



# A theoretical investigation on the structures, densities, detonation properties and pyrolysis mechanism of the nitro derivatives of toluenes

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## ABSTRACT

The nitro derivatives of toluenes are optimized to obtain their molecular geometries and electronic structures at the DFT-B3LYP/6-31G\* level. Detonation properties are evaluated using the modified Kamlet–Jacobs equations based on the calculated densities and heats of formation. It is found that there are good linear relationships between density, detonation velocity, detonation pressure and the number of nitro and methyl groups. Thermal stability and the pyrolysis mechanism of the title compounds are investigated by calculating the bond dissociation energies at the unrestricted B3LYP/6-31G\* level. The activation energies of H-transfer reaction are smaller than the BDEs of all bonds and this illustrates that the pyrolysis of the title compounds may be started from the isomerization reaction of H transfer. According to the quantitative standard of energetics and stability as an HEDC (high energy density compound), pentanitrotoluene essentially satisfies this requirement. In addition, we have discussed the effect of the nitro and methyl groups on the static electronic structural parameters and the kinetic parameter.

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## 1. Introduction

High energy density materials (HEDMs) have been receiving considerable attention because of their superior explosive performance over conventional energetic materials, such as having larger energy release with the smaller charging volume [1–4]. However, the previous molecular design of HEDM lacks quantitative criteria of identification, which is difficult to identify and to filtrate effectively HEDC. Therefore, in the past several years, our group has carried out a series of investigations on the molecular design for many typical categories of energetic compounds [5–17]. Considering the practical requirements and based on the results of these studies, a quantitative criteria associated both energy (including  $\rho$ ,  $D$ , and  $P$ ) and stability (BDE of the trigger bond) requirements, i.e.,  $\rho \approx 1.9 \text{ g/cm}^3$ ,  $D \approx 9.0 \text{ km/s}$ ,  $P \approx 40.0 \text{ Gpa}$ , and  $\text{BDE} \approx 80\text{--}120 \text{ kJ/mol}$  [18], are proposed and employed to filtrate and recommend potential HEDCs [14]. At the same time, we have also suggested a suit of simple while efficient methods to calculate  $\rho$ ,  $D$ ,  $P$ , and BDE.

Aromatic molecules having nitro groups are generally known as explosives. The nitro derivatives of methylbenzenes such as 2,4,6-trinitrotoluene (2,4,6-TNT), 1,3-dimethyl-2,4,6-trinitrobenzene (TNX), 1,3,5-trimethyl-2,4,6-trinitrobenzene (TNM) (see Fig. 1 for

the structural diagrams) are an important category of energetic compounds. TNT has been available as an explosive since around 1870, which is the most widely used explosive because of its compatibility with other explosives, low hygroscopicity, good thermal stability, relatively low sensitivity to impact and friction and its ability to be melt cast [19]. Exploring microscopic pyrolysis mechanism, which addresses the question of how an important impulse can initiate rapid exothermic reactions leading to the detonation of explosive solids, is always the research target of both theoretical and experimental chemists. Experimental studies on the pyrolysis mechanism of the nitro derivatives of toluene have touched upon many aspects, including the systematic theoretical studies on IR spectra and thermodynamic properties [20–33].

But to date, the systematic theoretical studies are few. Since studies on structure-performance relations are the foundations of molecular design, in this paper, the nitro derivatives of toluenes are studied in detail. The molecular geometries and electronic structure are obtained with the density functional theory method (DFT). Based on their optimized geometries, the molecular volume ( $V$ ) and theoretical density ( $\rho$ ) are calculated using Monte-Carlo method. The most important detonation properties, such as detonation velocity ( $D$ ) and detonation pressure ( $P$ ) are estimated by used modified K–J equation. Through calculations of bond dissociation energies (BDE) of the main bonds and H-transfer reaction, the pyrolysis mechanism, thermal stability and sensitivity are studied. The theoretical studies provide the abundance of information and rules, which not only quantitatively filtrate pentanitrotoluene as

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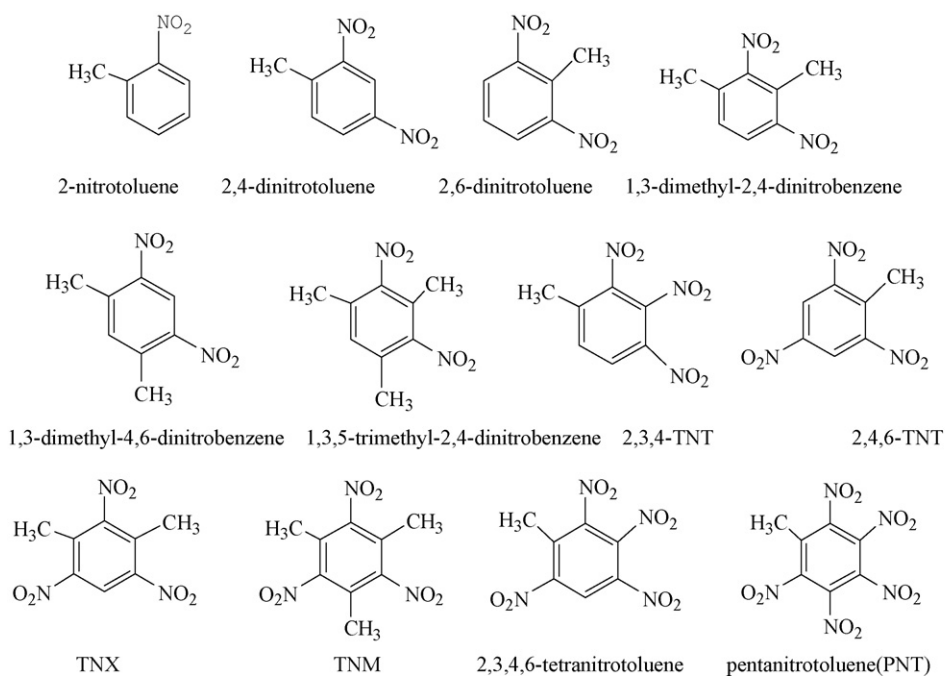


Fig. 1. Illustration of the molecular structures of the nitro derivatives of toluenes.

an HEDC, but also redound to further exploit and apply the title compounds.

