



## Structurally modified RDX - A DFT study



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### ABSTRACT

RDX is a nitramine type explosive which is widely employed in military and industrial applications. A hot topic in military area is lowering the sensitivity of explosives. Along this direction, one approach, which is still being applied, is to use coatings or additives for explosives, as in the example of *i*-RDX (reduced sensitivity RDX). Another attitude would be to make some slight molecular level chemical modifications in the explosive structure that cause a diminished sensitivity without substantial loss in explosive impact. RDX has three nitro groups. We assumed that by the conversion of these nitro groups to nitroso and amino groups, it might be possible to lower the sensitivity somewhat. We have correlated the bond dissociation energies with impact sensitivity. Additionally, the ballistic properties, i.e. detonation velocity (*D*), and detonation pressure (*P*) have been examined by using Kamlet-Jacobs equations. We have shown that the above mentioned molecular modifications are a successful way of lowering the sensitivity of RDX.

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## 1. Introduction

RDX, known as Research Department explosive, is a nitramine type explosive so long extensively employed in army and industrial applications [1]. It was synthesized as an explosive more influential than TNT, and it was broadly used in World War II. RDX is also called cyclonite, hexogen and T4 [2]. Its chemical name is hexahydro-1,3,5-trinitro-1,3,5-triazine, (cyclotrimethylenetrinitramine). RDX is a white, crystalline solid in its pure synthesized state. RDX is accepted as one of the most powerful military high explosives and quite stable under storage conditions [3]. It is frequently used as a component in mixtures including supplementary explosives and plasticizers, phlegmatizers or desensitizers. RDX is vital in the formulations of many well-known military explosives such as Composition A, B and C, CH-6, Torpex and particularly plastic bonded explosive (PBX) [4–9].

Desensitization of explosives (reduction of their sensitivity) is a hot research topic in military area. One approach covers the usage of additives and coatings of explosives where surface may play a significant role. There are many examples in the literature, especially on RDX [10].

Another approach, which is also adopted in the present study, is to apply some molecular level changes in the molecule structure of an explosive providing a decrease in impact sensitivity etc., without notable decrease of power. RDX has three nitro ( $-\text{NO}_2$ ) groups in the form of nitramine. Presently, it is assumed that conversion of these nitro ( $-\text{NO}_2$ ) groups to nitroso ( $-\text{NO}$ ) and amino ( $-\text{NH}_2$ ) groups (Fig. 1) might lessen the sensitivity. Moreover, a comprehension of the tendency in energetic character in going from RDX to derivatives discloses the factors which can be used in altering the sensitivity of explosives via structural modification. Desensitization produces much safer explosives in comparison to their parental molecules and prevents some unintentional detonations initiated by several factors like thermal and/or mechanical shock, static electric discharging, etc.

In the current article, some computational studies have been done on RDX itself and five dissimilar RDX derivatives.

## 2. Theoretical methods

The initial structure optimizations of RDX and further structures were accomplished following the basis set order: MM2 method, PM3 method, STO and HF/6-31G(d,p) and finally DFT, B3LYP/6-31G(d,p). There exists no imaginary frequency in the normal mode analysis of the molecules carried out at the same level of theory. The total electronic energies were calculated considering zero point vibrational energies (ZPE). The heats of formation of all the molecules were calculated by a T1 Thermochemical Recipe [11]

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### Abbreviations

B3LYP	Becke, 3-parameter, Lee-Yang-Parr
BDE	Bond Dissociation Energy
BSSE	Basis Set Superposition Error
DFT	Density Functional Theory
HF	Hartree Fock
HMX	Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine
PBX	Plastic Bonded Explosive
PM3	Parametric Method
RDX	Research Department Explosive; 1,3,5-Trinitroperhydro-1,3,5-triazine
STO	Slater-type orbital
TNT	2-Methyl-1,3,5-trinitrobenzene
T1	Thermochemical Recipe
QCISD	Quadratic configuration interaction

implemented in Spartan'08. The computational calculations were done using Spartan'08 software in standard conditions (298.15 K and 1.00 atm) [12]. Furthermore, the geometry optimizations and the single point calculations of all the structures were performed at UB3LYP/6-31G(d,p) theoretical level for bond dissociation energy (BDE) calculations. The basis set superposition error (BSSE) was achieved using the Boys and Bernardi counterpoise method in Gaussian 03 software package [13,14].

