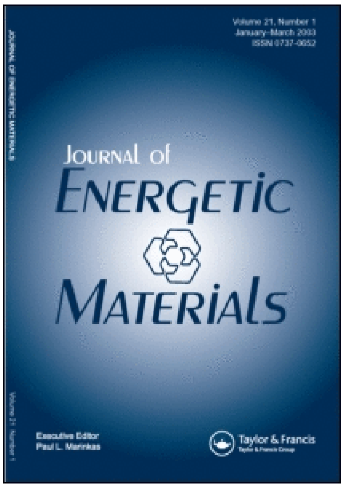

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Ab initio study on intermolecular interactions of energetic clusters

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AB INITIO STUDY ON INTERMOLECULAR INTERACTIONS OF ENERGETIC CLUSTERS

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ABSTRACT

Ab initio SCF and Møller-Plesset correlation correction methods (MP2) in combination with counterpoise procedure for BSSE correction have been applied to R_2N-NO_2 (R=H, Me), hydrazine and difluoroamine clusters. Of all the stable structures found for each polymer with the same degree of polymerization, only the most stable one is reported. The corrected binding energies of the most stable clusters are predicted to be -32.93, -20.11, -24.68, -18.39 and -9.19 kJ/mol for dimers of nitramine, methylnitramine, dimethylnitramine (DMNA), hydrazine and difluoroamine, and -47.27 and -19.22 kJ/mol for trimers of DMNA and difluoroamine respectively. The proportion of correlated interaction energy to their total interaction energy for all clusters is at least 18.1 percent, and the BSSE of ΔE(MP2) is at least 9.2 kJ/mol. Dispersion and/or electrostatic force are dominant in DMNA and difluoroamine clusters, whereas the H-bonds exist in nitramine, methylnitramine and hydrazine dimers. There exist cooperative effects in the trimers. As for R_2N-NO_2 dimers, the vibrational frequencies associated with N-O stretches or wags exhibit slight red shifts, but the modes associated with the motion of hydrogen atoms of the methyl group show somewhat blue shifts with respect to those of monomer. The N-H stretch mode exhibits large red shifts when it connects with other submolecules by H-bond as in the dimers of nitramine and hydrazine, otherwise it exhibits slight blue shifts.

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INTRODUCTION

Theoretical treatment of intermolecular interactions is emphasized by the fact that despite an enormous progress in various experimental techniques the unambiguous description of such process is still impractical. The binding energies of intermolecular interactions are much less than those of chemical bonding, and yet they play significant roles in a wide range of physical, chemical and biological fields. In the recent years, we have applied the intermolecular interactions to energetic systems and obtained some meaningful information [1-7] that will be helpful to the study and molecular design of energetic compounds. The behavior of molecular clusters is usually between two extremes: the gas phase and the crystal solid phase. Consequently, one can obtain valuable knowledge about the transition of these extremes by examining the properties of clusters of large size. Clusters containing more than two molecules behave cooperative effects [8-10], which is reflected in changes of some properties with increase in cluster size such as the interaction intensity increase and the frequency shift. Properly characterizing these phenomena is thus crucial to understanding the behavior of cluster. $R_2N\text{-}NO_2$ (R=H, Me) is a simple model of nitramine energetic compounds such as HMX and RDX that are especially used as explosives. Difluoroamine and hydrazine are other types of explosives. Researches already done on the above compounds have been emphasized mostly on their monomers [11-23]. To our knowledge, there are only two reports related to the molecular interactions of dimethylnitramine dimers using DFT method or molecule simulation method [24,25]. The intermolecular forces control such diverse phenomena as the diffusion, the aggregation and the detonation. To provide the fundamental information for further investigation on the mixture explosives, it is particularly necessary to study the intermolecular interaction. The aim of this paper is to investigate theoretically the structures, the frequency shifts, the binding energies, and the cooperative effects in the clustering processes by *ab initio* method. We also perform natural bond orbital (NBO) and Mulliken population analyses to probe the origin of the interaction.

COMPUTATIONAL METHODS

The monomer and all its possible stable dimers and trimers of the entitled molecules obtained from Chem3D software are fully optimized by the Berny method [26,27]. Natural bond orbital analyses and frequency calculations were performed on each optimized structure.

