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A Quantum Chemical Study on Thermolysis Initiation Mechanisms and Impact Sensitivity of Energetic Materials^{*)}

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Abstract: Thermolysis initiation mechanisms of polynitro compounds, tetrazole derivatives and their metallic salts, and cage high energy density compounds have been investigated using quantum chemical approaches. Our calculations showed that the trigger bonds whose breaking initiate a decomposition or an explosion were C-NO₂ or N-NO₂ bonds for nitro derivatives of benzene and aminobenzenes, CL-20 and polynitroadamantanes. Explosion of nitro derivatives of phenol and toluene were most likely triggered by the isomerization reactions involving the H-shift. Due to larger strain energy, the trigger bond was found to be the C-C bond in the framework of polynitrocubanes. Regarding tetrazoles and their metallic salts, opening of the tetrazole ring, i.e., scission of the N-N bond, followed by formation of N₂ molecules, initiate explosive reactions. We found for energetic materials having similar molecular structures and following similar thermal decomposition mechanisms, the bond orders of the trigger bond and the activation energy to break the bond were directly related to the impact sensitivity. We thus proposed two criteria used to evaluate the relative ordering of impact sensitivity for energetic materials with similar structures: the smaller the bond order, the more sensitive an energetic material, which was called the principle of the smallest bond order (PSBO). And the higher the activation energy, the less sensitive a material was. We demonstrated that in most cases the PSBO was equivalent to the activation energy criterion. The former was more convenient and easier to obtain while the latter could be applied more universally.

Keywords: thermolysis mechanism, impact sensitivity, PSBO, activation energy

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Introduction

Thermal decomposition directly related to the stability and deflagration of energetic materials. It is an important factor affecting the safety of production, usage and storage of energetic materials. Therefore, study of thermolysis mechanism is of great significance, and is a necessity in the field of explosive chemistry and technology. In the course of studying thermolysis mechanisms, we, in particular, paid great attention to the trigger step or initiation step not only because trigger step is usually rate-limiting step determined by molecular structure (the subsequent reaction steps are automatically accelerated, and thus not so important in the sense of determining the ordering of sensitivity), but also because the sensitivity of explosives is directly associated with thermolysis initiation step. Basing on the basic theory that thermolysis takes ahead of an explosion and the idea about the thermal entity of initiation [1-4], people always put thermolysis, initiation and sensitivity together to study.

During the last two decades, we have systematically investigated the mechanisms of thermal decomposition for various series of energetic materials including nitro compounds, nitroamines, nitroesters, azides, tetrazole derivatives and their metallic salts, metallic salts of NTO, specially organic cage high energy density compounds. In these studies, we adopted quantum chemical methods, combined with some experimental approaches.

We found that the relative order of impact sensitivity of energetic materials can be predicted by examining the bond order of the trigger bond or activation energy of the trigger bond breaking [5-12]. Most of the achievements were summarized in the monographs [13-15], respectively. Here we present and discuss some selected typical compounds only.

Materials and Methods

It is very difficult to perform the pyrolysis calculations on large systems at the high level. While semi-empirical MO methods [16-19], such as PM3, AM1, MNDO and MINDO/3 with unrestricted Hartree-Fock (UHF) model can give satisfactory results, and quickly predict the relative sensitivity for the compounds with similar structure and pyolysis mechanism. It should be pointed that, each bond chosen to break has the least Mulliken population in the corresponding molecule, respectively, and each transition state (TS) was found and confirmed by both the presence of only one imaginary frequency and the analysis of internal reaction coordinate (IRC).

Results and Discussion

Thermolysis initiation mechanisms

High energy density materials (HEDMs) have been receiving heated attention because of superior explosive performances over conventional energetic materials. Due to strain energy and compact structures, organic cage compounds are investigated as an important category of HEDMs. Typical examples of these compounds are hexanitrohexaazaisowurtzitane (CL-20) and octanitrocubane (ONC) [20]. Polynitrocubanes and polynitroadamantanes are also investigated as promising candidates of HEDMs [21].

ε-CL-20 (HNIW) [15, 22]

Figure 1 gives the molecular structure of ε -CL-20. Table 1 and Table 2 list bond orders and activation energies (E_a) of homolysis different kinds of the weakest bond C-C, C-N and N-N from UPM3 calculations, respectively. From Table 1,we can see that the bond whose bond order is the smallest in the same class, i.e., the weakest bond is C1-C3, C7-N2 and N2-N13, respectively.



