol), E_a the energy released by formation of nitric acid (cal), E_w the energy released by combustion of fuse wire (cal), E_c the energy that would have been released by combustion of residual carbon (cal) and Δt is the rise in temperature of calorimeter (K).

The standard enthalpy of combustion of the explosive in cal/mol was calculated by

$$\Delta H_{co} = \Delta E_{co} + 592.47(\frac{1}{2}d - \frac{1}{4}b + \frac{1}{2}c) \quad (28)$$

where b, c and d are subscripts in the formula of $C_aH_bO_cN_d$ explosive. Finally, the standard ‘heat of formation’ in cal/mol was calculated for each mole using the following equation:

$$\Delta H_f^0 = a\Delta H_f^0(CO_2, g) + \frac{1}{2}b\Delta H_f^0(H_2O, l) - \Delta H_{co} \quad (29)$$

Considering $\Delta H_f^0(CO_2, g)$ and $\Delta H_f^0(H_2O, l)$ equal to $-94\,051$ and $-68\,315$ cal/mol, respectively.

Using the above equation the ‘heat of combustion’ and standard ‘enthalpies of formation’ of 22 experimental organic explosives and one standard explosive (TNT) were determined. The results of these measurements, together with the reported crystal densities were used to calculate the detonation velocities and pressures by both Mader [18] and Kamlet–Jacobs methods [3]. With respect to the calculated velocities, there is a difference between both methods which ranges from -0.06 to ± 0.39 km/s, with an average of 0.176 km/s and standard deviation of 0.145 .

4.2. Quantitative structure–property relationship (QSPR) theory

Traditionally, ΔH_f^0 is estimated by additive calculation schemes, but the scheme can be created only on the basis of information about a large number of compounds. QSPR is another approach for quantitative evaluation of properties. It does not suggest the additive nature of a structure–property relationship and is applied for basis, with small or medium number of compounds. Moreover, the quality of predicting the parameters of substances becomes significantly higher when the results are calculated with the use of different approaches, and methods are compared. Therefore, use of additive scheme as well as QSPR approaches for estimating and predicting ΔH_f^0 are important.

Sukhachev and Pivina [19] developed ‘efficient modelling of molecular activity’ (EMMA) software to construct optimal linear regression models for determining the relationship between physico-chemical and sub-structural indices. These predicted properties based on structure–property relationship are effective in selection of potentially active structures for further synthesis.

On the basis of EMMA program, the structure and heat of formation relationship for non-aromatic polynitro compounds, may be predicted hypothetically by the following most stable and predictable correlation equation:

$$\begin{aligned} \Delta H_f^0 = & -98.86 + 1.14\text{SBE} + 49.77 \times 4\kappa_r/N_{\text{at}} - 437.78c_{\text{mid}} + \frac{61.76V_{\text{mid}}^2}{N_{\text{at}}} \\ & + 71.39\text{Fr}_1 - 195.44\text{Fr}_2 - 2933.25 \ln \left(\frac{\text{Fr}_3}{N_{\text{at}}} \right) \\ (R = 0.99, \text{S.D.} = 4.766, r = 368.49) \end{aligned} \quad (30)$$

where SBE is the enthalpy of the molecule where steric hindrance is absent (calculated on the basis of the molecular mechanics method). Here $4\kappa_r$ is the Randić’s index; c_{mid} the mean value of the diagonal elements in the inverse matrix of the weighed connectivity matrix G ; V_{mid} the mean value of the components of vector V , where V is the solution of the linear system $GV = C$, and C is the vector of corresponding vertex degrees in the structure graph; N_{at} is the number of atoms in the molecule; Fr_1 is the sum of the minimum charges at atoms in fragments of the type $-\text{C}-\text{C}-\text{NO}_2$; Fr_2 is the minimum of all the minimum charges at atoms in fragments of the type $\text{At}-\text{At}-\text{N}=\text{O}$, where At is an arbitrary atom; Fr_3 is the sum of maximum charges at atoms in all five-atom linear chains with single bonds in the structure.

Revealing the ‘structure–heat of formation’ relationship in cyclic nitrocompounds of aliphatic and nitramine nature, it was noted that substitution of eight nitro groups in the position of 1,3,5,7 of the eight membered molecular carcass when compared to four nitramine groups (e.g. HMX) increases ΔH_f^0 by 16.3 kcal/mol per position. Similar increase in the energy content by approximately 15.5 kcal/mol was observed in ten atom molecular cycle and twelve membered cycle, when compared to their respective five and six nitramine groups, i.e. substitution of two nitro groups for a nitramine groups in such compounds increases the energy content. A similar substitution in the polyhydrane series such as bis-homocubane and wurtzitane series with two nitramino groups increase ΔH_f^0 by 17.9 and 31.3 kcal/mol, respectively, as compared to those four nitro analogous. A remarkable increase in energy content was found in tetraaminoadamantane, when compared to adman-