The interaction energy of complex is evaluated as the sum of the HF interaction energy and the correlation interaction energy. The latter term could be determined by the Møller-Plesset perturbation theory [28-29]. The basis sets commonly used to calculate the energies in the above equation are far from being saturated and, hence, in any complex each subsystem will tend to lower its energy by using the basis functions of the other subsystem. The energies derived from the equilibrium geometry of the complex for each subsystem are lower than those calculated at the same geometry with the basis functions of the respective subsystem alone. This energy difference is the so-called BSSE that can be checked by Boys and Bernardi's counterpoise procedure (CP) [30-32]. For complex of two submolecules the BSSE is

$$\mathrm{BSSE}=\{E(\mathrm{A})-E(\mathrm{A[B]})\}+\{E(\mathrm{B})-E(\mathrm{B[A]})\}$$

where the $E(\mathrm{A[B]})$ and $E(\mathrm{B[A]})$ are the energies of A and B respectively when the other subsystem's basis sets are added.

The effects of cooperativity in the interaction could be estimated from various parameters such as structural changes undergone by clustering and the shifts in some vibrational frequencies. The more direct evaluation of the contributions of cooperativity in this paper is obtained by comparing the interaction energy of the cluster with the pairwise interaction energies calculated with the whole basis sets for the cluster in order to exclude BSSE [9,10]. Thus, for trimer the cooperativity contribution is,

$$E_{\text{nopair}} = \Delta E_{\text{ABC}}(\text{ABC}) - \Delta E_{\text{AB}}(\text{ABC}) - \Delta E_{\text{AC}}(\text{ABC}) - \Delta E_{\text{BC}}(\text{ABC})$$

where the terms in brackets mean that the whole basis sets for the cluster is used in calculations.

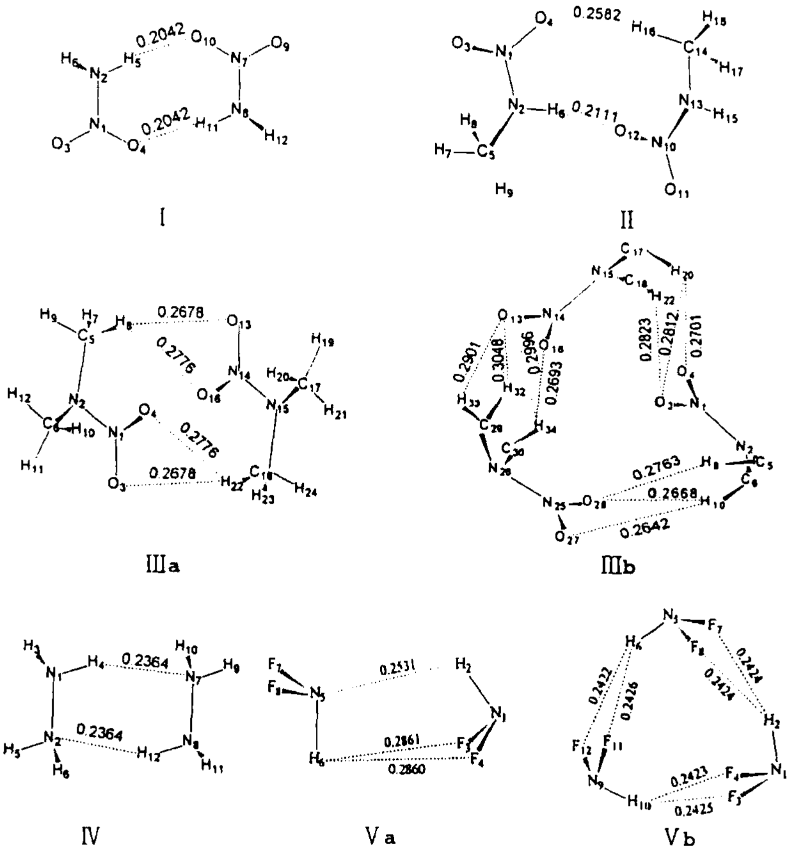
For this type of study, one should choose an appropriate basis set. Usually a substantial size of basis set is required for an accurate description of the structures and energies of clusters. However, the size of the clusters studied in this work excluded the use of very large sets, and hence we employed the 6-31G* basis set for nitramines, and 6-311G* for hydrazine and difluoroamine. All calculations are performed with Gaussian98 program [33] at the Compaq Workstation in our laboratory.