## 2. Computational methods

Many studies [14,34] have shown that the DFT-B3LYP method [35,36] in combination with the 6-31G\* [37] basis set is able to give accurate energies, structures, and a series of properties. In this paper, it is employed to obtain the fully optimized molecular geometries and electronic structure of the nitro derivatives of toluenes with the Gaussian03 program package [38].

Detonation velocity and pressure are the most important parameters for evaluating the detonation characteristics of energetic materials. For the explosives with CHNO elements, these parameters can be calculated using the Kamlet–Jacobs (K–J) equations [39,40]:

$$D = (1.011 + 1.312\rho_0)(N\bar{M}^{0.5}Q^{0.5})^{0.5} \quad (1)$$

$$P = 1.558\rho_0^2 N\bar{M}^{0.5}Q^{0.5} \quad (2)$$

where  $P$  is the detonation pressure (GPa),  $D$  is the detonation velocity (km/s),  $\rho_0$  is the packed density ( $\text{g}/\text{cm}^3$ ),  $N$  is the moles of gas produced by per gram of explosives,  $\bar{M}$  is the average molar weight of detonation products, and  $Q$  is the chemical energy of detonation (kJ/g).  $N$ ,  $\bar{M}$  and  $Q$  are decided according to the largest exothermic principle, i.e., for the explosives with CHNO elements, all the N atom converts into  $\text{N}_2$ , the O atom forms  $\text{H}_2\text{O}$  with H atom first and the remainder forms  $\text{CO}_2$  with C atom. The remainder of the C atom

will exist in solid state if the O atom does not satisfy full oxidation of the C atom. The remainder of the O atom will exist in  $\text{O}_2$  if the O atom is superfluous. Table 1 presents the methods for calculating the  $N$ ,  $\bar{M}$ , and  $Q$  parameters of the  $\text{CaHbOcNd}$  explosive.

Obviously, for the known explosives, their  $Q$  and  $\rho_0$  can be measured experimentally; thus their  $D$  and  $P$  can be calculated according to Eqs. (1) and (2). However, for those unsynthesized or hypothetical explosives, their  $Q$  and  $\rho_0$  cannot be evaluated from experimental measures. Therefore, in the molecular design of HEDC, in order to predict the detonation properties, we have recommended the modified K–J equations based on the calculation results of quantum chemistry [5–17].

In practice, the loading density of the explosives  $\rho_0$  can be replaced by the crystal theoretical density ( $\rho_{\text{cry}}$ ), while the chemical energy of the detonation reaction  $Q$  can be calculated as the difference between the heats of formation (HOFs) of products and that of reactants ( $Q_{\text{cal}}$ ). However, from the K–J equations, it is found that  $Q$  has much less effect than  $\rho$  on  $D$  and  $P$ . Therefore,  $Q$  and HOF estimated using the semi-empirical MO PM3 [41] method are precise enough to substitute the experimental data as has been proven in the previous studies [42]. Based on the  $\rho$  and  $Q$ , the corresponding  $D$  and  $P$  can be evaluated. In fact,  $\rho_0$  can only approximate to but not arrive at  $\rho$ , thus the  $D$  and  $P$  obtained from  $\rho$  can be seen as their upper limit (maximum values).

As is known to all, accurate prediction of crystal density is of much difficulty. “Group or volume additivity” method [43,44], although simple and rapid, cannot give reliable results owing to its inherent drawbacks; while the “crystal packing” method [45,46],

Table 1  
Methods for calculating the  $N$ ,  $\bar{M}$ , and  $Q$  parameters of the  $\text{CaHbOcNd}$  explosive.

Parameter	Stoichiometric ratio		
$N$	$c \geq 2a + b/2$	$2a + b/2 > c \geq b/2$	$b/2 > c$
$\bar{M}$	$(b + 2c + 2d)/4M$	$(b + 2c + 2d)/4M$	$(b + d)/2M$
$Q \times 10^{-3}$	$4M/(b + 2c + 2d)$	$(56d + 88c - 8b)/(b + 2c + 2d)$	$(2b + 28d + 32c)/(b + d)$
	$(28.9b + 94.05a + 0.239\Delta H_f^0)/M$	$[28.9b + 94.05(c/2 - b/4) + 0.239\Delta H_f^0]/M$	$(57.8c + 0.239\Delta H_f^0)/M$

$a$ ,  $b$ ,  $c$ , and  $d$  stand for the number of C, H, O, and N atoms in the explosive molecule, respectively;  $M$  in the formula is the molecular weight of the explosive (in g/mol);  $\Delta H_f^0$  is the standard heat of formation of the explosive (in kJ/mol).