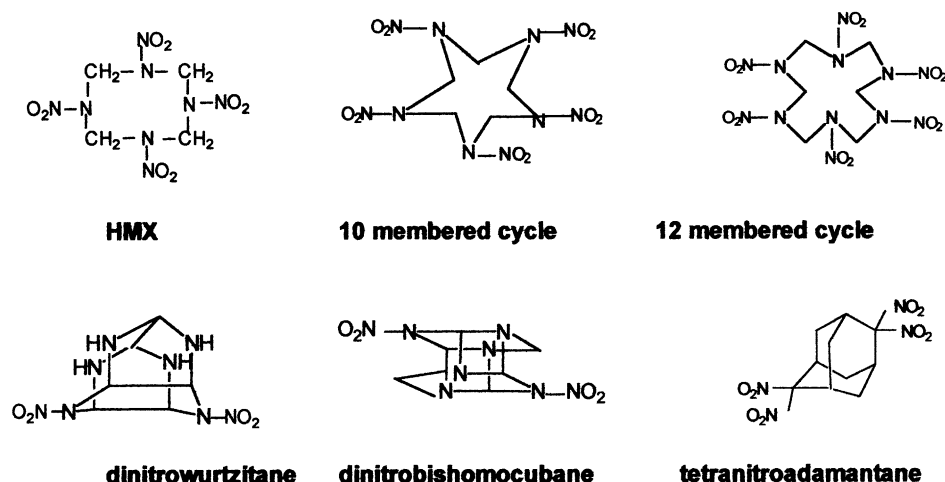


Fig. 2. Structures of some cyclic nitrocompounds used for ΔH_f^0 calculations.

tane ring which also depends on the increase in number of nitro groups and their substitution position as well. The substitution of the ester oxygen for the nitramine group increases the heat of formation substantially (Fig. 2).

4.3. Quantum mechanics

In the field of quantum chemistry, the development of new algorithms and techniques together with the continuing improvement in computers processing speed has meant that this technique can be applied to understand molecular problems with much more reliability, in terms of the predictions, and to much larger systems that has been the case until now [20]. In particular, there have been developments in the density functional methods for calculating molecular energies. These new methods provide near chemical accuracy for quantities such as bond strength and heat of formation.

However, all these methodologies must be tested against experimental data to gain an understanding of their limitations. Among the advanced methods developed in semi-empirical quantum chemistry for optimising the structure and determining the heat of formation of quite “large” molecules, the AM₁ and PM₃ parameterisation schemes have proved particularly effective. However, in general, the applicability of these methods is limited due to our inability to extend the accuracy of the calculation. On the other hand, ab initio theories, can in principle, be extended to any level of accuracy.

Heat of formation (ΔH_f^0) for various nitro compounds has been estimated from the semi-empirical molecular orbital methods like MNDO, MNDO/3, AM₁, PM₃ and molecular mechanics MM₂, are accurate enough for practical use.

Davis et al. [21] calculated physical properties for 105 nitro compounds utilising semi-empirical methods MINDO/3, MNDO and AM₁. They investigated the performance of each method in detail and concluded that MINDO/3 predicts ΔH_f^0 more accurately than MNDO

and AM₁. The properties evaluated include heats of formation, dipole moment, ionisation potential and molecular geometry.

Furthermore, MINDO/3 predicts correctly whether the heat of formation is exothermic or endothermic. However, MNDO and AM₁ always predict heats of formation, which are too endothermic. As more nitro groups are added to a molecule, MNDO and AM₁ predict increasingly more endothermic heats of formation, where as MINDO/3 does not show any trend. MINDO/3 predicts values close to the experimental heats of formation. As nitro content becomes large, the observed 'heat of formation' becomes more endothermic probably due to steric crowding.

Stewart [22] calculated properties of 763 compounds to estimate the performance of PM₃ and AM₁ methods selected from molecular orbital package (MOPAC) program. He found the average difference between calculated and observed ΔH_f^0 were 5.2 and 15.7 kcal/mol for PM₃ and AM₁, respectively. This discrepancy was corrected by Hawang et al. [23] by subtracting a constant value per nitro group from the calculated ΔH_f^0 and with the correction. Later, Yoshiaki et al. [24] calculated heat of formation of nitro compounds by semi-empirical method PM₃ and molecular mechanics (MM₂). They showed that PM₃ and MM₂ methods can estimate ΔH_f^0 more accurately than AM₁ for practical use. The calculated value differs by ± 0.07 and 0.06 kcal/g by PM₃ and MM₂, respectively, for both nitro alkanes and aromatic nitro compounds except, for tetranitromethane, where multi-nitro groups are on one carbon atom, resulting spatially very crowded, and ΔH_f^0 cannot be predicted accurately because of high steric energy.

Sana et al. [25] studied the heat of formation for some nitro compounds using isodemic procedure. They showed that ΔH_f^0 of nitro substituted paraffin increases quasi-linearly with the number of NO₂ groups. They introduced the concept of stabilisation energy which measures the special effects due to bond interaction, electron delocalisation, etc. and pointed out that, NO₂ substituent produces a large destabilisation energy. To estimate ΔH_f^0 of larger molecules, they also devised the concept of group energy, which contains the bond energies and the contribution of stabilisation energy.

To study the effect of polynitro aromatics, Yoshiaki et al. [26] calculated heat of formation of polynitro benzene and polynitro toluene with PM₃ and MM₂. They found that PM₃ semi-empirical method and MM₂ estimate ΔH_f^0 within ± 50 and ± 40 cal/g of observed value. In case of polynitrobenzene, MM₂ is more accurate than PM₃ and the neighbouring nitro groups raise ΔH_f^0 by about 10 kcal/mol. For polynitro toluenes, both methods showed fairly good values and the interaction between methyl and nitro groups raises ΔH_f^0 by about 5 kcal/mol.