## 3. Results and discussion

### 3.1. The geometries

All the structures considered in Fig. 1 have been supposed to be the potential nominees of explosives. The geometry optimizations of the molecules in Fig. 1 have been done at the B3LYP/6-31G(d,p) level. In the optimized structure, RDX has one nitro group in the axial and the other two in the equatorial positions. In structures 2–5, the conformational pattern of RDX is preserved, namely one axial and two equatorial positions occupied by the substituents. In structure-2 the nitro group is in the axial position. In structures-4 and -5 the axial position is occupied by the amino and nitro groups, respectively. Whereas in structure-6, the nitroso groups occupy the axial positions in that respect its conformation pattern is different from RDX. The amino and nitroso groups present in structure-3 prefer the equatorial positions. The calculated bond length data for the optimized geometries are shown in Table 1. The subscript numbers showing the bonds in Table 1 is arranged considering Fig. 2. The experimental X-ray diffraction data for RDX [15] are shown in Table 1 as well. The similarity between the experimental and theoretical bond length data for RDX and the absence of imaginary frequency in the potential energy diagrams assure the true geometry optimization of the molecules. This compatibility also assures that bond length data of all the molecules are close to the real values.

Overall, the experimental and theoretical bond length results for RDX are almost equivalent. There are slight differences between the

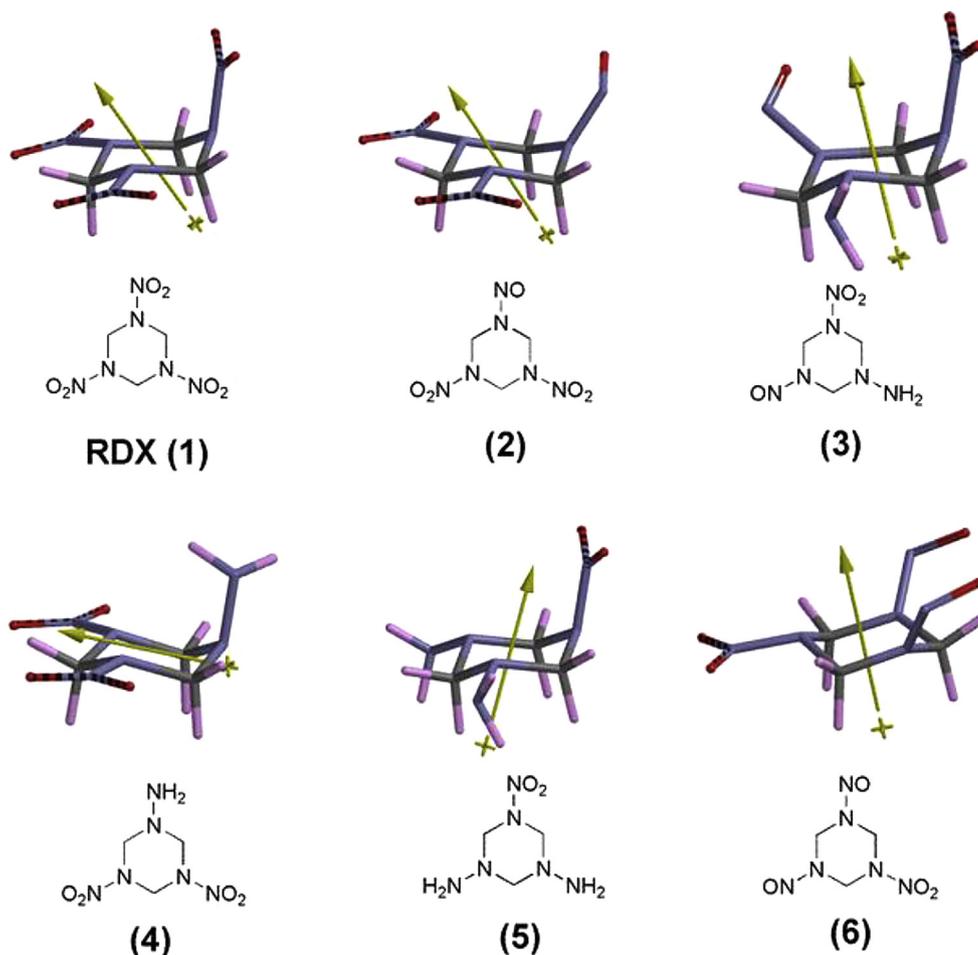
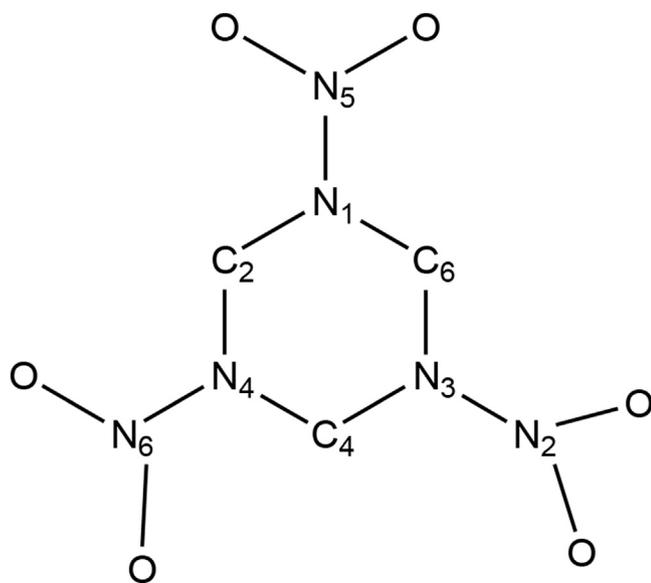


Fig. 1. The 3D geometries of RDX (1) and its derivatives.