**Table 2**  
Predicted densities and detonation properties of the title compounds.<sup>a</sup>

No.	Chemical name	OB <sub>100</sub>	Q	HOF	V	$\rho^b$	D	P
1	2-Nitrotoluene	5.11	1018.6	32.81	100.01	1.37(1.16)	4.69	8.15
2A	2,4-Dinitrotoluene	4.39	1220.9	7.60	117.07	1.55(1.52)	6.21	15.53
2B	2,6-Dinitrotoluene	4.39	1244.8	25.83	114.80	1.59(1.54)	6.33	16.43
3A	1,3-Dimethyl-2,4-dinitrobenzene	4.08	1169.3	-8.23	127.31	1.54	6.01	14.41
3B	1,3-Dimethyl-4,6-dinitrobenzene	4.08	1153.2	-21.41	128.25	1.53	5.95	14.11
4	1,3,5-Trimethyl-2,4-dinitrobenzene	3.81	1053.6	-41.38	142.23	1.48	5.77	13.04
5A	2,3,4-TNT	3.96	1408.0	44.16	133.83	1.70(1.62)	7.30	22.87
5B	2,4,6-TNT	3.96	1374.6	12.86	132.42	1.72(1.65)	7.37(6.93) <sup>c</sup>	23.46(19.1) <sup>c</sup>
6	TNX	3.73	1325.9	-0.223	142.38	1.69(1.64)	7.05	21.24
7	TNMs	3.53	1272.2	-24.94	159.77	1.60(1.48)	6.63	18.11
8	2,3,4,6-TetNT	3.68	1515.4	60.36	149.83	1.82(1.71) <sup>d</sup>	8.08(7.60) <sup>d</sup>	29.10(25.30) <sup>d</sup>
9	PNT	3.47	1621.5	115.42	164.08	1.93(1.76) <sup>d</sup>	8.79(8.23) <sup>d</sup>	35.69(31.20) <sup>d</sup>
	TNB	-1.41	1431.3	28.01	119.40	1.78(1.76)	7.68(7.35) <sup>c</sup>	26.03(21.90) <sup>c</sup>

<sup>a</sup> Units: HOF (kJ/mol), Q (J g<sup>-1</sup>), V (cm<sup>3</sup> mol<sup>-1</sup>),  $\rho$  (g/cm<sup>3</sup>), D (km/s), P (Gpa).

<sup>b</sup> The bracketed experimental values are taken from Ref. [49–51].

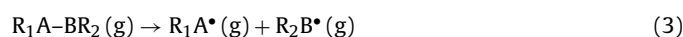
<sup>c</sup> The bracketed experimental values are taken from Ref. [52].

<sup>d</sup> The bracketed experimental values are taken from Ref. [53].

which is more reliable, has its limitation in routine calculation due to its extensive requirement in computational resources. Recently, a statistics average method has been worked out to predict the crystalline densities of energetic materials containing C, H, N and O elements. Subsequently, *D* and *P* are calculated. It was found that, this method is efficient and convenient [6–9,11]. Studies have indicated that, when the average molar volume *V* estimated by Monte-Carlo method based on 0.001 electrons/bohr<sup>3</sup> density space at the B3LYP/6-31G\*\* or 6-31G\* level is used, the theoretical molecular density  $\rho_{\text{mol}}$  ( $\rho_{\text{mol}} = M/V$ , *M* is the molecular weight) is very close to the experimental crystal density  $\rho_{\text{cry}}$ . It is worth noting that the average volume used here should be the statistical average of at least 100 volume calculations. For example, 45 energetic nitramines in Ref. [47] were calculated. It was further testified that,  $\rho_{\text{mol}}$  calculated at the B3LYP/6-31G\*\* level accords with  $\rho_{\text{cry}}$ . Whereas a larger basis set at the B3LYP level will overestimate *V* and underestimate  $\rho_{\text{mol}}$ , and, the densities predicted by the semiempirical MO methods are all systematically larger than the experimental ones.

In a word, the modified K–J equation has been endowed with the new connotation and its application range has been extended. And on the basis of quantum chemistry, it has been used to calculate *D* and *P* to quantitatively evaluate HEDC in molecular design. The modified method has resulted in satisfactory results [5–17].

To measure the strength of bonds and relative stabilities of the title compounds, the bond dissociation energies of various bonds in molecule are calculated. BDE is the required energy in homolysis of a bond and is commonly denoted by the difference between the total energies of the product and the reactant after zero-point energy correction. The expressions for the homolysis of A–B bond (3) and for calculating its BDE (4) are shown as follows [48]:



$$BDE_{(R_1A-BR_2)} = [E_{R_1A^\bullet} + E_{R_2B^\bullet}] - E_{(R_1A-BR_2)} \quad (4)$$

where *R*<sub>1</sub>*A*–*BR*<sub>2</sub> stands for the neutral molecules and *R*<sub>1</sub>*A*<sup>•</sup> and *R*<sub>2</sub>*B*<sup>•</sup> for the corresponding product radicals after the bond dissociation; *BDE*<sub>(*R*<sub>1</sub>*A*–*BR*<sub>2</sub>)</sub> is the BDE of the bond *R*<sub>1</sub>*A*–*BR*<sub>2</sub>; *E*<sub>(*R*<sub>1</sub>*A*–*BR*<sub>2</sub>)</sub>, *E*<sub>*R*<sub>1</sub>*A*<sup>•</sup></sub> and *E*<sub>*R*<sub>2</sub>*B*<sup>•</sup></sub> are the zero-point energy corrected total energies of the parent compound and the corresponding radicals, respectively.

All the calculations considered here were performed using the default convergence criteria given in the programs.