Recently, Stewart [22] and Dewar and Theil [27] calculated recently the geometric structures of polycyclic caged nitramine, HNIW or CL-20 using semi-empirical quantum chemical methods AM₁ and PM₃. In their calculations, all bond lengths, bond angles and dihedral angles were optimised. Among the existing four polymorphs α , β , γ and ϵ ; ϵ has the highest crystal density and stability, thus the greatest potential for application. The PM₃ calculated values of ΔH_f and detonation velocity of HNIW were found to be 448.7 kJ/mol and 9473 m/s (density 1.98 g/cm³), respectively. These values are close to reported values. Based on computation, it can be concluded that velocity of detonation is not very much sensitive to the heat of formation but quite sensitive to the density. Again the stability, sensitivity and performance as well of molecules varies from polymorphs to polymorphs. Thus, β -HMX is

the most stable polymorphs, whereas ϵ -HNIW has the highest performance among the all polymorphs existed in these two molecules [28]. Hence, it is desirable to obtain the right polymorphs access to right particle size distribution and adopt the morphology of the crystal (shape, porosity, internal defects, etc.) which are influential factor in the vulnerability of the energetic materials.

PM₃ is revised to reproduce (MOPAC superior to 5.0) the properties of nitro compounds, and PM₃ seem to be the most reliable method to obtain ΔH_f^0 of all the semi-empirical methods like MINDO/3, MNDO and AM₁. PM₃ can estimate the two centre bond energy which corresponds to dissociation energy and thereby suggest the role of nitrogroup substituents in the polynitroaromatics as it is unstable to heat and impact. MINDO/3 [29] has been used to calculate stabilisation energy of cyclic strained compounds such as 1,3,3-trinitroazetidine, tetranitrocubane, octanitrocubane etc.

Yoshaki et al. [30] calculated ΔH_f^0 in condensed phase by combining heats of vaporisation and sublimation obtained by additivity rule with ΔH_f^0 in gas phase from PM₃ and MM₂, correlating values of ΔH_v and ΔH_s , Laidler's [31] and Bondi's [32] values. This method provides accurate enough to estimate energy hazards of nitramines and nitrates.

Molecular modelling can potentially be a useful tool to gain insight into the mechanism of explosions, initiation process, and can provide a wealth of information regarding thermodynamic properties. Knowledge of thermodynamic properties, such as enthalpy, heat capacity and entropy, are necessary for predicting the direction and equilibrium concentration of chemical reaction. Zhou and Heming [33] reported thermodynamic properties of hydroxy tetrazoles in the gaseous phase. Ab initio MO calculation at MP2/6-31 level were formed on hydroxyl derivatives of tetrazoles and their anions. The results show that all the compounds are practically planar and aromatic. Also the nitrogen hydroxy tetrazoles are more stable than the carbon hydroxy tetrazoles. George and James [34] used semi-empirical code PM₃ to model the tetrazene decomposition. This was simulated by breaking the bond between the tetrazolyl group and azaaminoguanidinyll group.

An approach to the ab initio predictions of crystal structures and to the consideration of possible polymorphic transformation was also developed for HNIW by Piviana and Arnautova [35]. As a result, the energy-minimised structures with the densities close to 2.1 g/cm³ were predicted. There are five conformational forms, viz. α , β , ϵ , δ and ξ were for CL-20 were predicted, from which α , β and ϵ have been prepared and studied crystallographically. The results showed that predicted δ and ϵ forms correspond to deeper minima at the potential energy surface (-43.10 and -43.20 kcal/mol) than the other forms (α , -36.20 ; β , -35.90 and ϵ , -32.40 , respectively). Probably this difference is due to higher electrostatic energy of the former two polymorphic modifications. However, calculations of strain energy for CL-20 conformers indicate that the most strained framework among selected one is ξ -framework.

5. Crystal density

One property that is helpful in evaluating an explosive performance is its density. For example, we know from experiments that the detonation velocity (VOD) of explosive increases with increasing density. For most explosives, detonation velocity is a linear function a

density greater than unity. Also, the P_{c-j} pressure varies with the square of density, when density is in the range 1.0–1.6 g/cm³ [9]. Since a detonation wave proceeds through the body of the explosive, the energy which it releases within and behind itself will depend on the mass of explosive traversed per unit area of the wave front. Hence, the more the mass that is concentrated into a given volume of explosive, more the energy the mass front can release in order to sustain itself at a high velocity, provided the charge is a reasonable diameter and well confined. The velocity of detonation appears to be almost exactly proportional to loading density.

Several methods exist to estimate the density of compounds. These methods can be divided roughly into two broad categories: theoretical and empirical nature. The theoretical approach uses detailed information about the crystal structure in calculating density of compounds, i.e. the density of organic compounds can be calculated on fundamental basis if all inter- and intramolecular forces are known. The empirical method consists of estimating molar volume by additive constituent volumes and it is simple and relatively accurate.

Exner [36] was one of the first to consolidate the idea of the additivity of constituent volumes and to be concerned with the statistics related to calculated values. Exner also suggested that the molar volume is fundamentally more important property to consider. Nielsen [37] extended Exner's method to include constituent volumes related to multi-numbered ring system and chemical entities found in explosives. He found that 10- to 18-member ring system make a negative contribution to the molar volume, whereas all other ring systems make positive contribution. The actual error in his predicted densities seems to be larger than reported error of <5%.

Tarver [38] defined a different set of constituent volumes than those of Exner and Nielsen and reported that the calculated densities and observed densities are within 1.5% error. Immirizi and Perini [39] also defined a set of 15 constituent volumes that are basically atomic volumes, although ring contributions were also included. Their database consists of compounds where the ring systems were restricted to benzene and naphthalene derivatives.

All these empirical methods are concerned with estimating a compound's molar volume (cm³/mol) or equivalently its crystal volume (Å³ per molecule). The constituent volumes then include contributions from the actual volume occupied by the molecule (molecular volume) and the voids between the molecule.

