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Theoretical Studies on the Thermodynamic Properties and Detonation Properties of Cyclotrimethylene Trinitramine (RDX) with Aluminum and Boron Metals

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Abstract: The B3LYP/6-311++G(2df,2p) density functional theory (DFT) method was used to investigate the molecular geometry and thermodynamic properties of RDX and RDX derivatives containing Al and B metals. The detonation velocity (D) and detonation pressure (P), estimated by using Kamlet–Jacobs and literature equations, respectively. Total energies (E_t), frontier orbital energy (E_{HOMO}, E_{LUMO}), energy gap ($\Delta E_{LUMO-HOMO}$) and theoretical molecular density (ρ) were calculated with Spartan 14 software package program. It was shown that the presence of aluminum and boron atoms affects the good thermal stabilities. The results suggest that the composite RDX-Al, RDX-B derivatives have further detonation performance and higher density than RDX. RDX-Al derivatives appeared to be superior to RDX-B mixtures in terms of these parameters. These results provide information on the molecular design of new energetic materials.

Keywords: DFT calculations; detonation performance; aluminum and boron; RDX.

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INTRODUCTION

The studies on high-energy density compounds have been increasing recently due to their superior explosive performances [1–4]. Organic chemists and material scientists have been continuing research efforts to meet industrial and military requirements in order to develop new energetic materials with good thermal stability, higher performance, insensitivity, and economically and environmentally friendliness [5–8]. Detonation performance, good thermal stability, low impact, high pressure and density are all known to be important major parameters in explosives. Therefore, the objective of this study is to find the molecules with better detonation performance and thermal stability.

(RDX) ($C_3N_6O_6H_6$) is a significant energetic material which is used as propellants and explosives. In the literature, there are numerous studies on RDX explosives focusing on their detonation performance and thermal stability [9–12]. Since there are limited studies on the explosives with composite RDX-Al and RDX-B derivatives including their thermodynamic properties, this study is expected to contribute to fill this gap in the literature. Figure 1 presents the calculated substances and their chemical structures.

The metal additives used in explosives for civil and military purposes since the beginning of the 21st century, have been employed to strengthen the detonation characteristic of high explosives [13-14]. It has been discovered that compositions of high explosives with aluminum, boron or beryllium cause enrichment explosion heat and strength in demolition effect [15].