### 3. Results and discussions

#### 3.1. Densities and energies

Table 2 collects *V*,  $\rho$ , *D*, and *P* of the title compounds. The oxygen balances (OB<sub>100</sub>), calculated heats of formation HOF, and *Q* are also listed in this table.

The oxygen balances (OB<sub>100</sub>) are calculated using the formula (5), which can be used to rudely predict the impact sensitivities of the explosives [54].

$$OB_{100} = \frac{100(2n_O - n_H - 2n_C - 2n_{COO})}{M} \quad (5)$$

where *n*<sub>O</sub>, *n*<sub>H</sub>, and *n*<sub>C</sub> represent the numbers of O, H, and C atoms, respectively; *n*<sub>COO</sub> is the number of COO<sup>-</sup>, and here *n*<sub>COO</sub> = 0 for the nitro derivatives of toluenes; *M* is the molecular weight.

From Table 2, on the whole, we see that the calculated  $\rho$ , *D*, and *P* agree with the available experimental values, except for PNT. The calculated detonation properties of PNT in this paper are closed to that reported in Ref. [53]. In addition, Fig. 2 presents the relationship between the calculated and experimental densities. It is found that there is a linear relationship between them and the correlation coefficient is 0.9311, which indicates that the theoretical density calculated at the B3LYP/6-31G\* level is truly close to the crystal density. In a word, using the modified K–J equation based on the calculated densities, the method for predictions of the detonation properties of the title compounds is efficient and convenient. In fact,

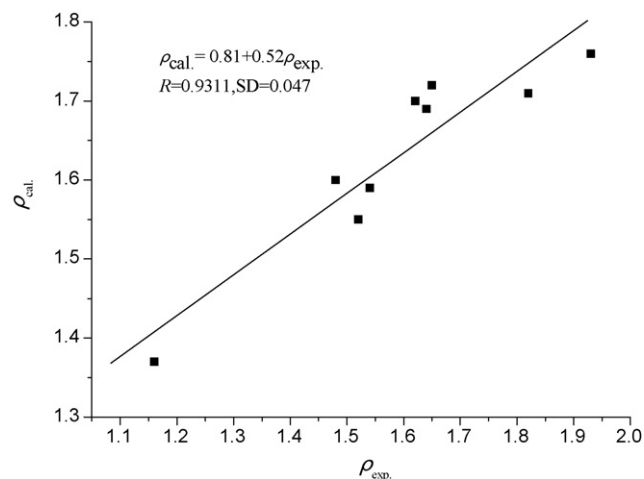


Fig. 2. The relationship between  $\rho_{\text{cal}}$  and  $\rho_{\text{exp}}$ .

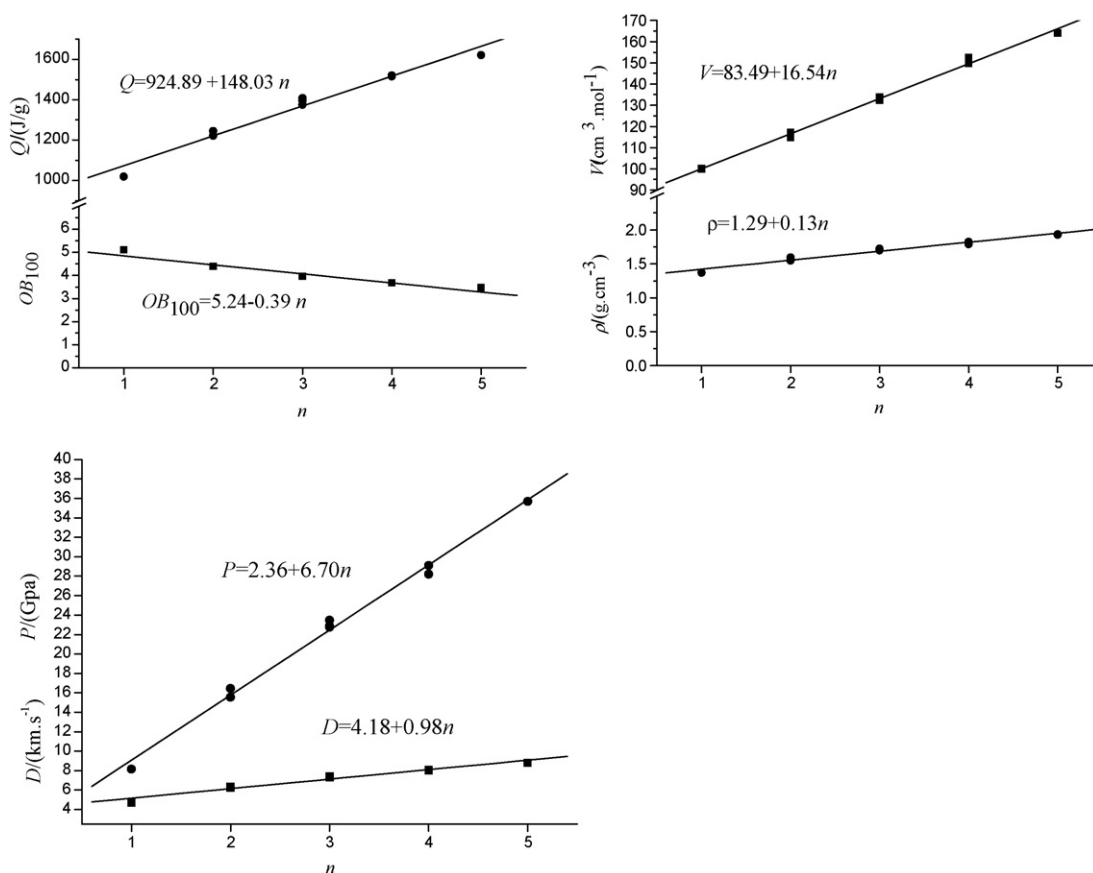


Fig. 3. Correlations between  $OB_{100}$ ,  $Q$ ,  $V$ ,  $\rho$ ,  $D$ ,  $P$  and the number of nitro group ( $n$ ) for the nitro derivatives of toluenes.

many previous studies have shown the reliability of the calculation method [14].