**Table 1**  
The bond length data (Å) of the optimized RDX and its derivatives computed at (DFT) B3LYP/6–31G(d,p) level.

Bond	RDX (1)	RDX <sup>a</sup>	2	3	4	5	6
N1-C6	1.450	1.457	1.440	1.458	1.444	1.456	1.441
C6-N3	1.471	1.441	1.474	1.466	1.486	1.463	1.478
N3-C4	1.463	1.463	1.465	1.466	1.462	1.459	1.479
C4-N4	1.463	–	1.462	1.449	1.465	1.462	1.441
N4-C2	1.471	–	1.470	1.458	1.484	1.461	1.458
C2-N1	1.450	–	1.447	1.462	1.448	1.459	1.458
N1-N5	1.441	1.431	1.383	1.426	1.428	1.421	1.376
N5-O	1.219	1.221	–	1.224	–	1.223	1.211
N5-O	1.219	1.221	1.208	1.222	–	1.225	–
N4-N6	1.400	–	1.400	1.363	1.397	1.423	1.375
N6-O	1.226	–	1.226	1.216	1.227	–	–
N6-O	1.226	–	1.226	–	1.228	–	1.211
N3-N2	1.400	1.395	1.399	1.422	1.393	1.422	1.397
N2-O	1.226	–	1.227	–	1.229	–	1.227
N2-O	1.226	–	1.226	–	1.227	–	1.227
Dipole moment (Debye)	4.23	–	3.62	6.34	3.75	5.33	4.23

<sup>a</sup> Experimental data recorded at 298 K stated in Ref. [15]. All molecules belong to C<sub>1</sub> point group.



**Fig. 2.** The numbering method of RDX and other derivatives.

experimental and calculated data. For instance, the X-ray bond length data for RDX has shorter nitramine N–NO<sub>2</sub> bonds approximately 0.01 Å than the computed values. These slight differences stem from the solid-state effect including the intermolecular interactions. These interactions are not available in the DFT computations employed presently [16].

### 3.2. Charges

Fig. 3 represents the electrostatic charge (in esu) development of the system computed at the B3LYP/6–31G(d,p) level and acquired in the direct output of the software. Moreover, the electrostatic potential  $VS(\mathbf{r})$  computed on the 0.001 au isodensity surface [17] has been superimposed on each structure (property range spans over –200 to 200 kJ/mol). As seen in Figs. 1 and 3 the dipole moments in all the structures except 4 are oriented upward. Note that the dipole moments of structures 1, 2, 4 are inclined over the equatorial groups (in structure-4 it is almost in the ring plane)

whereas in 5 its inclination is towards the axial group. Whereas, in 3 and 6 the dipole moment is almost vertical to the ring plane. The charges and bond lengths in the optimized geometries are arranged such that order of dipole moments (see Table 1) is  $2 < 4 < 1 = 6 < 5 < 3$ .

The orientation of the dipole moments indicate that the conformation of the substituents makes the bottom side of the molecules electron deficient contrary to the upper side. In structures-3 and -5 the region around the axial nitro group becomes relatively electron rich (see Fig. 3). In 4 the relatively electron rich region is around one of the equatorial nitro groups. The electrostatic potential  $VS(\mathbf{r})$  on the isodensity surface of 2 resembles the respective plot of RDX. Therefore it is not unexpected that most properties of 1 and 2 should be comparable.

### 3.3. The bond dissociation energies (BDE) vs. impact sensitivity

Numerous experimental studies show that nitramine (N–NO<sub>2</sub>) bond homolysis is the first step of thermal decomposition of RDX and other nitramines [18–21]. In this article, for the comparison of the nitramine bond strengths of the compounds, homolytic bond dissociation energy (BDE) calculations considering the removal of nitrogen dioxide moiety from the original geometry were computed at UB3LYP/6–31G(d,p) level. The equalities for the homolytic nitro bond (nitramine) break and calculation of the BDE are shown below



$$BDE(R-NO_2) = [E_{R^*} + E_{NO_2^*}] - E(R-NO_2) \quad (2)$$

R–NO<sub>2</sub> stands for the neutral molecule and R\* and NO<sub>2</sub>\* stands for the radicals occurring after the nitramine bond dissociation; BDE<sub>(R–NO<sub>2</sub>)</sub> denotes the bond dissociation energy of nitro bond; E(R–NO<sub>2</sub>), E<sub>R\*</sub>, and E<sub>NO<sub>2</sub>\*</sub> are the ZPE added total energies of the compounds and the radicals, respectively [22–24]. Additionally, the basis set superposition error (BSSE) analyses were carried out.