Figure 1. The structure and atomic numbering of ε -CL-20.

Table 1.	The Walliken bolid of der of 2-CE-20 from Of W19 calculations							
C-C	Bond order	C-N	Bond order	N-N	Bond order			
C1-C3	0.275	C7-N2	0.216	N2-N13	0.172			
C7-C10	0.279	C1-N9	0.223	N12-N28	0.177			
C6-C8	0.288	C1-N2	0.217	N4-N16	0.210			
		C10-N9	0.231	N5-N19	0.217			
		C8-N5	0.229	N9-N22	0.186			
		C8-N12	0.225	N11-N25	0.194			
		C6-N4	0.233					
		C6-N11	0.230					

Table 1.The Mulliken bond order of ε -CL-20 from UPM3 calculations

It's shown from Table 2 and Figure 2 that the activation energies for the homolysis reaction of N-NO₂ bond, 96.2 kJ mol⁻¹, is notably smaller than those for breaking the C-C and C-N bonds in the cage framework, 132.4 and 189.3 kJ mol⁻¹, indicating that the initiation step for ε -CL-20 is homolysis of the N-NO₂ bond on the side chain, and the framework consisting of cyclohexane and cyclopentane is rather stable.

Table 2. The heats of formation for reactants (R) and transition states (TS) and the activation energies (E_a) in different thermolysis reaction approaches of ε -CL-20

Homolysis bond	Heat of forma	E [lt I mol-1]	
	R	T S	L_a [KJ IIIOI ²]
C1-C3	1007.5	1139.9	132.4
C7-N2	1007.5	1196.8	189.3
N2-N13	1007.5	1103.7	96.2



Figure 2. Potential energy curves of C-C, C-N and N-N in the homolysis reaction of ε -CL-20 from PM3 calculation.

Polynitrocubanes [23]

Figure 3 shows the thermolysis mechanism of cubane. The diradical intermediate P1 is produced through the homolysis of the skeletal C-C *via* the transition state TS1. Further breaking of another C-C bond (*via* TS2) leads to the product. When 1,4-ditrinocubane and octanitrocubane are talked about, we just need replace -H with $-NO_2$ radical and this figure is also applicable.



Figure 3. Thermolysis mechanism of cubane.

In order to elucidate the pyrolysis mechanism of polynitrocubanes, two possible initial steps in the pyrolysis route are considered: (1) breaking the first C-C bond of the cube to form a transition state TS1 and diradical intermediate P1 and subsequently breaking the second C-C bond in P1 to form TS2 and product P2; (2) breaking a C-NO₂ bond to form a TS3 and the product P3 containing two radicals.

	Rupture of C-C bond		Rupture of C-NO ₂ bond
	E_{al}	E_{a2}	E_{a3}
1,4-Dinitrocubane	133.17	2.03	132.495
ONC	86.65	9.99	102.66

Table 3. MINDO/3 calculated the activation energies $[kJ mol^{-1}]^a$

^{*a*} E_{a1} and E_{a2} are the activation energies *via* the pyrolysis routes of R-TS1-P1 and P1-TS2-P2 respectively, E_{a3} are the activation energies *via* pyrolysis route for the rupture of C-NO₂ bond.

From Table 3, we can see that E_{a3} for breaking the C-NO₂ bonds in both ONC and 1,4-dinitrocubane molecules are larger than the corresponding E_{a1} for breaking the first C-C bonds in their cubic structures. This result indicates that the initial step in the pyrolysis of polynitrocubanes is the rupture of the C-C bond on cubane cage skeleton, which is different from the pyrolysis initiation step *via* breaking the bond between the ring and NO₂ for other caged energetic compounds such as CL-20 and polynitroadamantanes, and for many noncaged energetic compound such as TATB, RDX and HMX. Obviously, this difference is because the strain energies on cubane cage skeletons are much more than those on the ring in other caged and non-caged molecules.