Kitaigorodsky [40] estimated the molecular volume by assuming that the volume of each atom was defined by an empirically determined Van der Waal's radius. The method described by Stine [41] differs from the previous methods in that it is based as a much larger set of empirical data. Hence, the confidence limits may be determined more accurately.

Thus, for example, one constituent would be a carbon atom with four single bonds, designated as C(1,1,1,1) or if two of the bonds were in a ring system designated C(1,1,-1,-1). Another constituent would be a carbon atom with a double bond and two single bonds C(2,1,1). A negative value indicated that the bond is a part of ring system. A part of histogram of the error between the observed and calculated densities of 2000 compounds indicates that the calculated value is within 3–4% of the observed value (Table 3 and Fig. 3).

A new group additivity database has been determined to provide atom and functional volumes for calculation of solid state densities by Ammon and Mitchell [42]. Volumes for 78 atoms/groups were determined for C, H, N, O and F containing structures from 11 577 crystal structural data. The average percent difference between the observed

Table 3
Experimental and calculated values of density of organic energetic compounds

Compound	Observed density (g/cm ³)	Calculated density (g/cm ³)
Cyclo-1,3,5-trimethylene-2,4,6-trinitramine (RDX)	1.81	1.77
Pentaerythrol tetranitrate (PETN)	1.78	1.71
Hexanitrobenzene (HNB)	1.99	2.01
Diamino trinitrobenzene (DATB)	1.84	1.78
Tetranitropropanediurea (TNPDU)	1.93	1.93
2,4,6-Trinitrotoluene (TNT)	1.67	1.67
2,2',4,4',6,6'-Hexanitrostilbene (HNS)	1.74	1.73
2,2',4,4',6,6'-Hexanitroazabenzene (HNAB)	1.80	1.79
1,5-Bis(picrylamino)-2,4-dinitrobenzene	1.78	1.78
2,2',4,4',6,6'-Hexanitroazabenzene (HNAB)	1.80	1.79

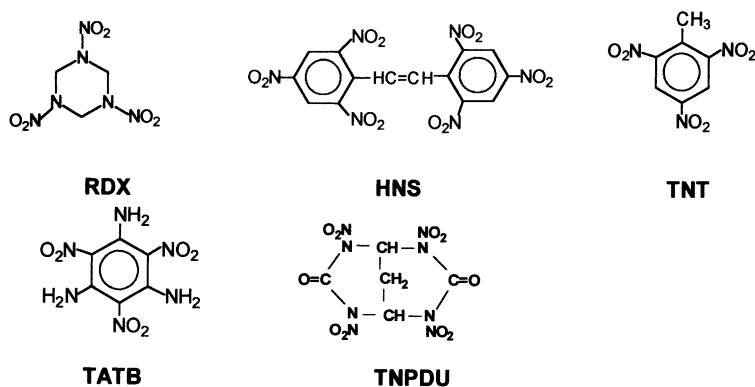


Fig. 3. structure of energetic compounds.

volume/densities for 485 structural database that was not used in the initial parameterisation is 2.04%.

Jayasurya [43] calculated the energy performance at different densities and heat of formation for octanitrocubane (ONC) which is one of the most powerful explosive known. The energy performance of ONC calculated at density 2.03 g/cm³ gave 20% more energy output than HMX. However, when the density was set at 2.13 g/cm³, which is 5% more than the previous value, the energy performance improved over 30% than HMX. The energy performance curve was calculated at density 2.23 g/cm³ which increases the energy output to over 40% than the current bench mark explosive's HMX. Hence, density is of particular interest in designing new explosives.

6. Structure–sensitivity relationships

Organic energetic materials are substances containing metastable molecules capable of undergoing very rapid and highly exothermic reactions. The study of energetic systems by

theoretical methods has accelerated dramatically over the last decade and has provided a considerable insight into the understanding of factors affecting their behaviour. An effort has been made significantly world-wide in order to understand better the relationship between the molecular structures of energetic compounds and their sensitivities to specific stimuli, e.g. impact and shock with the goal to design and manufacture less sensitive and less vulnerable munitions.

An ideal explosive is considered to be one which achieves high performance, but is insensitive enough to permit safe handling. However, it should not be, at the same time, so insensitive that detonation becomes difficult or impractical.

Many kinds of sensitivity have been identified in terms of nature of stimuli causing detonation; some of these include heat, friction, impact, shock and electrostatic charges. Two of the most commonly used measures are impact and shock sensitivity.

Impact tests involve subjecting a sample to the impact of standard weight falling from varying heights; the sensitivity is inversely proportional to the height at which there is a 50% probability of causing an explosion (called impact drop height or h_{50}). Shock sensitivity is often measured by a standard small scale gap test [44] and is interpreted as being directly proportional to the maximum gap width through which a given shock wave generated by another explosive (e.g. RDX) detonate the 50% of the time. Kamlet and Adolph [45] assessed impact sensitivity through correlation of oxygen balance (or OB_{100}). They demonstrated that for families of high energy molecules with similar decomposition mechanisms (e.g. trinitro-methyl, N- NO_2 and gem-nitro compounds and nitro aromatics with and without α -C-H linkages), there are approximately linear relationship between $\log h_{50}$ and OB_{100} as evidenced by the following formulae:

$$\log h_{50} = 1.332 - 0.026OB_{100} \quad (\text{with } \alpha\text{-H on carbon}) \quad (31)$$

$$\log h_{50} = 1.73 - 0.32OB_{100} \quad (\text{without } \alpha\text{-H on carbon}) \quad (32)$$

Kamlet and Adolph [45] also determined impact sensitivity of a large number of aliphatic and alicyclic explosives and found a good correlation ($r = 0.950$) of $\log h_{50}$ and OB_{100} using the following equations:

$$\log h_{50} = 1.372 - 0.168OB_{100} \quad (\text{N-}NO_2 \text{ explosives}) \quad (33)$$

$$\log h_{50} = 1.753 - 0.233OB_{100} \quad (\text{C-}NO_2 \text{ explosives}) \quad (34)$$

It was found that polynitroaliphatic containing at least one N- NO_2 linkage are more sensitive than nitroaliphatic explosives containing only C- NO_2 linkages. In these correlations, as $\log h_{50}$ increases OB_{100} decreases for any one family of molecule, i.e. the more impact sensitive explosives are those with the more positive OB_{100} values (Table 4).