The sensitivity behavior of an explosive under different heat, impact, friction conditions may vary. In this work, the “sensitivity” term designates the “impact sensitivity” of the focused explosive. Impact sensitivity behavior of explosives can be determined experimentally by the drop height test. The impact sensitivity can also be examined by theoretical methods. Murray et al. [25] have put out an association between the BDEs of the nitro bonds and the electrostatic potentials on the molecular surfaces of some energetic molecules. The several appreciated studies in the references [26–29] have indicated that there is a parallel correlation between the BDE for the weakest nitro bond of the molecule and its impact sensitivity. The typical tendency is that the larger the BDE data of nitro bond, the lower the sensitivity is.

Desensitization of explosives (reducing their vulnerability) becomes more of an issue in military applications. Our methodology in the current work is to apply small structural changes in the explosive that lead to the probable decrease in impact sensitivity without substantial loss of explosive power. RDX has three nitro groups. We foresaw that the conversion of nitro (–NO<sub>2</sub>) groups to nitroso (–NO) and amino (–NH<sub>2</sub>) groups might enable a decrease in the impact sensitivity. The lowest sensitivity has been attributed to the highest nitramine (N–NO<sub>2</sub>) bond dissociation energy. Also, a comprehension of the tendency of energetic character in going from RDX to the derivatives might reveal the features which can be used in changing the impact sensitivity of explosives via structural modification. Table 2 shows the computed BDE data. The consistency of our BDE value (without BSSE) and the calculated literature data (the datum excerpted from the reference is without BSSE) [30]