From Table 3 we can also find that for the two compounds, E_{a2} for breaking the second C-C bonds are much smaller than E_{a1} for breaking the first C-C bond in their cubes. This means that compared with the first C-C bond, the rupture of the second C-C bond is very easy. So, in the pyrolysis initiation reaction of polynitrocubane, the rate-controlling step is to form a diradical by the single C-C bond breaking in the cube. The second C-C bond breaking is easily followed to form a nitrocyclooctatetraene for ONC. The corresponding energy level diagram calculated by MINDO/3 method in the pyrolysis of ONC is shown in Figure 4.



Figure 4. Thermolysis potential energy curve of octanitrocubane from MINDO/3 calculation.

Theoretical criteria of impact sensitivity

Polynitro aromatic compounds

Much attention has been paid to polynitro aromatic compounds. TATB (1,3,5-triamino-2,4,6-trinitrobenzene) and TNT (2,4,6-trinitrotoluene) *et al.* are among the most effective and widely-used explosives and monopropellants.

Nitro derivatives of benzene and aminobenzenes [7, 8]

UHF-SCF-AM1 method [18] has been applied to study the pyrolysis initiation reactions for seven nitro derivatives of benzene and seven nitro derivatives of aminobenzenes. From Table 4, one can see that for each series of compounds there is a good linear relationship between the bond order (B_{C-N}) of the trigger bond (C-NO₂) and the activation energy (E_a) of the homolysis reaction of the bond. Comparing the experimental impact sensitivity values ($h_{50\%}$), (B_{C-N}) and E_a , one can find that there are parallel relationships between them. That is, for homologous compounds, the smaller the bond order of the trigger bond, (there is less electron density around this bond, thus the bond is relatively weak) the lower the activation energy to break the bond. Therefore thermal decomposition proceeds more easily. Accordingly it is easier for this compound to be initiated to explosion or equivalently its sensitivity is larger. The finding that the smallest bond order corresponds to the largest sensitivity is called the principle of the smallest bond order (PSBO) used for estimating the sequence of impact sensitivity. In the case of nitro derivatives of benzene and aminobenzenes, PSBO leads to the same conclusion as that derived from the activation energy (E_a) criterion.

Table 4. The AM1 calculated Wiberg bond order of the weakest C-NO₂ bonds in the nitro derivatives of benzene and aminobenzenes ($B_{\text{C-N}}$), the activation energies (E_a) of pyrolysis initiation reactions and the experimental impact sensitivity of them ($h_{50\%}$)

· · · ·			
Compounds	B _{C-N}	$\begin{bmatrix} E_a \\ [kJ mol^{-1}] \end{bmatrix}$	$h_{50\%}$ [m]
Nitro derivatives of benzene			
Nitrobenzene	0.857	140.069	75.83
<i>m</i> -Dinitrobenzene	0.852	131.429	3.75
p-Dinitrobenzene	0.848	129.379	
s-Trinitrobenzene	0.844	124.226	0.60
o-Dinitrobenzene	0.839	118.996	
1,2,3,4-Tetranitrobenzene	0.812	96.678	
Hexanitrobenzene	0.797	84.185	0.05
Nitro derivatives of aminobenzenes			
TATB (1,3,5-triamino-2,4,6-trinitrobenzene)	0.934	157.21	>>320
o-Nitroaniline	0.889	146.21	
DATB (1,3-diamino-2,4,6-trinitrobenzene)	0.882	140.40	3.20
2,6-Dinitroaniline	0.880	135.35	
TNA (2,4,6-trinitroaniline)	0.871	130.64	1.77
2,3,4,6-Tetranitroaniline	0.806	95.94	0.41
Pentanitroaniline	0.801	88.63	0.15

Table 5 lists Mulliken bond order (M_{C-N}) calculated at the density functional theory (B3LYP/6-31G* [24, 25] level and the experimental impact sensitivity values. Data at the first principle level (Table 5) further corroborate the validity of PSBO previously derived based on semi-empirical molecular orbital calculations.