RESULTS AND DISCUSSION

Optimized geometries

Of all the stable clusters, only the most stable structures of $R_2N\text{-}NO_2$, $H_2N\text{-}NH_2$ and NHF_2 clusters are shown in Figure 1. Table 1 lists some optimized geometrical parameters of the clusters. Both the monomers of $Me_2N\text{-}NO_2$ and $H_2N\text{-}NO_2$ have C_s symmetry with $N\text{-}NO_2$ coplanar. These results are in quite good agreement with all

FIGURE.1 Optimized structures, intermolecular distances (nm) and atomic numbering of the clusters (only the intermolecular contact hydrogens are shown for DMNA trimers)



I

II

IIIa

IIIb

IV

Va

Vb

previous theory work or with low temperature crystalline form but differ from the experimental gas-phase geometry of C_{2v} symmetry [34,35]. This discrepancy is due to the fact that the planar or pyramidal nature of amino group is sufficiently weak and capable of altering the geometry [21]. The hydrazine monomer has C_2 symmetry, which is also in agreement with the experimental result [36]. The most stable structure of DMNA dimer is very similar to that from the DFT result that emphasized the existence of two O···N contacts by 0.308 nm [25] instead of two additional O···H contacts as in Figure

1-IIIa. Both of the O···N contacts in IIIa are 0.3097 nm. Compared to the geometries of monomer, all the N-N lengths of nitramines (I , II , IIIa and IIIb) decrease by 1.0-2.4 pm, whereas those of N-O in the intermolecular interaction rings increase by 0.1-1.3 pm. The

TABLE 1 Optimized geometries of the clusters [a]

Clusters	Parameters and Values				
I	R_{1-2} 134.0(-1.6)	R_{7-8} 134.0(-1.6)	R_{2-5} 100.2(0.4)	θ_{2-1-4} 116.9(0.4)	$\varphi_{4-1-2-5}$ 24.8(-0.8)
	R_{1-4} 120.4(1.3)	R_{7-10} 120.3(1.2)	R_{8-11} 100.2(0.4)	θ_{2-1-5} 112.3(1.8)	$\varphi_{4-1-2-6}$ 160.3(3.8)
II	R_{1-2} 133.6(-1.1)	R_{10-11} 119.2(-0.1)	R_{10-13} 133.6(-1.1)	θ_{2-1-4} 116.6(0.4)	$\varphi_{2-1-4-3}$ 178.3(0.2)
	R_{1-3} 119.3(0.0)	R_{10-12} 120.1(0.6)	R_{13-14} 145.5(0.4)	$\theta_{10-13-14}$ 119.5(1.3)	$\varphi_{4-1-2-5}$ 161.8(1.4)
	R_{1-4} 120.2(0.7)				
IIIa	R_{1-2} 133.3(-1.1)	R_{2-5} 145.9(0.4)	R_{18-22} 108.2(-0.3)	R_{14-15} 133.3(-1.1)	θ_{2-5-8} 111.7(0.7)
	R_{1-3} 119.8(0.1)	R_{2-6} 145.7(0.2)	R_{13-14} 119.8(0.1)	R_{15-17} 145.7(0.2)	$\varphi_{3-1-2-4}$ 178.3(-0.4)
	R_{1-4} 120.3(0.6)	R_{5-8} 108.2(-0.3)	R_{14-16} 120.3(0.6)	θ_{2-1-4} 117.8(0.4)	$\varphi_{13-14-16-15}$ 178.2(-0.5)
IIIb	R_{1-2} 132.8(-1.6)	R_{6-10} 108.1(-0.4)	R_{18-22} 108.2(-0.3)	θ_{1-2-6} 116.5(0.7)	$\theta_{25-26-30}$ 116.8(1.0)
	R_{1-3} 120.4(0.7)	R_{13-14} 120.2(0.5)	R_{25-26} 132.0(-2.4)	θ_{2-6-10} 111.5(1.5)	$\theta_{26-30-34}$ 111.5(1.5)
	R_{1-4} 120.0(0.3)	R_{14-16} 119.9(0.2)	R_{25-28} 120.8(1.1)	$\theta_{13-14-15}$ 117.7(0.3)	$\varphi_{3-1-2-4}$ 177.9(-0.8)
	R_{2-5} 145.7(0.2)	R_{14-15} 133.4(-1.0)	R_{26-30} 145.9(0.4)	$\theta_{14-15-18}$ 115.9(0.1)	$\varphi_{13-14-16-15}$ 177.7(-1.0)
	R_{2-6} 146.0(0.5)	R_{15-17} 145.8(0.3)	R_{30-34} 108.0(-0.5)	$\theta_{15-17-20}$ 111.5(1.5)	$\varphi_{27-25-26-28}$ 178.9(0.2)
	R_{5-8} 108.2(-0.3)	R_{17-20} 108.2(-0.3)	θ_{3-1-2} 117.9(0.5)	$\theta_{27-25-26}$ 118.2(0.8)	
IV	R_{1-2} 141.5(0.4)	R_{1-4} 99.8(0.2)	R_{2-6} 100.0(0.1)	θ_{2-1-4} 107.5(-0.5)	$\varphi_{4-1-2-5}$ 156.8(3.1)
Va	R_{1-2} 100.1(0.0)	R_{5-6} 101.1(0.0)	R_{5-7} 134.1(-0.2)	θ_{2-1-3} 101.9(-0.3)	θ_{6-5-7} 102.8(0.6)
	R_{1-3} 134.6(0.3)				
Vb [b]	R_{1-2} 100.0(-0.1)	R_{1-3} 134.8(0.5)	θ_{2-1-3} 101.9 (-0.3)		