As for the isomers with the same  $OB_{100}$ , no conspicuous discrepancy of their respective  $Q$ ,  $V$ ,  $\rho$ ,  $D$ , and  $P$  is found. As a whole,  $Q$ ,  $V$ ,  $\rho$ ,  $D$  and  $P$ , except  $OB_{100}$  that linearly decreases, increase with the increasing number of  $-NO_2$  groups. Fig. 3 presents the relationships between  $OB_{100}$ ,  $Q$ ,  $V$ ,  $\rho$ ,  $D$ ,  $P$  and the number of nitro group ( $n$ ), which all exist linear relationships, obviously showing good group additivity. The corresponding correlation coefficients are  $-0.9626$ ,  $0.9856$ ,  $0.9975$ ,  $0.9844$ ,  $0.9796$  and  $0.9967$ , respectively. This strongly supports the claim that introducing more nitro substituents (moderately increasing the oxygen balance) into an energetic molecule usually helps to increase its detonation performance [40].

In addition, for the title compounds with the same number of nitro groups (such as TNB, TNT, TNX and TNMs), HOF,  $Q$ ,  $V$ ,  $\rho$ ,  $D$ , and  $P$  are good linearly related with the number of methyl groups ( $n'$ ), respectively. This obviously shows good group additivity on the detonation properties. The correlation equations are as following:

$$HOF = 29.72 - 17.19n', \quad R = -0.9893, \quad SD = 4.0167$$

$$Q = 1429.9 - 52.6n', \quad R = -0.9996, \quad SD = 2.3130$$

$$V = 118.83 + 13.11n', \quad R = 0.9941, \quad SD = 2.2667$$

$$\rho = 1.78 - 0.06n', \quad R = -0.9812, \quad SD = 0.0178$$

$$D = 7.70 - 0.35n', \quad R = -0.9972, \quad SD = 0.0414$$

$$P = 26.11 - 2.60n', \quad R = -0.9977, \quad SD = 0.2809$$

where  $R$  and  $SD$  are the correlation coefficient and standard deviation, respectively.

In a word, it shows that introduction of nitro group can improve the detonation properties of the nitro derivatives of toluenes. Compared with famous nitroaromatic explosive TNT (*s*-trinitrotoluene) ( $\rho = 1.72 \text{ g/cm}^3$ ,  $D = 7.37 \text{ km/s}$ ,  $P = 23.46 \text{ GPa}$ ), they all have better detonation performance when the number of nitro groups is not less than 4, which indicates that they are all potential energetic compounds. However, introduction of methyl group can depress the detonation properties. Therefore, in the design of the molecule, we could adjust the detonation properties by changing the substituted group. According to our suggested energy criterion for HEDC, i.e.,  $\rho \approx 1.9 \text{ g/cm}^3$ ,  $D \approx 9.0 \text{ km/s}$ , and  $P \approx 40.0 \text{ GPa}$ , it is found from Table 2, that pentanitrotoluenes satisfies the requirements.

### 3.2. Pyrolysis mechanism, stability and identification of sensitivity

#### 3.2.1. Static electronic structural parameters

Bond overlap populations (or bond order) reflect the electron accumulations in the bonding region, and they can provide us with detailed information about the chemical bond. As a whole, the less Mulliken bond populations a bond has, the easier the bond breaks. Though Mulliken population analysis [55] suffers from some shortcomings, such as the basis set dependence, results derived from Mulliken population analysis at the same calculation level are still meaningful for comparing trends in the electron distribution for homologous compounds as was done here. The bond overlap populations and the net charge on the nitro group  $Q_{-NO_2}$  obtained from the Mulliken population analysis for the title compounds at the B3LYP/6-31G\* level are listed in Table 3.

**Table 3**The static electronic structural parameters of the titled compounds.<sup>a</sup>

No.	$M_{C-NO_2}$	$M_{C=C}$	$M_{C-CH_3}$	$M_{C-H}$	$M_{N=O}$	$Q_{-NO_2}(e)$
1	0.1678	0.4549	0.3689	0.3490	0.2702	-0.4214
2A	0.1542	0.3748	0.3725	0.3524	0.2766	-0.3867
2B	0.1571	0.4574	0.3792	0.3551	0.2717	-0.3897
3A	0.1516	0.4387	0.3609	0.3565	0.2674	-0.3999
3B	0.1560	0.3681	0.3684	0.3516	0.2751	-0.4020
4	0.1478	0.4299	0.3604	0.3572	0.2719	-0.4125
5A	0.1383	0.3476	0.3682	0.3578	0.2748	-0.3140
5B	0.1468	0.3786	0.3819	0.3362	0.2745	-0.3560
6	0.1463	0.3727	0.3742	0.3554	0.2536	-0.3755
7	0.1447	0.4122	0.3609	0.3521	0.2675	-0.3818
8	0.1342	0.3459	0.3827	0.3583	0.2692	-0.2979
9	0.1263	0.3111	0.3673	0.3526	0.2670	-0.3077

<sup>a</sup>  $M_{C-NO_2}$ ,  $M_{C=C}$ ,  $M_{C-CH_3}$ ,  $M_{C-H}$  and  $M_{N=O}$  are the weakest bond overlap populations of the C–NO<sub>2</sub>, C=C, C–CH<sub>3</sub>, C–H, N=O bonds in each molecule;  $Q_{-NO_2}$  is the net charge on –NO<sub>2</sub> group of the corresponding bond.