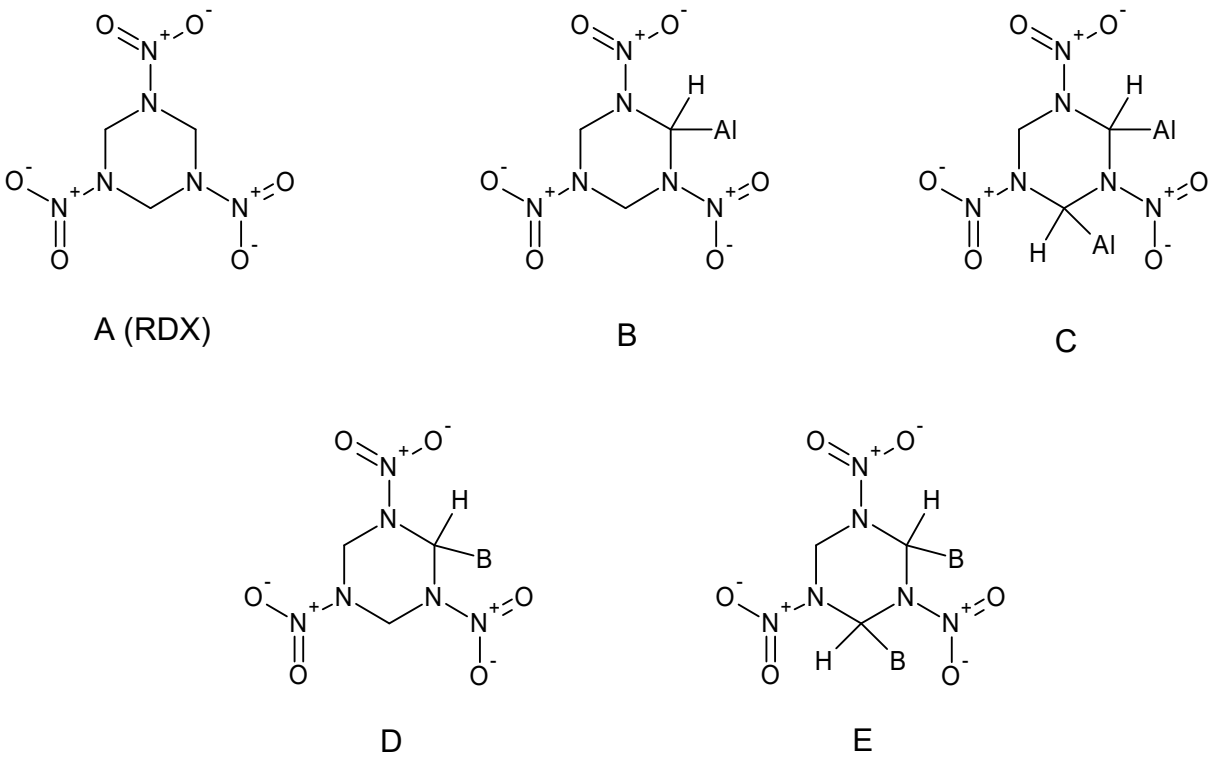

Figure 1. Chemical structures of calculated RDX derivatives.

The aluminized explosives are an energetic material widely used in the defense industry since the 20th century in various formulations (*e.g*. Ammonal, Tritonal, aluminized plastic bonded explosives, *etc*). There is presently an increased interest to discover more detonation characteristics of aluminized explosives [16]. Reaction temperature and reaction time increase when Al is added into the explosives [17]. When the metal participates in the reaction zone, aluminized explosives exhibit eigenvalue detonation behavior since the aluminum unreacted or partially reacted at the initial point in the reaction zone [18-19]. The properties of explosives containing boron have not been widely investigated though these materials have significant impact [20-21]. Boron flames at 2067 ºC, and its boiling temperature is 3865 ºC. It appears that it is stronger than steel, harder than corundum, and lighter than aluminum. Unlike aluminum, boron's oxidizing products are gases, not solids. In addition, the boron powders of sub-micrometer size particle are easily available, and the boron particles are not coated by the oxide film. A positive effect of boron on the explosion heat exceeds even that of aluminum [22].

To the best of our knowledge, there have been no precedents on a theoretical study about thermodynamic features and detonation velocities of additive metals (Al and B) RDX type plastic explosive mixtures so far. In this study, novel additive metals including RDX derivatives were examined comparatively.

MATERIALS AND METHODS

Computational methods

In the present study, quantum chemical calculations were carried out by using Spartan 14 software program at 298.15 K and under vacuum [23]. The B3LYP/6-311++G(2df,2p) (DFT) method was employed for detonation performance and thermodynamic properties. AM1 geometry was used in the calculations for the initial state and the geometry optimization was carried out $5x10^5$ cycles.

Detonation performance

Density: The density of RDX compounds needs the data of the molecular volume. The molecular volume was defined as inside a contour of 0.001 electrons/bohr^3 density that was evaluated by Monte-Carlo integration. In this study, all compounds' density (A, B, C, D, E) were calculated by using molecular weight, molecular volume and molecular interactive length in SPARTAN 14 software package program and the results were shown in Table 2. Calculated data in the Table 2 supplies some ideas about the characteristics features of the compounds. RDX derivative compounds with different additive metal groups have different density values. Incorporation of metal groups in explosives increase and affect detonation performance of compounds.

It seems that the density of explosive increases when Al and B metals are composited with RDX. It appears that there is more increase in density when Al is added rather than B. Table 2 shows the density comparison as follows; $\rho A<\rho B<\rho C$ and $\rho A<\rho D<\rho E$. In the literature, the explosive performances are better with the increasing density [24].

Detonation velocity: The detonation properties (*i.e.* detonation energy, velocity, pressure, and density) before synthesis, needs to be taken into consideration as it decreases the cost for synthesis and characterization of the energetic compounds. Detonation performance includes two important parameters; detonation pressure (P, GPa), and detonation velocity (D, km.s^{-1}) to calculate performance of explosive compounds. In this study, Kamlet–Jacobs empirical equations (1,2) were used to determine $C_aH_bO_cN_d$ (RDX)(A) compounds [25-26].

$$P = 1.558\ N.M^{1/2}.Q^{1/2}\ .\ \rho^2 \qquad \text{(Eq. 1)}$$

$$D = 1.01(N.M^{1/2}.Q^{1/2})^{1/2}.(1 + 1.30\ \rho) \qquad \text{(Eq. 2)}$$

As for the $C_aH_bO_cN_d$ type explosives, the parameters N, M, and Q were computed and each was shown in Table 1.