In 1990 Stine [46,47] proposed a sensitivity index, based on the geometric properties of a regular tetrahedron, which has been shown to correlate with OB_{100} values. However, these useful correlations although good for a number of classes of compounds, do not allow one to distinguish between structural isomers which may have quite different sensitivities. This consideration has prompted considerable attention to the idea of the key “trigger linkage” in explosives as proposed by Kamlet and Adolph [45].

Due to the importance of nitroaromatics as a class of explosives, considerable interest has been generated in their properties, mechanisms of decomposition and factors affecting their

Table 4
Oxygen balance and impact sensitivity of some explosives

Explosive	OB ₁₀₀	<i>h</i> ₅₀ (cm)
2,4,6-Trinitrotoluene (TNT)	−3.08	160
TNB	−1.46	100
Picric acid	−0.48	64
Triamino trinitrobenzene (TATB)	−2.33	320
Tetryl	−1.04	25
Diamino trinitrobenzene (DATB)	−2.33	>200
2,2',4,4',6,6'-Hexanitrobenzene (HNB)	3.45	11
CL-18	−0.79	56
CL-12	−1.32	67
Cyclo-1,3,5-trimethylene-2,4,6-trinitramine (RDX)	0	24
Tetranitrotetraazacyclooctane (HMX)	−1.33	34

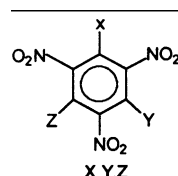
sensitivities. In general, any group or group of substituent influences aromatic ring because of the presence of the polarisable π -electron and the possibility of the conjugation, where both resonance and inductive effects play prominent roles in determining the distribution of charge in the system. It is noteworthy that the role of resonance is determined by using a general relation, $\sigma_P - \sigma_I = \sigma_R$, where the Hammett constant σ_P is defined in terms of *para*-substituted aromatics (e.g. benzoic acid) for which resonance interactions by resonance donors can be quite significant and σ_I is determined independently for series of compounds such as substituted acetic acids for which inductive effect predominates.

The commonly used nitroaromatics explosives are benzene derivatives which contain three or more nitro groups and as mentioned earlier that the sensitivity has been shown to be highly dependent upon the nature of the additional substituents on the aromatic ring. Except for sensitising effect of OH group [48], electron donating substituents (e.g. $-\text{NH}_2$, $-\text{OCH}_3$, $-\text{CH}_3$) generally desensitise (Table 5). In contrast, electron-withdrawing groups (including another NO_2 group) increase sensitivity. Further Dick et al. [49,50] measured the shock strength in single crystal of pentaerythritotetranitrate (PETN), where he observed shear stress based on the crystal orientations. This also corroborates same order as obtained in the analysis for increasing steric hindrance to shear under shock conditions. Owens [51] has demonstrated for a group of 11 trinitroaromatics and concluded that impact sensitivity varies inversely with the total donating ability of non-nitro substituents on the ring. Reasons for this behaviour is that resonance donors strengthen to some degree the C– NO_2 bonds as shown in Fig. 4.

However, it is noted that the degree of resonance electron withdrawn by the nitro groups into the C– NO_2 bond region is believed to be small, even with strong electron donors present; and the resonance structures (b) and (d) may play only a minor role.

In general, impact sensitivity increases as the largest V_{mid} of trinitro aromatic molecule $V_{\text{mid,max}}$ increases (V_{mid} is the electrostatic potential at the midpoint of the C– NO_2 bond as approximated from atomic charges). In view of the relationship between V_{mid} and a bond energy expression developed by Fliszar [52], it can be inferred that the instability of individual C– NO_2 linkage may be a key factor in initiating decomposition induced by impact. The presence of electron donating groups such $-\text{NH}_2$, $-\text{OCH}_3$ and $-\text{CH}_3$ tends to diminish

Table 5
Impact sensitivity of some substituted polynitroaromatics

 X, Y, Z	Impact drop height (cm)
NH ₂ , NO ₂ , H	41
Cl, H, H	79
OH, H, H	87
H, H, H	100
COOH, H, H	109
CH ₃ , H, H	160
NH ₂ , H, H	177
OCH ₃ , H, H	192
OCH ₃ , OCH ₃ , H	251
NH ₂ , NH ₂ , H	320
NH ₂ , NH ₂ , NH ₂	>320

$V_{\text{mid,max}}$, thereby suggesting that these may reduce the instabilities of the C–NO₂ linkages relative to those of trinitro benzene. The –OH group is an exception to this pattern even though of its electron-donating nature such as hydroxynitroaromatics have anomalously high sensitivities due to nitronic acid formation as suggested by Politzer et al. [53]. The proton transfer mechanism for the formation of nitronic acid was predicted at the HF/3-21G level to the significant extent which is accompanied by disruption of aromaticity resulting in a contribution to the observed sensitivity effects of hydroxyl substituents in nitroaromatics (Fig. 5).