[a] bond length in pm, bond angle and dihedral angle in degree, values in parentheses are the differences from the corresponding monomer, [b] bond lengths of the other two submolecules are nearly as the same as the first submolecule (±0.1pm)

changes of bond lengths for I and IIIb are larger than those of II and IIIa, owing to the shorter intermolecular contact distance in I and cooperative effects in IIIb. The X-NO_2 (X=N,C,O) bond in nitro explosives is often referred to as a detonation trigger [12,15,17].

The interaction causes the shortening of N-NO_2 bond for all clusters, especially for structure IIIb. It can be speculated that the interaction may lower the sensitivity in a certain degree. Bond lengths in the intermolecular H-bond ring in IV increase by 0.2~0.4 pm. The N-F lengths in Vb increase by 0.5 pm, whereas all the other bond lengths are nearly unchanged. In general, shorter intermolecular contact distance or cooperative effect in the system containing three molecules causes larger change of bond length. The bond angles and the dihedral angles of all clusters change slightly from their corresponding monomer, which implies that the influence of interaction on bond bending or internal rotation around single bond is very small.

Vibrational frequencies and their shifts

The characterized vibrational frequencies (IR), their intensities (KM/mol) and the shifts from those of monomers are shown in Table 2. For I and III, the frequencies associated with the N-O stretches exhibit slight red shifts with respect to those of its

TABLE 2 Vibrational frequencies, shifts and intensities

clusters	Frequency (shifts, intensity)
I	$\nu_{\mathrm{N-O,str}}$ /1884(-18, 1291) $\nu_{\mathrm{N-N,str.}}$ /1645(+11, 527) $\nu_{\mathrm{N-H}}$ /3748~3914(-44~-15, 0~456)
II	$\nu_{\mathrm{N-N,str.}}$ /1653(+5, 226) $\nu_{\mathrm{H-N-N,rock.}}$ /1878(-11, 564) $\nu_{\mathrm{N-H\&C-H}}$ /3736~3869(0~+3, 0~289)
IIIa	$\nu_{\mathrm{N-O,str.}}$ /1816(-16, 913) $\nu_{\mathrm{N-C-H,rock.}}$ /1674(+5, 312) $\nu_{\mathrm{C-H}}$ /3242~3366(-3~+17, 0~43)
IIIb	$\nu_{\mathrm{N-O,str.}}$ /1812(-20, 994) $\nu_{\mathrm{N-C-H,rock.}}$ /1676(+7, 200) $\nu_{\mathrm{C-H}}$ /3248~3370(+3~+17, 0~47)
IV	$\nu_{\mathrm{N-H,wag\&rock}}$ /1009(-84, 171) $\nu_{\mathrm{N-N,str.}}$ /1220(-4, 9) $\nu_{\mathrm{N-H}}$ /3722~3829(-7~-9, 0~49)
Va	$\nu_{\mathrm{N-F,str}}$ /1177(+13,250) $\nu_{\mathrm{N-H,str.}}$ /3770~3772(+6~+7, 10~14)
Vb	$\nu_{\mathrm{N-F,str.}}$ /1159(-5, 508) $\nu_{\mathrm{N-H,str.}}$ /3790~3792(-7~-9, 0~45)