Table 1. Calculations of the N, M and Q are determined with the following formula [27].

	Stoichiometric Relations		
Parameter	**c ≥ 2a + b/2**	**2a + b/2 > c ≥ b/2**	**b/2 > c**
N	(b + 2c + 2d)/4M_i	(b + 2c + 2d)/4M_i	(b + d)/2M_i
M_{ave}	4M_i/(b + 2c + 2d)	(56d + 88c – 8b)/ (b + 2c + 2d)	(2b + 28d + 32c)/ (b + d)
Qx10^{-3}	(28.9b + 94.05a + 0.239ΔH°f)/M_i	[28.9b + 94.05(c/2 – b/4)+ 0.239ΔH°f]/M_i	(57.8c + 0.239ΔH°f)/M_i
M_i molecular weight of the compound (g/mol)			

Detonation velocity of RDX molecule was calculated with Kamlet-Jacobs equations, and Equation 3 was used in the calculation for the detonation velocity (D, km.s^{-1}) of B, C, D, and E compounds [28]. These results point out that the following simple equation can provide the suitable pathway for predicting D [28]:

$$D\ (km.s^{-1}) = y_1 + y_2 a + y_3 b + y_4 c + y_5 d + \sum_{i=6} y_{iSSPi} \qquad \text{(Eq. 3)}$$

Velocity values obtained for RDX were placed into Equation 3 because of existing special and structural variants (SSPi). Due to the fact that the co-efficients a, b, c, d have a linear relation with detonation velocity, the equation becomes linear, too. Based on these results for different a, b, c, d obtained by Spartan 14 software package program, y_i coefficients were found out by regression method by means of Mathematica 8 [29]. After that, addition of an inorganic element into the explosive molecule was performed by using y_6 coefficient. It is e=1 for one Al or one B, and it is e=2 for two Al or two B. After y_i and e parameters were found, theoretical explosive velocities were calculated for B, C, D, E compounds. Table 2 presents calculated theoretical ρ(g.cm^{-3}), D(km.sn^{-1}), and P (GPa) of the RDX derivations. As can be seen in Table 2, all RDX derivatives have good detonation properties (Q=1369.74-1473.91 J.g^{-1}, D=8.76-8.98 km.s^{-1}, P=34.32-40.28 GPa). Meanwhile, as the number of metallized groups increase, ρ, D, and P of the corresponding compounds increase. Molecule C was calculated as having the highest D, ρ and P values among RDX derivative compounds.

Table 2. Predicted densities and detonation properties of RDX, RDX derivatives containing Al and B metals.

Molecule	Formula	φ	N	M	Q	ρ[e]	D[f]	P[g]
A	$C_3H_6N_6O_6$	6.65	0.034	27.2	1426.6	1.82	8.768	343.3
B	$C_3H_5AlN_6O_6$	5.91	0.029	284	1438.5	2.03	8.943	379.3
C	$C_3H_4Al_2N_6O_6$	5.15	0.026	29.7	1369.7	2.24	8.986	402.8
D	$C_3H_5BN_6O_6$	6.36	0.031	28.4	1456.4	1.90	8.839	357.7
E	$C_3H_4B_2N_6O_6$	6.06	0.029	29.7	1473.9	1.98	8.888	370.2

[e] g/cm^3, [f] km/s, [g]kbar

When Figure 2 and 3 are examined, it can be seen that D (km.s^{-1}) and ρ (g.cm^{-3}) linearly increase with the addition of explosive metallized groups. However, compounds having Al increase the D and ρ relatively much more than compounds having B. Aluminized explosives, in particular, had been thoroughly investigated as they were extensively employed. Hence, the results are consistent with the literature [30].