Table 5. The Mulliken bond order of the weakest C-NO₂ bonds (M_{C-N}) from B3LYP/6-31G* calculations and the experimental impact sensitivity ($h_{50\%}$ and E)

Compounds	$M_{ ext{C-N}}$	<i>h</i> _{50%} [m]	<i>E</i> /Nm
<i>m</i> -Dinitrobenzene	0.1611		39
s-Trinitrobenzene	0.1511	71	74
1,2,3,5-Tetranitrobenzene	0.1346	33	
Pentanitrobenzene	0.1211	7	
Hexanitrobenzene	0.1323	15	
TATB	0.1788	>>320	
DATB	0.1640	320	
TNA	0.1567	177	
2,3,4,6- Tetranitroaniline	0.1350	41	
Pentanitroaniline	0.1169	15	

Nitro derivatives of phenols and methylbenzenes [9, 10]

Table 6 and Table 7 list the results of the nitro derivatives of Phenols and methylbenzenes calculated by UAM1 method. Data in Table 6 show that for nitro derivatives of phenols, the activation energy for breaking C-NO₂ bond (E_a^h) is larger than that for the H-shift isomerization reaction (E_a^i) . Hence it is reasonable to assume that O-H bond is the trigger bond in nitro derivatives of phenols. In fact, the experimental impact sensitivity results vary in parallel with the bond order $(B_{\text{H-O}})$ and E_a^i .

Table 6. The experimental impact sensitivity $(h_{50\%})$ of six nitro derivatives of Phenols, the activation energies of two kinds of reactions $(E_a^{\ h} \text{ and } E_a^{\ i})$ and the Wiberg bond order in the reactant molecules $(B_{\text{C-N}} \text{ and } B_{\text{H-O}})$

No. of compound ^{<i>a</i>}	(1)	(2)	(3)	(4)	(5)	(6)
$h_{50\%}$		>3.2	2.96	0.87	0.43	0.27
E_{a}^{h} (kJ mol ⁻¹) ^b	136.859	146.289	143.369	133.691	132.495	142.812
E_{a}^{i} (kJ mol ⁻¹)	94.889	97.613	81.350	85.475	72.094	67.354
$B_{\text{C-N}}^{c}$	0.859	0.879	0.885	0.852	0.858	0.886
B _{H-O}		0.886	0.885	0.878	0.877	0.869

^{*a*}(1),(2)...,(6) indicate 2,4-dinitrophenol, 4,6-dinitroresorcinol, 2,4-dinitroresorcinol, 2,4,6-trinitrophenol, 2,4,6-trinitroresorcinol and 2,4,6-trinitro-1,3,5-trihydroxyl benzenes, respectively

 $^{b}E_{a}^{\ h}$ and $E_{a}^{\ i}$ correspond to the activation energies of the homolysis and isomerization reactions, respectively $^{c}B_{C-N}$ and B_{H-O} stand for the Wiberg bond orders of the weakest C-NO₂ and H-O bonds in the reactant molecules, respectively.

Table 7. The experimental impact sensitivity (impact energy) of seven nitro derivatives of methylbenzenes, the activation energies of two kinds of reactions $(E_a^h \text{ and } E_a^i)$

Compounds	impact energy	$E_a{}^h$	$E_a{}^i$
Compounds	$[10^{-4}$ kg m ⁻²]	[kJ mol ⁻¹]	[kJ mol ⁻¹]
2,4-Dinitromethylbenzene	18.9	134.076	79.194
4,6-Dinitro-1,3-dinitromethylbenzene	14.6	129.691	74.760
2,4-Dinitro-1,3-dinitromethylbenzene		120.068	68.572
2,4-Dinitro-1,3,5-trinitromethylbenzene	13.8	121.650	68.382
2,4,6-Trinitromethylbenzene	11.4	114.504	64.446
2,4,6-Trintro-1,3-dinitromethylbenzene	5.7	111.516	61.768
s-Trinitromethylbenzene	5.9	112.813	69.626

It is obvious in Table 7 that our calculated $E_a{}^h$ for cleaving the C-NO₂ bond in nitro derivatives of methylbenzenes is larger than the one for the H-shift isomerization reaction ($E_a{}^i$), indicating that the trigger bond is the α -C-H bond. There is basically a parallel relationship between $E_a{}^i$ and the impact sensitivity values.

Tetrazole derivatives and their metallic salts [11-12]

Tetrazole is a kind of five-membered heterocyclic compound containing four nitrogen atoms. A series of investigations on tetrazole derivatives show that 5-substituted (or C-substituted) tetrazoles are more stable than the 1- and 2-substituted (or N-substituted) isomers. The impact sensitivity of 5- substituted tetrazole derivatives follows the following order [26, 27]: R: $CH_3 < NH_2 < H < NHNO_2 < Cl < NO_2 < N_3 < N_2^+$ (R are substitutents; see Figure 5). The sensitivity of some metal salts of tetrazole derivatives has also been measured [28] (see Table 8). Various efforts have been made to explain the experimentally observed sensitivity order. Unfortunately none of them can explain the observed order of sensitivity satisfactorily.