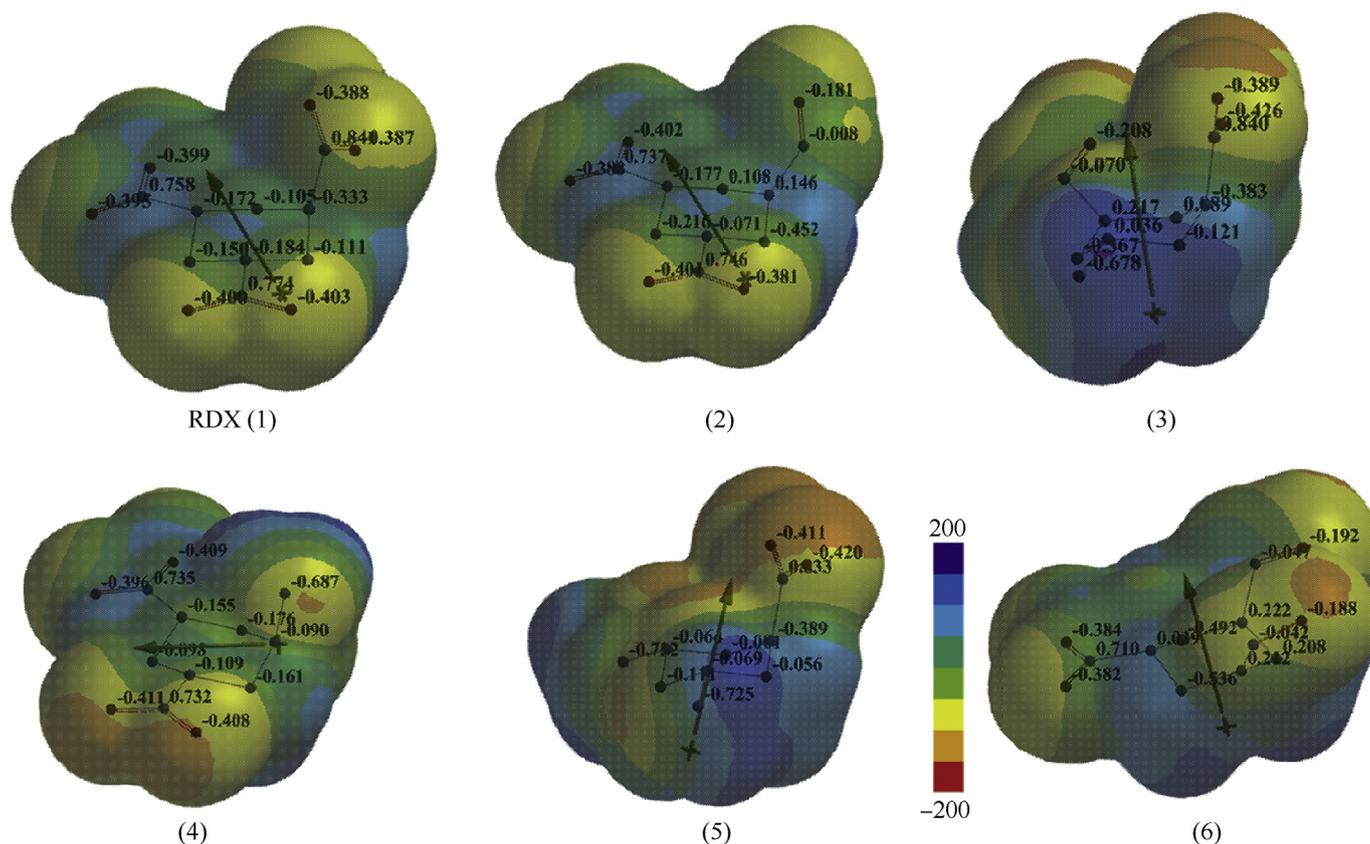


Fig. 3. Electrostatic charges on the atoms of the species superimposed with electrostatic potential  $VS(r)$  computed on the 0.001 au isodensity surface (The Hydrogens are not shown).

**Table 2**  
The homolytic bond dissociation energies, BSSE and corrected BDEs of N–NO<sub>2</sub> bonds of RDX and other derivatives calculated at (DFT) UB3LYP/6–31G(d,p) theoretical level.

Molecule	Bond	BDE/ (kJ·mol <sup>-1</sup> )	BSSE/ (kJ·mol <sup>-1</sup> )	BDE <sub>corr</sub> / (kJ·mol <sup>-1</sup> )
1	N <sub>(1)</sub> -N <sub>(5)</sub> O <sub>2</sub>	152.83 (151.73)	18.14	134.69
	N <sub>(3)</sub> -N <sub>(2)</sub> O <sub>2</sub>	145.87	18.06	127.81
	N <sub>(4)</sub> -N <sub>(6)</sub> O <sub>2</sub>	146.01	18.12	127.89
2	N <sub>(3)</sub> -N <sub>(2)</sub> O <sub>2</sub>	145.47	18.15	127.32
	N <sub>(4)</sub> -N <sub>(6)</sub> O <sub>2</sub>	143.27	18.15	125.12
3	N <sub>(1)</sub> -N <sub>(5)</sub> O <sub>2</sub>	161.99	18.63	143.36
	N <sub>(3)</sub> -N <sub>(2)</sub> O <sub>2</sub>	157.15	18.51	138.64
4	N <sub>(4)</sub> -N <sub>(6)</sub> O <sub>2</sub>	160.53	18.28	142.25
	N <sub>(1)</sub> -N <sub>(5)</sub> O <sub>2</sub>	172.41	17.71	154.70
5	N <sub>(3)</sub> -N <sub>(2)</sub> O <sub>2</sub>	153.94	18.21	135.73

\*Datum in parenthesis is the computed literature data from Ref. [30] for BDE of nitro bond of RDX. The subscript numbers in parenthesis indicate the positions.

for RDX increases the reliability of the technique adopted in the current article (see Table 2).

We have compared the impact sensitivity of explosives in the present study on the basis of BDE values such that attributing the highest sensitivity to the lowest nitramine bond dissociation energy value. We have changed the nitro groups with amino and/or nitroso group(s) and examined the nitramine BDE values. An increase in the nitro BDE has been interpreted as a more insensitive explosive, and a decrease in nitro BDE has been evaluated as a more sensitive explosive. When a nitro group of RDX is changed with nitroso group (structure-2), the BDE for nitramine bond decreases by 2.69 kJ/mol, resulting in a more sensitive explosive. However, replacement of both of the nitro groups by nitroso groups (structure-6) creates a more insensitive explosive compared to RDX that is, BDE value of nitramine bond increases by 7.92 kJ/mol.

Likewise, the replacement of one nitro group with an amino

group (structure-4) induces an increase in nitramine BDE by 10.83 kJ/mol. The substitution of both nitro groups by amino groups (structure-5) increases the BDE value by 26.89 kJ/mol. The results showed that amino replacements produce the most insensitive explosives of all. The amino groups balance the electron demand of nitro groups existing in the system.

The introduction of one nitroso and one amino groups instead of nitro groups of RDX accomplishes structure-3. Meanwhile, the BDE increases by 15.55 kJ/mol in going from RDX to structure-3, resulting in a more insensitive explosive.

All the conversions considered, except for structure-2, cause a notable increase in BDEs, therefore an effective decrease in impact sensitivity is expected theoretically. This type of variation of functional groups of RDX is very supportive for decreasing the sensitivity.

Insensitivity concept has been correlated with Bond dissociation

energy (BDE). The higher the BDE, the more insensitive the explosive is. Since the BDE values are in the following order:  $2 < 1 < 6 < 4 < 3 < 5$  (as seen from the chart in Fig. 3 and Table 2); the insensitivity is in the same order. For structures 2–6, there exists an inverse relationship between the BDE and detonation velocity. The structure-5 has been assigned as the most insensitive RDX derivative and the structure-2 has been identified as the most sensitive RDX derivative.