• Positive/negative signs indicate blue/red shifts, respectively monomer, accompanied by the increasing of intensities. The shifts demonstrate that the N-O bonds are somewhat weakened. There are slight blue shifts in the 3242-3370 cm^{-1} ranges for III, these modes are associated with the motion of hydrogen atoms of the methyl group. For II, the H-N-N rocking exhibits red shift. The N-H stretch modes in the 3722-3914 cm^{-1} for I, IV and Vb exhibit some red shifts, and the N-H *wagging or rocking mode in* IV *shows large red shift* (-84cm^{-1}). The N-H stretch mode in Va exhibits slight blue shift owing to its long contacting distance and thus weak interaction. It is known that the normal hydrogen bonding causes a large red shift in the X-H (X=O, N, F or Cl) stretch frequency. Therefore, there is H-bonding effect in I and IV, but this effect is negligible in all the other clusters.

Interaction energies and cooperative effects

Table 3 gives both the uncorrected and corrected interaction energies and the contributions of cooperativity. There are no imaginary frequencies for all structures in Table 3, which convicts that all the structures in Figure 1 correspond minima on their potential energy surfaces. The binding energy of IIIa is between the values of -11 kcal/mol and -5 kcal/mol obtained at the SCF+$E^{(20)}_{disp}$ and the DFT levels respectively [24,25]. The proportion of correlated

TABLE 3 Interaction energies and cooperative energies (kJ/mol) [a]

Energies	I	II	IIIa	IIIb	IV	Va	Vb
ΔE(HF)	-40.85	-26.54	-29.42	-55.89	-23.10	-14.97	-40.59
ΔE(MP2)	-49.82	-32.70	-48.21	-91.14	-35.96	-21.61	-56.41
		(18.8)	(39.0)	(38.7)	(35.8)	(30.7)	(28.0)
$\Delta E(HF)_c$	-35.43	-21.72	-18.12	-35.51	-17.92	-9.90	-21.11
$\Delta E(MP2)_c$	-36.89	-22.45	-28.37	-53.89	-25.39	-12.37	-25.06
$\Delta E(MP2)_{c,ZPE}$	-32.93	-20.11	-24.68	-47.27	-18.39	-9.19	-19.22
$E_{nopair,MP2}$				-2.97			-2.17

[a] The values in parentheses represent [ΔE(MP2)-ΔE(HF)]/ΔE(MP2) × 100; 6-31G* is used for nitramines and 6-311G* for hydrazine and difluoroamine

interaction energies to their total interaction energies (viz. $[\Delta E(\mathrm{MP2}) - \Delta E(\mathrm{HF})]/\Delta E(\mathrm{MP2})$, see Table 3) for all clusters is at least 18.1 percent, so it is imperative to include the electron correlation energies into interaction energies. The discrepancies between $\Delta E(\mathrm{MP2})_c$ and $\Delta E(\mathrm{MP2})$ are at least 9.2 kJ/mol for all clusters, indicating that it is also necessary to correct the BSSE. The ZPE corrections for the interaction energies are generally less than those of BSSE. The BSSE and ZPE corrected interaction energies of I is the largest. Considering that there are only two intermolecular contacts in II and IV, and yet their binding energies are -20.11 kJ/mol and -18.39 kJ/mol respectively. The average binding energy for each intermolecular contact in II or IV is larger than those of III and V. This means that there exist H-bonds in I, II and IV. Based on the changes of binding energies upon addition of a new molecule to a cluster, the transition from the dimer to the trimer involves the contributions of cooperativity as in the cases of IIIb and Vb.