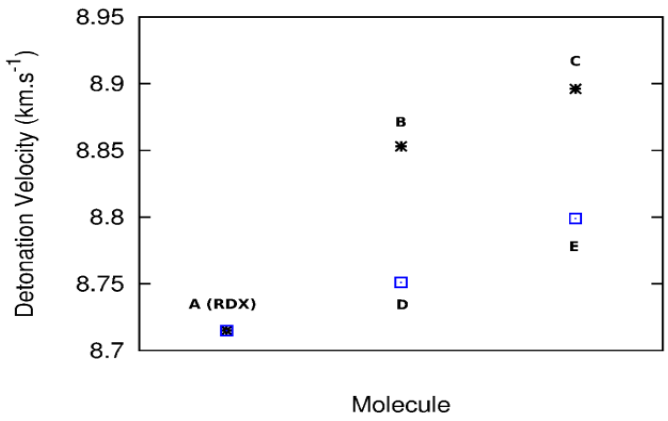

Figure 2. Prediction of detonation velocity (km.s^{-1}) of RDX derivatives.

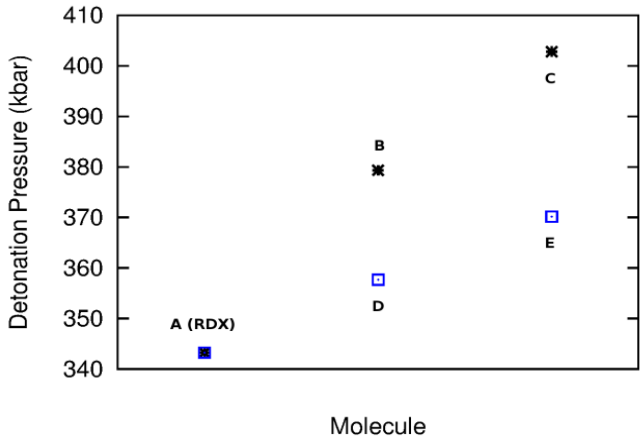

Figure 3. Prediction of detonation pressure (kbar) of RDX derivatives.

Thermal stability: Studying HOMO and LUMO demonstrates whether or not the reaction is feasible and the relative thermal stability of an individual molecule in the gas phase [1]. The higher value of energy gap (ΔE) resulting from higher energy of LUMO and lower energy of HOMO indicates that neither losing nor capturing an electron would happen on the title compound easily, so it is more stable.

Table 3 shows the zero-point energy (ZPE), HOMO and LUMO energies, energy gap $\Delta E_{LUMO-HOMO}$, total energies geometry of the optimized compounds which were calculated at the theoretical level of B3LYP/6-311++G(2df,2p). When Table 3 is considered, it is obvious that the ZPE and total energies of compounds get lower from A to E. It is known that as the molecular weight of compounds get higher, the total electronic energy values get lower. The average values of frontier orbital energy gap $\Delta E_{LUMO-HOMO}$ of A, B, C, D and E at B3LYP/6-311++G(2df,2p) levels are 5.75, 3.84, 2.15, 4.02 and 3.43 a.u., respectively. As can be seen in Figure 4, it is notable that compound C has the smallest energy gap, which indicates that this compound is the least stable among the five compounds studied, while compound A has the largest energy gap and is, therefore, the most stable of them. Thermal stability order of them are as follows:

(least stable) C<E<B<D<A (most stable)

Table 3. ZPE, E_{HOMO}, E_{LUMO} and energy gaps ($\Delta E_{LUMO-HOMO}$) for RDX derivatives.

Molecules	Weight[a]	Total Energy[b]	HOMO[b]	LUMO[b]	Energy Gap[b]	ZPE[c]
A	222.117	24426.79	-8.06	-2.31	5.75	359.54
B	248.091	31007.16	-6.59	-2.75	3.84	332.30
C	274.065	37586.68	-5.87	-3.72	2.15	302,91
D	231.92	25083.65	-7.41	-3.39	4.02	336.62
E	241.723	25739.75	-7.36	-3.93	3,43	308.62

[a] amu. [b] eV. [c] kJ/mole.
The total electronic energies were corrected for zero point energies (ZPE) taking into consideration Total energies listed in the table were included ZPE.

Inspection of Figure 5 and Table 3 reveals that the presence of Al and B metals appreciably raises the HOMO level and decreases the LUMO level compared to RDX.