### 3.4. Explosive properties

Explosive effects of energetic materials can be assessed by the determination of the ballistic properties, especially detonation velocity ( $D$ ) and detonation pressure ( $P$ ). The use of empirical Kamlet-Jacobs [31–34] equations enables one to calculate these properties by means of Eqs. (3) and (4).

$$D = 1.01 (N M_{av}^{1/2} Q^{1/2})^{1/2} (1 + 1.30 \rho) \quad (3)$$

$$P = 1.558 \rho^2 N M_{av}^{1/2} Q^{1/2} \quad (4)$$

The terms in Kamlet Jacobs Equations (3) and (4) are shown as:  $D$ , detonation velocity (km/s);  $P$ , detonation pressure (GPa);  $\rho$ , density of a compound ( $\text{g}/\text{cm}^3$ );  $N$ , moles of gaseous detonation products per gram of explosive;  $M_{av}$ , average molecular weight of gaseous products;  $Q$ , chemical energy of detonation (kcal/g). The parameters  $N$ ,  $M_{av}$ , and  $Q$  are calculated according to the chemical composition of each explosive as revealed in Ref. [16]. For a  $\text{C}_a\text{H}_b\text{O}_c\text{N}_d$  type explosive, if  $2a + b/2 > c \geq b/2$  equality is fulfilled,  $N$  is calculated using  $(b+2c+2d)/4M$ ,  $M_{av}$  is calculated as  $(56d + 88c - 8b)/(b+2c+2d)$ , and  $Q$  is calculated as  $[28.9b+94.05(c/2-b/4)+0.239\Delta H_f^0]/M$ . If  $b/2 > c$  equality is satisfied,  $N$  is calculated as  $(b + d/2M)$ ,  $M_{av}$  is calculated as  $(2b + 28d + 32c)/(b + d)$ ,  $Q$  is calculated as  $[(57.8c + 0.239\Delta H_f^0)/M]$ . The coefficient (0.239) of  $\Delta H_f^0$  in the relations is a conversion factor from kJ/mol to kcal/mol. “ $M$ ” is the molecular weight of the compound (in g/mol);  $\Delta H_f^0$  is the standard heat of formation of the compound (in kJ/mol). The standard heat of formation ( $\Delta H_f^0$ ) was calculated using T1 Thermochemical Recipe. This recipe follows the G3(MP2) recipe, by replacing HF/6-31G(d) for the MP2/6-31G\* geometry, omitting both the HF/6-31G(d) frequency and QCISD(T)/6-31G(d) energy and approximating the MP2/G3MP2 large energy using dual basis set RI-MP2 techniques [35]. The density ( $\rho$ ) of each compound is calculated by ratio of molecular weight to the molar volume. The statistical average of hundred single-point molar volume calculations results in the molecular volume of each optimized molecule. The Monte Carlo integration in the Gaussian 03 software package was used for molar volume calculations [14]. The density of each compound was anticipated from the molecular volume divided by

molecular weight. Structures 1, 2, 4, and 6 are in accordance with  $2a + b/2 > c \geq b/2$  relation, whereas, structures-3 and -5 are in accordance with  $b/2 > c$  relation. The calculated oxygen balance ( $\Omega$ ), heat of formation ( $\Delta H_f^0$ ), the chemical energy of detonation ( $Q$ ), density ( $\rho$ ) and detonation velocity ( $D$ ) and pressure ( $P$ ) are listed in Table 3. It also includes experimental values of RDX [16,36,37] taken from the literature.

Table 3 shows the oxygen balance ( $\Omega$  %) values of the explosives considered in the present study. For a  $\text{C}_a\text{H}_b\text{O}_c\text{N}_d$  type explosive, %  $\Omega$  is calculated as  $1600(2a + b/2 - c)/M$ . It is an expression that indicates the degree to which an explosive can be oxidized. If an explosive molecule has sufficient amount of oxygen to produce  $\text{CO}_2$  from carbon,  $\text{H}_2\text{O}$  from hydrogen molecules, sulfur dioxide from all of its sulfur, and all metal oxides from metals with no excess, the molecule is supposed to have a zero oxygen balance. The molecule is supposed to have a positive oxygen balance if it has more oxygen than is required and a negative oxygen balance if it contains less oxygen than needed. In this work, all the considered molecules have negative oxygen balances, like a well-known explosive, TNT.

The heat of formation ( $\Delta H_f^0$ ) values of all molecules was calculated with a thermochemical recipe, T1. The comparability of the calculated ( $\Delta H_f^0$ ) value of RDX and the literature value [16] raises the credibility of the method. When density ( $\rho$ ) data are considered, replacement of the nitro groups with amine groups (structures 4 and 5) causes a dramatic decrease in the density. The nitroso group substitutions (structures 2 and 6) also cause a slight decrease in the density.