Figure 5 illustrates the thermal decomposition of C-substituted tetrazole derivatives and their metal salts. A systematic investigation on a series of tetrazole derivatives shows that the rate-controlling step of thermal decomposition is the first step, i.e., the opening of the tetrazole ring. Thus it is reasonable to predict the sensitivity order for tetrazole derivatives just by comparing the activation energy of this step. We employed both DFT-B3LYP and semi-empirical PM3 methods.



Figure 5. Illustration of the thermolysis initiation step of 5-substituted tetrazoles and their metallic salts (R = substituent, M = metal atom for tetrazole metal salts).

5-Substituted tetrazole derivatives

Table 8.	Activation	energies	obtained	from	B3LYP/6-31G	and	PM3
	calculations	, respectiv	ely [kJ mo	1-1]			

	, I , I	L .	
R	No.	$E_a(\text{DFT})$	$E_a(PM3)$
N_{2}^{+}	1	89.02	99.11
OH	2	97.46	124.45
N_3	3	103.01	132.16
NO ₂	4	108.21	132.76
Cl	5	103.24	133.66
NHNO ₂	6	100.08	134.24
NH ₂	7	99.53	134.55
Н	8	110.14	138.05
CH ₃	9	114.32	140.85

It is notable in Table 8 that all activation energies from B3LYP calculation are smaller than the PM3's results. The average difference between two sets is 27.19 kJ mol⁻¹. PM3 produces the similar trend for activation energy as B3LYP. For example, both methods predict that $5-N_2^+$ -tetrazole has the smallest reaction barriers (89.02, 99.11 kJ mol⁻¹, respectively), and 5-methyltetrazole the largest ones (114.32, 140.85 kJ mol⁻¹, respectively). The lower the barrier, the more easily the thermal decomposition proceeds. Thus the compound will be more sensitive, provided that the reaction barrier of this step is the decisive factor for detonation of 5-substituted tetrazoles. According to the obtained activation energies from B3LYP calculation, we might conclude that $5-N_2^+$ -tetrazole is the most sensitive whereas 5-methyltetrazole the most stable, which is in line with experiments. Accordingly, we can obtain the following theoretical sensitivity order for the eight derivatives (1, 3, 4, 5, 6, 7, 8, and 9): CH₃ < H < NO₂ < Cl < NHNO₂ < N₃ < NH₂ < N⁺₂. Comparing the experimental sensitivity ordering $(CH_3 < NH_2 < H < NHNO_2 < Cl < NO_2 < N_3 < N_2^+)$, one can see that there are some discrepancies between the two sets. In our opinion there are two reasons for it. First, the discrepancies might be due to the different decomposition pathway undergone by 5-nitroaminotetrazole, 5-nitrotetrazole, and 5-aminotetrazole. The self-consistent reaction field (SCRF) calculations show that unlike most C-substituted tetrazoles, 5-NO2 and 5-NHNO2 tetrazole derivatives exist mainly in the 2H-tetrazole (not 1H-isomer) forms in condensed phase. Therefore in the cases of 5-nitro- and 5-nitroaminotetrazoles, explosion is initiated, most probably by the decomposition of 5-substituted 2H-tetrazole derivatives. For 5-aminotetrazole, there is indeed experimental evidence indicating that the pyrolysis mechanism of 5-aminotetrazole is different from Figure 5. The second reason for the discrepancies is the smaller activation gap (see especially the reaction barrier from compound 3 to compound 7), which is beyond the accuracy of our theoretical calculation. Analysis of activation energy from PM3 calculation shows that the activation energies E_a (PM3) are in the following increasing order: N₂ > N₃ > $NO_2 > Cl > NHNO_2 > NH_2 > H > CH_3$, in accordance with the experimental sensitivity order except for 1H-tetrazole and 5-aminotetrazole.

Metallic salts of 5-substituted tetrazole derivatives

Table 9 contains the activation energies and the experimental impact insentivities for metallic salts of 5-substituted tetrazole derivatives.