From these data in Table 3, we can see clearly that, the overlap population of the C–NO<sub>2</sub> bond ( $M_{C-NO_2}$ ) is the least in each molecule, which predicts that the C–NO<sub>2</sub> bond with least overlap population may be the trigger bond during thermolysis initiation processes. Meanwhile, on the whole, with the number of nitro and methyl groups increasing,  $M_{C-NO_2}$  decreases as expected. This suggests that the stability of the title compounds decreases and that their sensitivities increase accordingly, which confirms that the nitro and methyl groups have an effect on activity. For example, the order of the stability for the titled compounds is  $9 < 8 < 5B < 2 < 1$ ,  $4 < 3A < 2A$ , and  $7 < 6 < 5B$ . As to isomers, it is found that the relative positions of the substituents have an influence on the stability of the molecules. In general, the nearer the distance between the

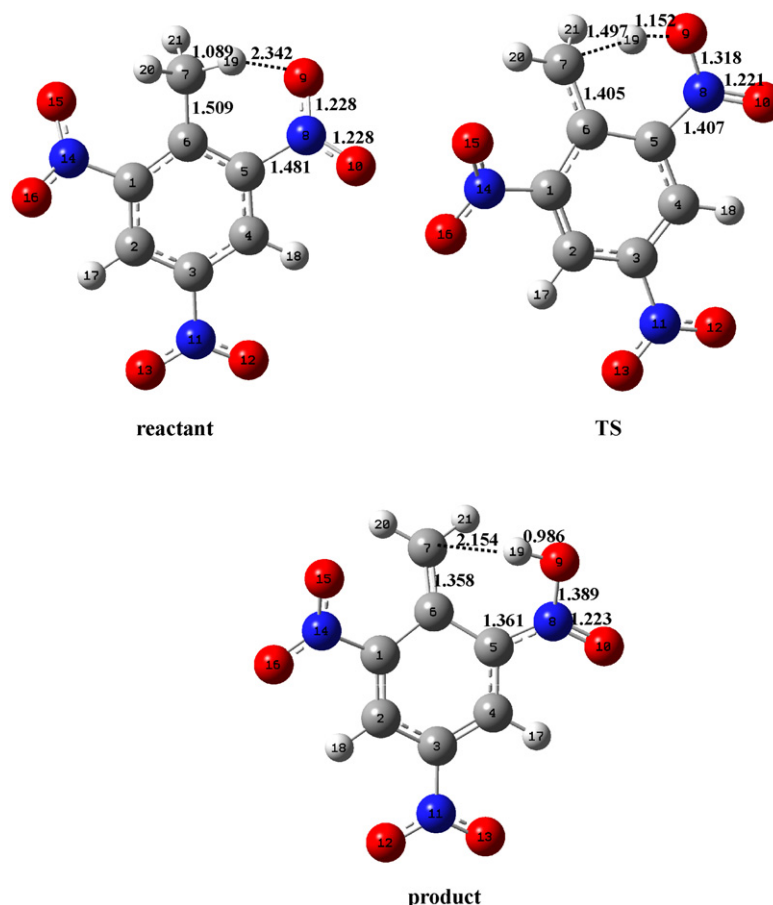
groups is, the more unstable the compound is, which attributes to the electron-withdrawing effect and the steric hindrance effect. For instance,  $3A < 3B$ , and  $5A < 5B$ .

Additionally, for the nitro derivatives of toluenes,  $-Q_{-NO_2}$  decreases with the number of nitro groups increasing, which suggests that the larger the  $-Q_{-NO_2}$  is, the more stable and therefore less sensitive the compound is.

In a word, because the bond orders of chemical bonds and the net charges on the atoms are obtained from the Mulliken population analysis, the parallel relation between  $M_{C-NO_2}$  and  $Q_{-NO_2}$  of the homologous compounds are necessarily provided, i.e., the smaller  $M_{C-NO_2}$  has, the smaller the negative net charge on –NO<sub>2</sub> group is. This induces that, for the homologous energetic materials, the smaller the stability is, the larger the sensitivity is. Therefore, it is entirely parallel to identify the relative magnitude of impact sensitivity using “PSBO” and  $Q_{-NO_2}$  [6,56]. Where “PSBO” is the principle of the smallest bond orders, i.e., for the series of the energetic materials with the similar molecular structure and pyrolysis mechanism, the smaller the overlap population of the trigger bond is, the larger the impact sensitivity is. Here, it is proved again.

### 3.2.2. Kinetic parameter

Another main concern for the energetic materials is whether they are kinetically stable enough to be of practical interest. Thus, studies on the bond dissociation or pyrolysis mechanism are important and essential for understanding the decomposition process of the energetic materials, since they are directly relevant to the sensitivity and stability of the energetic compounds. In this paper, four possible initial steps in the pyrolysis route are considered for the



**Fig. 4.** The structures of reactant, TS and product fully optimized for the H-shift isomerization reaction of 2,4,6-TNT and the part of the related geometric parameters.



**Table 4**  
Comparison of theoretical BDEs (kJ/mol) for typical C–C, C–N, and N–N bonds at the G2 and B3LYP/6-31G\* levels.