The detonation velocity and detonation pressure values for RDX both agree well with the experimental literature data [2,16,36]. When Table 3 is considered, it is obvious that the explosive performances of all molecules are superior to the well-known explosive, TNT. The performances of RDX and other derivatives are in the following manner (See Fig. 4):  $\text{TNT} < 5 < 3 < 4 < 6 < 2 < \text{RDX}$ . The replacement of nitro groups with nitroso groups (on going from RDX to structures 2 and 6) slightly decreases the ballistic properties. Similarly, the amino group substitutions (from RDX to structures 4 and 5) lead to an average decrease in detonation velocity and pressure. The structure-3 has one nitro, one nitroso and one amino group. The presence of the nitro and nitroso groups instead of nitro groups also lowers the detonation properties inappreciably.

The explosive properties and sensitivity characteristics of the structures considered should be evaluated together. Amino group replacement (structures 4 and 5) is an effective method in decreasing sensitivity; however, these replacements deteriorate the detonation properties. Also, nitroso substitutions (structures 2 and 6) bring about higher BDEs than RDX (more insensitive compounds) with lower detonation velocity values. Similarly, conversion of RDX to structure-3 results in decreasing the sensitivity with worse detonation properties. Among them, structure-6 (the

**Table 3**

Anticipated density data and detonation properties of RDX and its derivatives at B3LYP/6–31G(d,p) level.

Molecule	$\Omega$ /%	$\Delta H_f^0$ <sup>a</sup> (kJ·mol <sup>-1</sup> )	$Q$ / (kcal·g <sup>-1</sup> )	$V^b$ / (cm <sup>3</sup> ·mol <sup>-1</sup> )	$d$ / (g·cm <sup>-3</sup> )	$D$ / (km·s <sup>-1</sup> )	$P$ / (GPa)
RDX (1)	-21.61	210.88 (191.63)	1642.72	125.44	1.78 (1.81)	8.94 (8.75)	35.23 (34.30)
2	-31.05	283.96	1626.82	119.55	1.74	8.71	32.95
3	-63.59	335.83	1440.16	110.93	1.60	8.08	26.90
4	-49.96	266.59	1534.94	117.46	1.65	8.25	28.58
5	-88.81	338.50	1211.83	110.76	1.48	7.71	23.26
6	-42.08	344.13	1592.01	111.32	1.73	8.54	31.56
TNT	-73.98	52.47	1417.5	137.32	1.64	7.11	19.00

<sup>a</sup> The heat of formation values acquired by T1 Thermochemical Recipe.

<sup>b</sup> Average molar volumes from hundred single point calculations at the B3LYP/6–31G(d,p) level. Data in parenthesis are the experimental values obtained from Refs. [2,16,36].

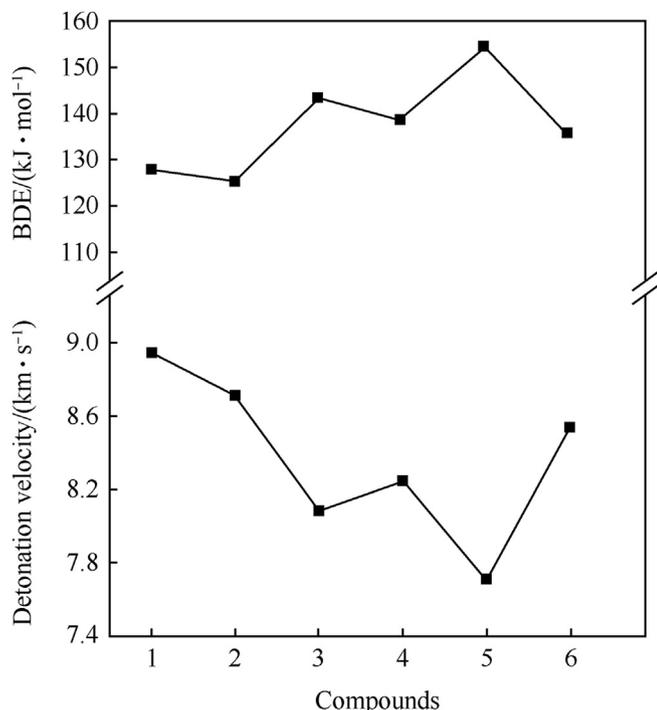


Fig. 4. The Detonation velocity and bond dissociation energy of the weakest bonds for RDX and other derivatives.

Table 4

The number of moles of gaseous decomposition products of RDX and its derivatives using the Kistiakowsky–Wilson Rules.