Natural bond orbital and Mulliken populations

The donor and the acceptor of NBO between intermolecules, and their interacting stable energies obtained from MP2 analysis of Fock matrix in NBO basis are collected in Table 4. The stable energies are proportional to the NBO interacting intensities. The oxygen or nitrogen atoms donate their lone pairs to the neighbor C-H or N-H antibonds, which strengthens the intermolecular O···H or N···H interactions. The interacting stable energies of F to N-H are all small due to both the relative longer F···H distances to the sum of their atomic radii and the large electronegetivity of fluorine atom. The NBO interacting in I is the greatest, followed by those of II, IIIb and IV, which is another indication of stronger interactions as in I, II and IV, or cooperativity effect as in IIIb.

TABLE 4 Intermolecular natural bond orbital interacting and the corresponding stable energy (kJ/mol) [a]

Cluster	Donor	Acceptor (BD*)	*E*	Cluster	Donor	Acceptor (BD*)	*E*
I	LP(1)O_{10}	N_2-H_5	5.31	IIIb	LP(1)O_4	C_{17}-H_{20}	1.17
	LP(2)O_{10}	N_2-H_5	4.80		LP(2)O_4	C_{17}-H_{20}	3.64
	LP(1)O_4	N_8-H_{11}	5.31		LP(1)O_{27}	C_6-H_{10}	1.09
	LP(2)O_4	N_8-H_{11}	4.80		LP(2)O_{27}	C_6-H_{10}	2.59
					LP(1)O_{28}	C_5-H_8	1.34
II	LP(1)O_{12}	N_2-H_6	4.75		LP(2)O_{28}	C_6-H_{10}	1.21
	LP(2)O_{12}	N_2-H_6	0.97				
	LP(1)O_4	N_{14}-H_{16}	0.63	IV	LP(1)N_2	N_8-H_{12}	2.41
	LP(2)O_4	N_{14}-H_{16}	0.61		LP(1)N_7	N_1-H_4	2.45
IIIa	LP(1)O_3	C_{18}-H_{22}	0.84	Va	LP(1)F_3	N_5-H_8	0.16
	LP(2)O_3	C_{18}-H_{22}	1.84		LP(1)F_4	N_5-H_7	0.16
	LP(2)O_4	C_{18}-H_{22}	0.79		LP(1)F_5	N_1-H_2	0.39
	LP(1)O_{13}	C_5-H_8	0.84				
	LP(2)O_{13}	C_5-H_8	1.84	Vb	LP(1)F_3	N_9-H_{10}	0.25
	LP(2)O_{16}	C_5-H_8	0.79		LP(1)F_4	N_9-H_{10}	0.27
					LP(1)F_7	N_1-H_2	0.26
IIIb	LP(1)O_{16}	C_{30}-H_{34}	1.13		LP(1)F_8	N_1-H_2	0.29
	LP(2)O_{16}	C_{30}-H_{34}	2.22		LP(1)F_{11}	N_5-H_6	0.27
	LP(1)O_3	C_{18}-H_{22}	1.51		LP(1)F_{12}	N_5-H_6	0.26
	LP(2)O_3	C_{17}-H_{20}	1.13				

[a] LP means lone pair, BD* represents antibond

Apart from the NBO analyses, the Mulliken population of intermolecular O···H can also provide physical insight into the nature of intermolecular interaction. The Mulliken populations of O···H contacts are as follow: 0.0247 for I, 0.0105~0.0153 for II, 0.0032~0.0062 for IIIa, 0.0017~0.0084 for IIIb, 0.0243 for IV, 0.0031~0.0081 for Va and 0.0090~0.0117 for Vb. With the exception of I, II and IV, all the values above are less or much less than that of a normal H-bonding, which reveals again that the dispersion and/or electrostatic force, other than the H-bonding, is dominant in III and V, and which also demonstrates that the interaction in trimer is more intensive than that of dimer for the same molecule.

CONCLUSIONS

From *ab initio* calculations in the paper, the following conclusions can be drawn:

(1) There exist H-bonds in I, II and IV, whereas the dispersion and/or electrostatic force, other than the H-bond, are dominant in III and V. There exist cooperative effects in the trimers.

(2) The stronger the interaction is, the more the bond length in the intermolecular contacting ring changes, and also more red shifts on the N-H or O-H vibrational mode take place.

(3) This report together with our previous work [1-7] will be fundamental to developing energetic composite with favorable detonation performances for the corresponding compounds.

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