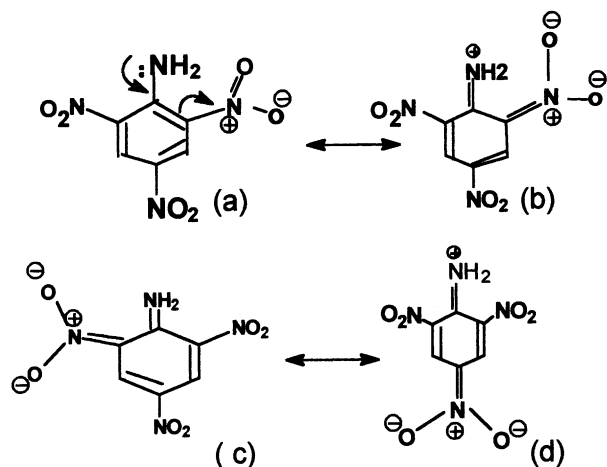


Fig. 4. Resonance donors strengthen C–NO₂ bonds of 2,4,6-trinitroaniline.

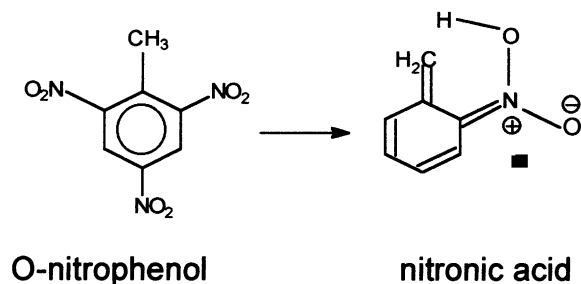


Fig. 5. Predicted proton transfer mechanism, thermodynamically highly unfavourable.

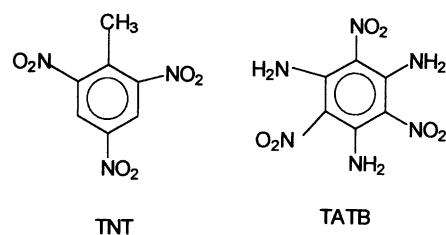


Fig. 6. Model compounds for hydrogen transfer reactions.

Murray et al. [54], studied hydrogen transfer reactions for two nitroaromatic explosives, 2,4,6-trinitrotoluene (TNT) and 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) using computational model systems (Fig. 6).

TNT is thermally labile, self-igniting at temperatures between 200 and 210°C and has intermediate impact and shock sensitivities. TATB, on the other hand, is stable to temperature well above 300°C and is so insensitive for impact and shock that it is impractical as an explosive. The results for *o*-nitrotoluene indicate that intramolecular hydrogen transfer form a bicyclic tautomer which is highly favoured thermodynamically at HF/3-21G level and on further loss of water to form anthranil (Fig. 7).

An interesting feature of these results is that there is no formation of nitronic acid tautomer but rather the thermodynamically favoured bicyclo systems. On the contrary, Cox and Hillier [55] using ab initio HF/STO-3G level for TNT found that it was thermodynamically highly unfavourable due to the formation of nitronic acid (Fig. 8).

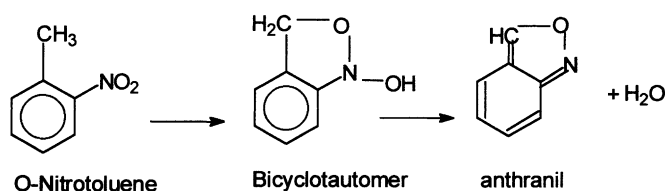


Fig. 7. Intramolecular hydrogen transfer mechanism of *o*-nitrotoluene.

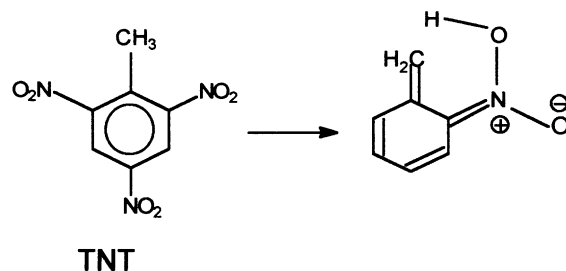


Fig. 8. Nitronic acid formation of TNT at HF/STO-3G level.

This five membered cyclic system was further evidenced by the intramolecular rearrangement in low temperatures studies of TNT as reported by Rogers [56] in 1967 and by Dacon et al. [57] in 1970. The energy produced during this process could help to stimulate further reactions. Further studies on TATB for thermal decomposition and under water shock and impact using the HF/3-21G level calculation, Sharma et al. [58] found the evidence of formation of five membered furazan ring formation which could explain its very low sensitivity [59] (Fig. 9).

The presence of nitro groups in an organic molecule introduces some degree of charge separation or local polarity, due to strongly electron attracting power of NO_2 group, this phenomenon occurs even if the symmetry of the molecules is such that the overall dipole moment is zero.

Brinck et al. [60] introduced a term polarity index, Π for a variety of molecules, which is a quantitative measure of local polarity and demonstrated its relationship to dielectric constants, an experimentally determined bulk property of molecules. A general trend in molecule bearing nitro group is that Π increases as the carbon to NO_2 ratio decreases, e.g. Π -values for $\text{C}_6\text{H}_5\text{NO}_2$, $p\text{-C}_6\text{H}_4(\text{NO}_2)_2$ and CH_3NO_2 are 12.3, 16.5 and 19.9 kcal/mol, respectively. This observation has led to a conclusion that there is a for a relationship between Π and impact/shock sensitivities of nitroaromatics [61].