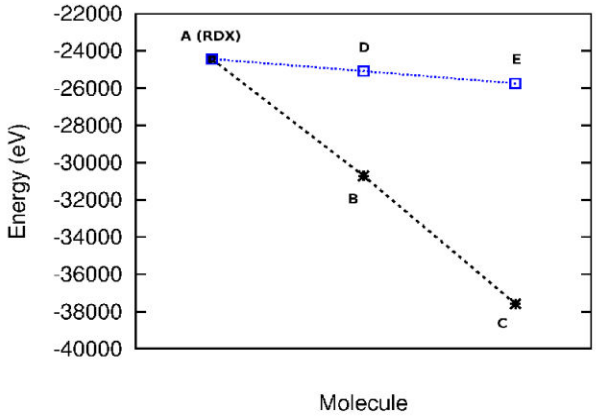

Figure 4. Calculated energy gap of all compounds.

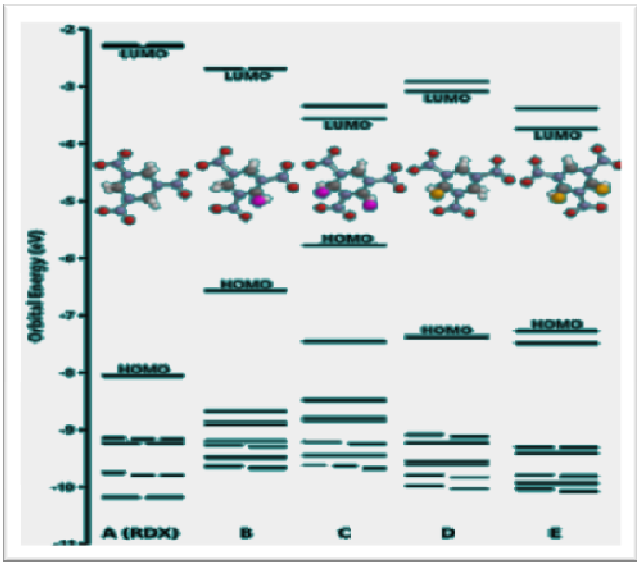

Figure 5. Molecular orbital energy spectra of the species [B3LYP/6-311++G(2df,2p), energies in eV].

RESULTS AND DISCUSSION

In this study, we have studied the detonation performance and thermal stability of RDX and RDX derivatives containing Al and B metals by the DFT- B3LYP method. As a result of our theoretical study, the following conclusions are drawn:

(1) The calculated detonation performance (D, P, ρ) are very helpful for enhancing detonation performance. Considering the detonation performance and thermal stability, additive metal groups (Al, B) can be regarded as potential candidates in high energetic materials. These results supply theoretical calculation for basic information about the molecular design of new high energetic materials and experimental synthesis.

(2) As for the RDX compounds contain metals, as number of metals increases, D, P and ρ linearly increase, however energy gap and ZPE linearly decrease.

(3) Calculated results showed that aluminum and boron metals groups can be added to explosives, as an enhancement to their performances. In addition, results indicate that aluminum is more effective than boron.

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Türkçe Öz ve Anahtar Kelimeler

Alüminyum ve Bor Metalleri içeren Siklotrimetilen Trinitramin (RDX) Bileşiklerinin Termodinamik ve Patlama Özellikleri Üzerine Teorik Çalışmalar

Nilgün ŞEN, Bayram YÜKSEL

Öz: B3LYP/6-311++G(2df,2p) yoğunluk fonksiyonel teorisi (DFT) yöntemi kullanılarak RDX ile Al ve B metali içeren RDX türevlerinin moleküler geometrisi ve termodinamik özellikleri incelendi. Patlama hızı (D) ve patlama basıncı (P) Kamlet-Jacobs ve literatürdeki eşitliklere göre hesaplandı. Toplam enerjiler (E_t), sınır orbital enerjisi (E_{HOMO}, E_{LUMO}), enerji aralığı ($\Delta E_{LUMO-HOMO}$) ve teorik moleküler yoğunluk (ρ) Spartan 14 program paketi ile hesaplandı. Alüminyum ve bor atomlarının varlığında iyi ısıl kararlılık elde edildiği gösterildi. Sonuçlara göre RDX-Al, RDX-B türevlerinin daha ileri patlama performansına sahip olduğu ve yoğunluklarının RDX'e göre daha yüksek olduğu bulundu. RDX-Al türevlerinin bu parametreler ışığında RDX-B türevlerine göre daha üstün olduğu gözlendi. Bu sonuçlar yeni enerjetik malzemelerin moleküler tasarımında bilgi verecektir.

Anahtar kelimeler: DFT hesaplamaları; patlama performansı; alüminyum ve bor; RDX.

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