Compounds			E_a	S
Mercuric	NitroTzc	(I)	130.76	15
Mercurous	NitroTz	(II)	156.68	50
Mercuric	nitroaminoTz	(III)	183.43	70
Lead	nitroaminoTz	(IV)	217.01	100
Thallous	AzoTz	(V)	232.94	150
Potassium	NitroTz	(VI)	233.36	200

Table 9. Activation energies obtained from PM3 calculations $[kJ mol^{-1}]$ and relative sensitivity (*S*)

It is notable from Table 9 that the smaller the activation energy, the smaller S is, thus the more sensitive the compound is. Figure 6 illustrates the relationship between the calculated activation energies E and the sensitivity S.



Figure 6. Activation energy of the N (1)-N (2) bond breaking to the experimental impact sensitivity of some tetrazole metal salts.

From Table 9 we can also see that the calculated activation energy for potassium nitrotetrazole VI is a little smaller, which results in that the last point in Figure 6 deviates from the line a little. This might be due to the use of the potassium-like sparkle model as the parameter for potassium in the program. Regressing the line for the first five points, we obtained:

$$E_a = 122.6 + 0.779S$$

The correlation coefficient is 0.973. The higher correlation coefficient indicates that the proposed 'substituent model' for treating the metal salts of tetrazole derivatives is successful.

Applications in molecular design

As for polynitroadamantanes (PNAs), the promising candidates of HEDMs, there have been little reports on their experimental sensitivity and thermolysis mechanisms. So, we use the two theoretical criteria to study the relative sensitivity for them to find the object compounds. In order to elucidate the pyrolysis mechanism of PNAs, two possible initial steps in the pyrolysis route are considered: (1) breaking the C-NO₂ bond (2) breaking the C-C bond on the skeleton. Table 10 gives the results of the homolysis of the C-C and C-NO₂ bonds using UHF-PM3 method [29].



Figure 7. The structure and atomic numbering of adamantane.

From Table 10, we can see that, E_a for breaking C-NO₂ bonds are much smaller than that for breaking C-C bonds of PNAs. These results indicate that the initial step in the pyrolysis of PNAs is the rupture of C-NO₂ bond, not C-C bond on cage skeleton. As a whole, with the number (n) of nitro groups increasing, E_a for the homolysis of C-NO₂ bonds decrease. In addition, we found that E_a are also related with the electronic structure parameters, such as bond orders of C-N (B_{C-N}) of PANs.



Figure 8. Linear relationship between E_a and C-N bond orders (B_{C-N}).

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	Heats of f	ormation	E		
Compounds ^a	Dopatanta	Transitio	on States	1	2 <i>a</i>
	Reactants	C-C	C-NO ₂	C-C	C-NO ₂
1-	477.60	663.77	621.66	186.17	144.06
2-	485.00	668.65	630.12	183.65	145.12
1,2-	498.92	661.15	630.01	162.23	131.09
1,3-	483.23	674.17	621.27	191.04	138.04
1,4-	487.09	674.11	628.24	187.02	141.15
2,4-	498.44	683.07	638.79	184.63	140.35
2,6-	493.05	677.41	635.48	184.36	142.43
2,2-	535.73	707.09	635.98	171.36	100.25
1,3,5-	499.07	695.03	631.41	195.96	132.34
1,4,4-	545.08	719.10	641.72	174.02	96.64
1,2,3-	533.28	694.21	650.30	160.93	117.02
2,4,6-	515.96		651.23		135.27
1,3,8-	510.85		636.63		125.78
1,3,6-	500.88		635.56		134.68
1,3,5,7-	523.96	729.43	651.24	205.47	127.28
2,2,4,4-	649.74	826.75	731.40	177.01	81.66
2,4,6,8-	555.99		682.18		126.19
1,4,4,7-	564.62		659.76		95.14
2,2,6,6-	606.21		703.64		97.43
1,3,4,5,7-	592.61		692.52		99.91
2,4,6,8,10-	598.29		721.31		123.02
2,2,4,4,6,6-	778.29		848.69		70.40
1,3,4,5,6,7-	657.83		750.84		93.01
2,4,6,8,9,10-	642.75		761.76		119.01
1,2,3,4,5,6,7-	743.90		837.25		93.35
1,3,4,4,5,7,8-	745.42		819.33		73.91
2,2,4,4,6,6,8,8-	979.53		1042.72		63.19
1,2,3,4,5,6,7,8-	820.39		913.29		92.90
1,2,3,4,5,6,7,8,9-	932.45		1026.02		93.57.
1,2,3,4,5,6,7,8,9,10-	1046.12		1121.99		75.87
2,2,4,4,6,6,8,8,10,10-	1343.26		1369.28		26.02
1,2,3,4,4,5,6,7,8,9,10-	1198.78		1223.55		24.77