	Formula	N <sub>2(g)</sub>	H <sub>2</sub> O <sub>(g)</sub>	CO <sub>(g)</sub>	H <sub>2(g)</sub>	C <sub>(s)</sub>	n <sub>gas total</sub>
<b>RDX</b>	C <sub>3</sub> H <sub>6</sub> N <sub>6</sub> O <sub>6</sub>	3	3	3	–	–	9
<b>2</b>	C <sub>3</sub> H <sub>6</sub> N <sub>6</sub> O <sub>5</sub>	3	3	2	–	1	8
<b>3</b>	C <sub>3</sub> H <sub>8</sub> N <sub>6</sub> O <sub>3</sub>	3	3	–	1	3	7
<b>4</b>	C <sub>3</sub> H <sub>8</sub> N <sub>6</sub> O <sub>4</sub>	3	4	–	–	3	7
<b>5</b>	C <sub>3</sub> H <sub>10</sub> N <sub>6</sub> O <sub>2</sub>	3	2	–	3	3	8
<b>6</b>	C <sub>3</sub> H <sub>6</sub> N <sub>6</sub> O <sub>4</sub>	3	3	1	–	2	7
<b>Picric Acid</b>	C <sub>6</sub> H <sub>3</sub> N <sub>3</sub> O <sub>7</sub>	3/2	3/2	11/2	–	1/2	8.5

molecule having two nitroso and one nitro group) is the optimum. It is not only more insensitive than RDX, but also as good as RDX in performance.

### 3.5. Detonation products and explosive power

The small molecules, i.e., CO<sub>2</sub>, CO, H<sub>2</sub>O, etc. are the main detonation products of C<sub>a</sub>H<sub>b</sub>O<sub>c</sub>N<sub>d</sub> type explosives. In order to elucidate the number and type of the decomposition products, a series of rules was proposed by Kistiakowsky and Wilson [37,38]. Table 4 displays the moles of detonation products of the compounds investigated in this article.

The total quantity of gas produced upon detonation has been found by adding the moles of H<sub>2</sub>O, N<sub>2</sub>, CO and H<sub>2</sub>, except for the moles of solid C. When total amount of gas is measured, the structures 2–6 produce 7–8 mol of gas upon detonation.

The main products of an explosive reaction are heat and hot gases. The volume of produced gas gives information on how much work done by the energetic materials. Standard conditions should be adopted to calculate the volume of generated gas, because the volume of gas changes with the changing temperature. The standard conditions (273 K, 1 atm) also enable the scientist to make comparisons among different explosives. Division of the value of

Table 5

The power index data of RDX, its derivatives, Picric Acid, TNT and HMX.

Compound	Q/(kcal·g <sup>-1</sup> )	V/(dm <sup>3</sup> ·g <sup>-1</sup> )	Q·V	Power index/%
<b>RDX</b>	1642.72	0.908	1490.98	127
<b>2</b>	1626.82	0.869	1414.36	120
<b>3</b>	1440.16	0.890	1282.06	109
<b>4</b>	1534.94	0.816	1252.65	106
<b>5</b>	1211.83	1.105	1339.23	114
<b>6</b>	1592.01	0.825	1313.01	111
<b>PA</b>	1417.61	0.831	1178.12	100
<b>HMX</b>	1639.83	0.908	1488.35	126
<b>TNT</b>	1424.11	0.740	1053.35	89

total volume of gas produced upon detonation by the molecular weight gives an idea of how much gas is released per gram of explosive [39–42].

The heat of explosion “Q” and the volume of produced gas “V” can be combined to obtain the explosive power data as indicated below [36]

$$\text{Explosive Power} = Q \cdot V \quad (5)$$

The value for the explosive power is then compared with the explosive power of a standard explosive, namely Picric Acid (PA), to obtain power index, as shown in the following equation

$$\% \text{ Power Index} = \frac{Q \cdot V}{Q_{\text{PA}} \cdot V_{\text{PA}}} \times 100 \quad (6)$$

Table 5 displays the power index values of RDX, the other RDX derivatives, Picric Acid, TNT, and HMX. The power index values of RDX and RDX derivatives presently considered are in between 106 and 127% and in the subsequent manner: HMX ~ RDX > 2 > 5 > 6 > 3 > 4 > PA > TNT. The structure-2 has the highest power index value after RDX. All the structures (2–6) are better in terms of the power index than the well-known explosives PA and TNT. All the molecules in the present study can easily be employed when higher amount of gas is required as an alternate to RDX.

## 4. Conclusion

Currently, computational studies have been completed on RDX itself and five different RDX derivatives. The bond length data of the structurally optimized (at the theoretical level of DFT B3LYP/6-31G(d,p)) RDX were compared to experimental values quite satisfactorily. The lowest bond dissociation energies of the nitramine bond were associated with impact sensitivity concept. The possibility of decreasing the sensitivity of an explosive without significant loss in power by the conversion of nitro groups of RDX to nitroso and amino groups has been proven. All the compounds were evaluated as a better explosive than TNT. The conversion of nitro groups to amino groups creates more insensitive explosive when compared to nitroso conversions. All the compounds examined in this article showed better explosive properties than TNT. They are all possible nominees for insensitive high explosives. Thereby, they are all alternative to renowned explosive RDX whenever lower sensitivity applications are required. This study has shown that molecular modification is an operative method in desensitization of RDX.

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