Compound	CH <sub>3</sub> –CH <sub>3</sub>	CH <sub>3</sub> –NO <sub>2</sub>	NH <sub>2</sub> –NO <sub>2</sub>	(CH <sub>3</sub> ) <sub>2</sub> N–NO <sub>2</sub>	CH <sub>3</sub> NH–NO <sub>2</sub>
B3LYP/6-31G*	364.39	242.55	196.14 (196.65) <sup>a</sup>	172.49	193.07
G2	369.45	255.22	213.72 (213.80) <sup>b</sup>	205.64	216.31

<sup>a</sup> Ref. [58].

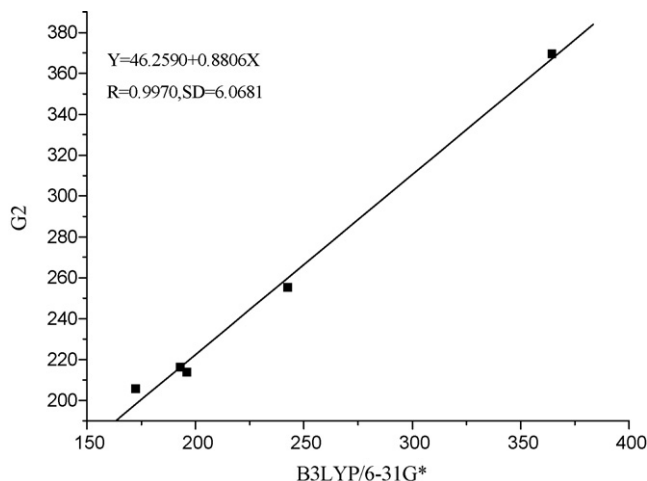
<sup>b</sup> Ref. [59].

title compounds by breaking the following bonds: (1) C–NO<sub>2</sub>; (2) C–CH<sub>3</sub>; (3) C–H, and (4) H-transfer isomerization reactions of C–H bond. In all these studies, the C–NO<sub>2</sub>, C–CH<sub>3</sub>, and C–H bonds are selected as the breaking bonds according to the smallest one of the same kind of the bonds at the B3LYP/6-31G\* level. It is worthy to be mentioned that at the B3LYP/6-31G\* level we succeeded to locate the in-plane TSs of the H shift reactions (see Fig. 4), which was consistent with the results at PM3 level. Taken 2,4,6-TNT for the example, Fig. 4 illustrates the structures of reactant, transition state (TS) and product of H-transfer isomerization reactions fully optimized at the DFT-B3LYP/6-31G\* level, including the part of the geometric parameters related with the reaction. The full geometric parameters of reactant, TS and product are listed in Tables 1S–3S of Appendix.

First, a benchmark calculation on several small molecules with C–C, C–N, and N–N bonds by using Gaussian-2 (G2) theory [57] was carried out to check the accuracy of BDE computed with the B3LYP/6-31G\* method. Table 4 summarizes the computed BDE values at the G2 and B3LYP/6-31G\* levels. Fig. 5 shows a very good linear relationship between the B3LYP/6-31G\* and G2 calculated BDEs ( $R = 0.9970$ ). On this basis, we might expect reliable calculated results for the title compounds.

The BDEs and the activation energies for the isomerization reactions of the H transfer ( $E_a$ ) for the title compounds at the B3LYP/6-31G\* level are listed in Table 5. Compared with BDE<sup>0</sup>, BDE parallelly descends 5.4–38.7 kJ/mol, which indicates that using BDEs with or without correction for zero-point energy will not have influences on the identification of trigger linkage and pyrolysis mechanism.

Generally speaking, the less the energy is required to break a bond, the weaker the bond is, and the easier the bond becomes a trigger bond, that is to say, the corresponding compound is more unstable and the sensitivity is larger. From Table 5, it can be seen that, for the nitro derivatives of toluenes, the activation energies of H-transfer reaction at the B3LYP/6-31G\* level is smaller than the BDEs of all other bonds and this illustrates that the trigger linkage is initiated from the isomerization reactions of the H transfer. At the same time, BDEs of trigger bonds for the title compounds are



**Fig. 5.** Comparison of the BDEs calculated by the B3LYP/6-31G\* and G2 theory.

quiet large and suffice the stability request of BDE  $\approx 80$ – $120$  kJ/mol suggested previously.

Fig. 6 presents the correlations between the activation energies, BDE<sub>C–NO<sub>2</sub></sub>,  $M_{C–NO_2}$ ,  $Q_{–NO_2}$  and the number of nitro groups ( $n$ ). For the nitro derivatives of toluenes, with the number of nitro groups increasing, the activation energies of BDE<sub>C–NO<sub>2</sub></sub> and H-transfer reaction decrease, indicating that the stability decreases and their sensitivities increase accordingly. For example, the order of the compounds with one methyl group is  $9 < 8 < 5A$  and  $5B < 2A$ , e.g., the activation energies of 5A (2,3,4-TNT), 8 (2,3,4,6-TetNT), 9 (PNT) and 5B (2,4,6-TNT), 2A (2,4-dinitrotoluene) are 180.85, 177.41, 173.86 and 174.11, 177.06 kJ/mol, respectively and in turn, the impact sensitivities are 0.56, 0.19, 0.18 m and 18.9, 11.4 kg/m<sup>2</sup>. With the number of methyl groups increasing, the activation energies decrease, e.g., the activation energies of 5B (2,4,6-TNT), 6 (TNX), and 7 (TNM) are 174.11, 180.68, and 187.97 kJ/mol, respectively and in turn, the impact sensitivities are probably  $5B > 6 > 7$ , namely, the descending order of the stability is  $5B < 6 < 7$ .