Secondary nitramines are an important class of explosives of which, two of the most widely used military explosives nitramines are 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclo-octane (HMX). Organic amines and aza

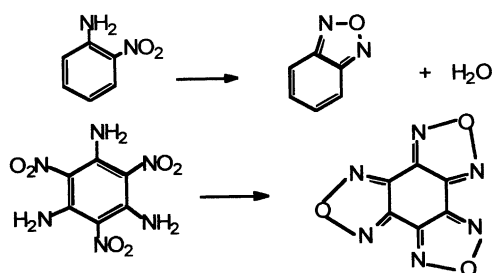


Fig. 9. Thermodynamically neutral furazan ring of TATB.

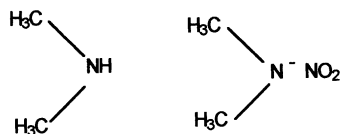


Fig. 10. Structure of dimethylamine and dimethylnitramine.

nitrogens are characterised by the presence of “lone pair” of electrons which give rise to strongly negative region in the molecular electrostatic potentials; however, these are significantly weakened by the substitution of electron withdrawing nitro group on the amine nitrogen [62]. As an example the negative potential in the lone pair region of dimethyl amine reaches a value of ~ 100 kcal/mol (at the HF/STO-SG computational level), whereas dimethyl nitramine there is no negative potential associated with the amine nitrogen [63]. An interesting feature of aza nitrogens is an anomalous stabilisation that is associated with their presence, which can be attributed to σ -conjugation of their lone pairs. These findings were further supported by several computational studies on nitramines [64] (Fig. 10).

Because of their importance as energetic material, a great deal of interest has been directed towards the stability and thermal decomposition mechanisms of nitramines. The rupture of N–NO₂ bond is a key step in the process of decomposition initiated by heat, shock or impact, although there may be important competing pathways, which may even predominate in some instances [65]. The recent computational studies [66] revealed two modes, that support bond rupture and molecules dissociation. One is a ring mode, while the other involves a stretching of the N–NO₂ bonds; the corresponding bond breaking processes are shown as in Fig. 11.

The energetic analysis in terms of activation barrier in the study led to the conclusion that ring fragmentation is roughly competitive with N–NO₂ bond breaking as an initial step in the thermal decomposition. An identical pathway is depicted for 1,3,5-triazacyclohexane and its trinitroderivative (RDX) while using ab initio calculations and local density functional (LDF) [67] methods with predicted activation energies are in the range 72–75 kcal/mol (Fig. 12).

However, extension of experimental evidence pointing to N–NO₂ scission as a key step in nitramine decomposition argue that the strengths of these bonds should be explicitly

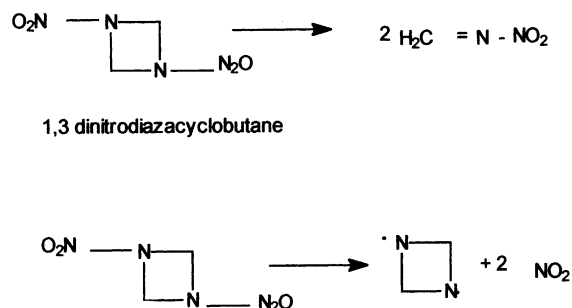


Fig. 11. Thermal decomposition pathways of 1,3-dinitro-diazacyclobutane.

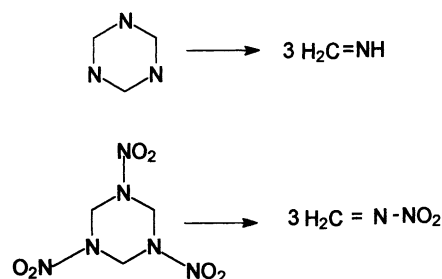


Fig. 12. Ab initio calculation level of decomposition pathway of triazacyclohexane and RDX.

reflected to a measure of sensitivity. The decomposition pathways of cubane and azacubanes have been outlined using ab initio MO method to determine the most feasible ring opening mechanism [68,69]. The optimisations have been carried out at 6-31G level of basis set and the first transition state was determined by using the eigen value transition state technique. The activation energy barrier for ring opening pathway of cubane and azacubane are 34 and 16.26 kcal/mol, respectively.

However, due to the simultaneous presence of $-\text{NO}_2$ and $-\text{NH}_2$ groups on adjacent tertiary carbons in some strained molecule, e.g. 1-nitro-3-aminobicyclobutane and 1-amino-2-nitro cubane there is marked weakness of C–C bonds, as measured by means of calculated bond order. This phenomenon has been attributed to a “push–pull” mechanism, which in the limiting case would lead to a rupture of the C–C bond as illustrated below [70,71] (Fig. 13).

“Push–pull” mechanism is actually the consequence of two separate effects, associated with the $-\text{NH}_2$ and $-\text{NO}_2$ groups individually, which can in some instances reinforce each other. In studies of aminocubanes, aminoazacubanes, aminotriprismanes and aminoazatriprismanes, a consistent direction has been observed, where specific bond weakening is observed in one of the C–C or C–N bonds adjacent to the site of $-\text{NH}_2$ substitution. The weakened C–X bond (where X = C or N) is invariably coplanar with the C–NH₂ bond and the position of the most electrostatic potential is associated with the amine nitrogen lone pair (Fig. 14).