Table 10. The HOFs of the reactants, transition states and activation energies (E_a) for homolysis of C-C and C-NO2 bond of PNAs

*1- and 1,2- denote 1-nitroadamantane and 1,2-dinitroadamantane, respectively, the others are similar.

From Figure 8, we can see that there is good relationship between E_a and $B_{\text{C-N}}$ with linear correlation coefficient 0.9747, which proves the reliability of PSBO again. And the thermal stability and impact sensitivity for PANs can be identified. In addition, based on the quantum chemical calculation of heats of formation, molecular volumes and theoretical densities, we also calculated the detonation velocity (*D*) and detonation pressure (*P*) of PANs using Kamlet-Jacobs equation [30]. Conventionally a material is considered to be an HEDM if its density ρ is larger than 1.9 g cm⁻³, detonation velocity *D* greater than 9 km s⁻¹ and detonation pressure *P* higher than 40 GPa. Taking the sensitivity of PNAs into account, we can find that only PNAs with 8 ~ 10 nitro groups, can be the candidates as HEDMs from Table 11.

Compds. ^a	ρ	D	P	Compds. ^a	ρ	D	P
1-	1.34	4.32	6.77	2,2,4,4-	1.75	7.35	23.58
2-	1.34	4.36	6.92	2,2,6,6-	1.77	7.32	23.89
1,2-	1.49	5.99	14.12	1,3,4,5,7-	1.80	7.75	26.67
1,3	1.49	5.66	12.61	2,4,6,8,10-	1.82	7.84	27.44
1,4-	1.48	5.65	12.49	1,3,4,5,6,7-	1.90	8.76	35.15
2,4-	1.53	5.81	13.52	1,3,4,4,5,7-	1.92	8.45	32.93
2,6-	1.49	5.70	12.77	2,4,6 8,9 10-	1.89	8.33	31.68
2,2-	1.50	5.79	13.25	1,2,3,4,5,6,7-	1.95	8.77	35.74
1,3,5-	1.64	6.49	17.66	1,3,4,4,5,7,8-	1.96	8.81	36.21
2,4,6-	1.62	6.47	17.41	1,2,3,4,5,6,7,8-	2.03	9.24	40.59
1,4,4-	1.64	6.47	17.53	2,2,4,4,6,6,8,8-	2.00	9.18	39.82
2,4,6,8-	1.72	7.18	22.72	1,2,3,4,5,6,7,8,9-	2.02	9.39	41.86
1,3,5,7-	1.71	7.11	21.74				

Table 11. The theoretical densities (ρ) , detonation velocities (D) and pressures (P) for PNAs^a

^a Units: ΔH_{f} : kJ mol⁻¹ V: cm³ mol⁻¹, ρ : g cm⁻³, D: km s⁻¹, P: GPa.

^b1- and 1,2- denote 1-nitroadamantane and 1,2-dinitroadamantane, respectively, the others are similar.

Conclusions

We have studied molecular geometries, electronic structures, thermolysis initiation mechanisms and theoretical criteria of impact sensitivity for series of energetic materials by quantum chemical methods. Our systematic work leads to following conclusions:

1. The thermolysis initiation step of energetic compounds can be determined

by comparing the bond orders of neighboring atoms, or more safely, *via* comparing the activation energies of bond breaking reactions.

- 2. For energetic materials with the similar molecular structures and thermolysis mechanisms, there is normally a parallel relationship among the bond order of the trigger bond, the activation energy to break the bond and the experimental impact sensitivity.
- 3. The relationship between structure and property for energetic compounds, such as the two criteria of identifying relative impact sensitivity, can be used for molecular design in looking for new HEDMs.

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