**Table 5**  
BDEs for main kinds of the bonds and the activation energies ( $E_a$ ) of the H transfer in C–H bond (kJ/mol) at the B3LYP/6-31G\* level.<sup>a</sup>

No.	BDE <sup>0</sup>				BDE				Impact sensitivities <sup>b</sup>	
	C–NO <sub>2</sub>	C–C	C–H	H transfer ( $E_a^0$ )	C–NO <sub>2</sub>	C–C	C–H	H transfer ( $E_a$ )	Impact energies (10 <sup>–4</sup> )	$h_{50\%}$
1	299.80	442.43	407.69	201.82	280.22	412.31	371.87	187.74		
2A	285.14	449.44	460.07	191.10	266.41	419.45	419.08	177.06	18.90	
2B	265.65	428.82	394.63	184.49	247.72	398.58	358.81	170.52		
3A	266.95	448.48	403.75	195.82	249.02	419.24	368.38	182.35	14.96	
3B	289.67	449.11	467.63	198.19	271.07	418.74	426.47	184.31	14.60	
4	273.17	443.18	411.60	200.30	255.78	413.28	376.07	187.50		
5A	256.70	453.56	403.54	194.50	239.48	423.36	368.21	180.85		0.56
5B	290.68	442.26	400.76	188.00	273.71	411.94	365.36	174.11	11.40	
6	274.47	446.54	413.91	193.76	257.80	417.23	378.42	180.68		
7	260.36	448.39	416.85	200.96	243.98	418.49	381.61	187.97		
8	255.74	448.60	402.11	191.21	239.23	418.07	366.87	177.41		0.19
9	229.40	457.38	404.59	187.12	213.78	427.14	369.43	173.86		0.18

<sup>a</sup>  $E_a = E_{TS} - E_R$ ,  $E_a^0$  denotes the activation energies for the isomerization reactions of the H transfer without zero-point energy corrections, while  $E_a$  denotes the activation energies including zero-point energy corrections.

<sup>b</sup>  $h_{50\%}$ : The height from which a given weight (2.5 kg) must be dropped on the compound to produce 50% initiation probability, unit: m; the impact energies are the corresponding energies requested to make the explosives explode, unit: kg/m<sup>2</sup>. The experimental values are taken from Ref. [23,60].

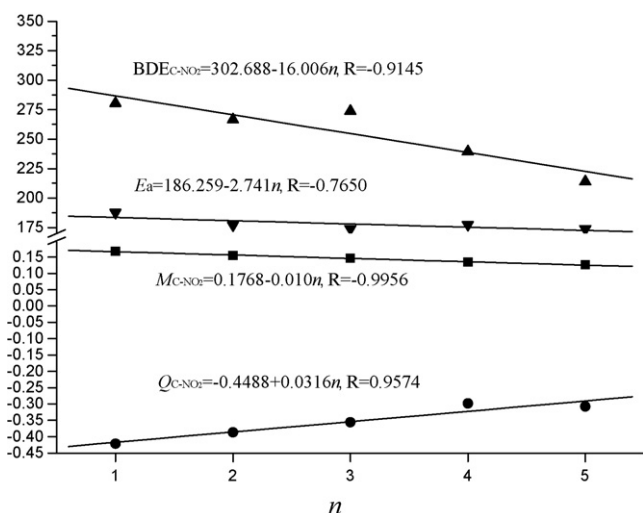


Fig. 6. Correlations between the activation energies,  $BDE_{C-NO_2}$ ,  $M_{C-NO_2}$ ,  $Q_{C-NO_2}$  and the number of nitro groups ( $n$ ).

In a word, the static electronic structural parameters and the kinetic parameter not only can be used to identify the trigger bond and illustrate the pyrolysis mechanism, but also to identify the stability and the relative magnitude of the sensitivity.

#### 4. Conclusions

Based on DFT-B3LYP/6-31G\* calculations and modified K-J equation, we have theoretically studied the structures and the performance for the nitro derivatives of toluenes, and the conclusions of this work are as following:

For the nitro derivatives of toluenes, with the increase in the number of nitro groups, heat of formation, heat of detonation, volume, density, detonation velocity and detonation pressure linearly increase, except the oxygen balance linearly decreasing close to zero oxygen balance; with increasing the number of methyl groups, the other properties linearly decrease, except the volume linearly increasing.

The activation energy of H-transfer reaction is smallest among the BDEs of all other bonds and these illustrate that the pyrolysis of the title compounds is started from the isomerization reactions of the H transfer. Moreover, the activation energies decrease and increase with the increase in the number of nitro and methyl groups, respectively.

The static electronic structural parameters and the kinetic parameter all can be parallelly or equivalently used to identify the stability and the relative magnitude of impact sensitivity for homologous energetic materials.

In theory, among the title compounds, pentanitrotoluenes ( $\rho = 1.99 \text{ g/cm}^3$ ,  $D = 9.10 \text{ km/s}$ ,  $P = 38.91 \text{ GPa}$ ) essentially satisfies the quantitative criteria for the energy and the stability as HEDCs.

This paper has provided the detailed structure-performance information for the nitro derivatives of toluenes for the first time, which will be helpful for the reasonable use of the synthesized compounds and further exploitation of the nonsynthesized compounds.

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#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jhazmat.2009.12.088.

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