This delocalisation, which weakens the C–X bond, can occur most effectively when the latter is coplanar with the lone pair. It has been found that this effect is stronger when X = N (rather than X = C), consistent with the anomeric effect being most commonly invoked

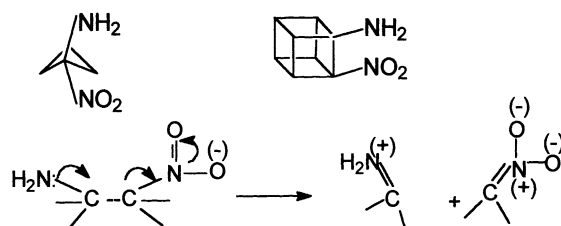


Fig. 13. Rupturing of the tertiary C–C bond of “push–pull” mechanism.

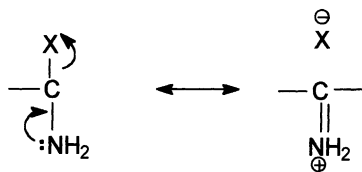
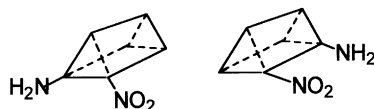


Fig. 14. Anomeric effect of a C–X bond.

Fig. 15. Effect of NO₂ group on adjacent C–C bonds in nitrotriprismane.

for molecules in which X is an electronegative atom [72], e.g. N, O or F. However, the situation involving NO₂ group alone is less straightforward than that of the –NH₂, because it can strengthen some bonds and can weaken other depending upon its conformation [73]. Again Murray et al. [74] predicted that neighbouring –NO₂ and –NH₂ groups may also act upon different bonds as shown below in nitroamino triprismane, where –NO₂ weakens the adjacent C–C bonds in three membered ring, while –NH₂ acts on the bond in the four membered ring (Fig. 15).

The studies of nitro derivatives of aza cage-like systems has created an interest the design of new energetic materials. The C–C bond weakening with NO₂ group in the systems does not occur to any significant degree when there is an adjacent aza nitrogen [75]. This is because of overall stabilising influence of aza nitrogens, thence through diminishing the molecular strain energy. Thus, the potential high-energy molecule tetranitrotetraazacubane is feasible from the standpoint of synthesis and stability (Fig. 16).

High nitrogen content molecules as potential energetic materials, have prompted a variety of theoretical studies. Nitrogen catenation is often associated with instability and/or sensitivity as being observed in the powerful explosives 1,3,5-triazido-2,4,6-trinitrobenzene which undergoes a slow conversion to hexanitrosobenzene and N₂, thereby eventually losing its initiating power [76].

The insensitivity to impact and a high level of thermal stability of high nitrogen content compounds may be accounted due to considerable delocalisation of charge (through –N=N– and –C=C– double bonds) caused by different resonating structures. Again, the instability/sensitivity to impact varies from isomer to isomer in triazole series of compounds

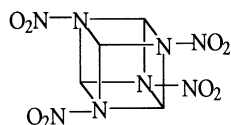


Fig. 16. Structure of tetranitrotetraazacubane.

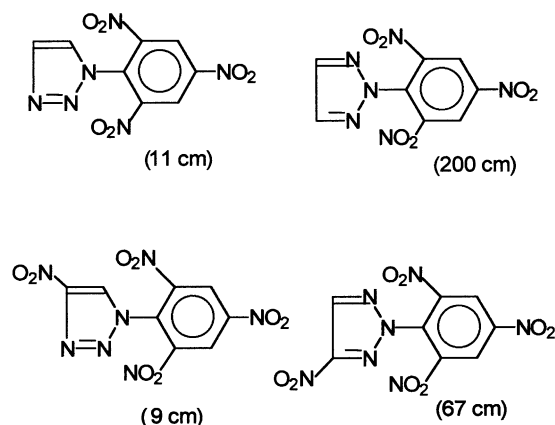


Fig. 17. Impact sensitivity of isomeric triazoles.

because of the presence of shorter and stronger N–N bonds which facilitate decomposition [77] through the loss of N_2 (Fig. 17).

7. Conclusions

The theoretical calculations and various empirical methods complementing to computer calculations of the factors related to detonation velocity, detonation pressure, crystal density, oxygen balance and heat of formation are described. The interaction between theory and synthesis appears to the realisation that sensitivity, density and heat of formation of a molecule are the most important parameters to screen potential explosives. However, high nitrogen content is one of the factors that influence performance. Indeed, it is imperative that all of the factors are to be considered simultaneously because there are very few molecular constituents that contribute in a positive way to each of these factors.

The shock sensitivity relationships for nitramine and nitro aliphatic suggest that the strengths and number of X–NO₂ (X = C or N) linkages in relation to overall molecular size are important in determining sensitivity. For a few nitramines, the sensitivity varies directly with local polarity (I) which increases as the number of X–NO₂ linkages per unit volume increases. In the area of nitro aromatics, correlation between impact/shock sensitivity and total electron donating ability of the non-nitro substituents suggest that the strengthening of C–NO₂ linkages lead to decrease sensitivity. A direct relationship between impact sensitivity and local polarity of nitro aromatics is again not consistent. Molecules, which do not fit general types of relationships such as the high sensitivities of hydroxynitroaromatics, may be due to formation of small quantities unstable nitronic acid tautomers.

Thus, an universal relationship between sensitivity and molecular parameters cannot be established. In general, nitramines are more sensitive to impact/shock than the nitroaromatics due to lower rotational energy barrier of C–NO₂ bonds in nitroaromatics relative to N–NO₂ in nitramines there by there is dissipation of thermal energy.

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