

Density functional study on the derivatives of purine

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Abstract The derivatives of purine are designed through substituting the hydrogen atoms on it for nitro and amino functional groups. Geometries and frequency are analyzed at the B3LYP/6-31 G** level of density functional theory (DFT). Heats of formation (HOF), bond dissociation energy (BDE) and detonation parameters (detonation velocity and detonation pressure) are obtained in detail at the same level. It is found that the BDE values of all derivatives are over $120\text{KJ}\cdot\text{mol}^{-1}$, and have high positive heats of formation. These derivatives possess excellent detonation properties, for B1, B2, and C, the detonation velocity are 9.58, 9.57, and $9.90\text{ km}\cdot\text{s}^{-1}$, and the detonation pressure are 43.40, 46.05, and 46.37 Gpa, respectively, the detonation performances are better than cyclotrimethylenetrinitramine (RDX) and cyclotetramethylenetetranitramine (HMX). Hence, the derivations of purine may be promising well-behaved high energy density materials.

Keywords Bond Dissociation Energy · Density Functional Theory · Detonation properties · Heats of formation · Isodesmic reaction

Introduction

As the good prospects of nitro and amino substituents in the low sensitivity, high energy density explosives field, it has attracted a lot of attention in the last several decades [1–5].

Most research works are focused on nitroazole, nitroazine, and nitropyridine and some important results have been achieved. For example, three derivatives of 2,4,5-tri nitroiminazole (PTNI) are synthesized by Talawar [6], the 1-methyl-2,4,5- trinitroiminazole (MTNI) are confirmed to have performance relative to the RDX [7], and some derivatives of tetrazine with high performance are synthesized [8], and so on. These molecules are broadly researched because the heterocycles usually have high nitrogen content and high positive heat of formation, which can increase substantially the energy density of molecules. Furthermore, π aromatic bonding can also be located in these heterocycles and stabilize the molecule. These molecules are usually insensitive to the static, friction, and impact. To our knowledge, purine has high nitrogen contents and conjugate action in system [9], but we cannot find that it is studied as high energy density compounds (HEDCs) so far. Purine is a heterocyclic molecule with four nitrogen atoms, and it has been known as an important biomolecule because it is one of the basic groups to combine nucleonic acids [10–13]. Moreover, the purine has been studied in drug by Hongli Zhao and Lixin Zhou [14], and they obtained satisfying consequence. Purine has a nitrogen content of above 46%, and it is also fascinating because four hydrogen atoms are located at the ring and can be substituted by additional functional groups, such as high-energy nitro group or amino group as Lewis base. In fact, amino-substituted purine and nitro-substituted purine have been synthesized in experiment [15]. In general, the introduction of nitro will make the molecule more explosive, but the introduction of amino will make the molecule more insensitive because they can form intermolecular and intramolecular bonds to stabilize the molecule and increases crystal density. If we introduced these two groups into purine and varied the positions and the numbers of substituent, we could expect a molecule

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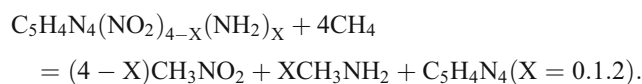
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with appropriate sensitivities and high energy densities. Therefore, 11 derivatives of purine are designed through substituting the hydrogen atoms in purine for amino or nitro groups, and the geometry, thermodynamic characters, and detonation performance are calculated in detail by using B3LYP method with 6-31 G** basis set

Calculation methods

All geometries are optimized using at G03 program package [16] on a desktop computer. The calculation method used was the density functional theoretical (DFT) method using Beche's 3-parameter exchange functional plus the correlation functional of Lee, Yang, and Parr (abbreviated B3LYP) [17] along with the standard Gaussian basis set labeled 6-31 G** [18]. Figure 1 shows the optimized geometries of the derivatives of purine. All optimized structures were characterized to be the local energy minimum on the potential energy surface by vibrational analysis. Based on these structures, Wiberg bond orders are calculated by using nature bond orbital (NBO) analyses [19].

It is well understood that the heat of formation (HOF), enthalpy, and so on, are important parameters to measure the explosive performance of HEDCs. So in this paper, we designed isodesmic reactions [20, 21] to get the heats of formation of the derivatives of purine. In isodesmic reactions, the bonds and electronic pairs of the reaction are kept equivalent in the products and the reactants, resulting in a remarkable reduction of the calculations' error for the heat of formation. Additionally, isodesmic reactions could counterbalance the error of electronic correlation energies and also result in a remarkable reduction of calculations' errors. In this paper, the used isodesmic reaction is designed as the following:



So, the heats of formation can be deduced from

$$\begin{aligned} \Delta_r H^0(298\text{K}) &= \sum \Delta_f H^0(\text{p}) - \sum \Delta_f H^0(\text{r}) \\ &= \sum E(298\text{K}, \text{p}) - \sum E(298\text{K}, \text{r}) + \Delta(\text{PV}) \\ &= \sum E(0\text{K}, \text{p}) - \sum E(0\text{K}, \text{r}) + \Delta\text{ZPE} + \Delta\text{HT} + \Delta n\text{RT} \end{aligned}$$

where $\sum \Delta_f H^0(\text{p})$ and $\sum \Delta_f H^0(\text{r})$ are the heats of formation of product and reactant at 298 K, respectively. The experimental thermodynamic parameters of CH_4 , CH_3NO_2 , CH_3NH_2 , from the references [22], the thermodynamic parameters of $\text{C}_5\text{H}_4\text{N}_4$ are obtained by theoretical calculation [23], which are listed in Table 1. $\sum E(0\text{K}, \text{p})$ correspond to the energies sum of products at 0 K, $\sum E(0\text{K}, \text{r})$ is sum of the energies of reactant at 0 K. ΔZPE is sum of the zero

point correction energies of products and reactants. ΔH_T is the thermal correction value, $\Delta(\text{PV})$ equal $\Delta n\text{RT}$ for ideal gas, and it will be zero because Δn is zero in an isodesmic reaction. All values are calculated by us and the final results are listed in Table 2.

Bond dissociation energies (BDE) are equal to the energies arousing a homolytic cleavage reaction of chemical bond [24]. For many organic molecules, the terms "bond dissociation energy" and "bond dissociation enthalpy" often appear interchangeably in the literature [25]. Generally, it can be described by subtracting the reactant energy from the product energy. The trigger bond was described according to the principle of the smallest bond order (PSBO) [26]. The values of the bond order are obtained by NBO analysis. For example, a homolytic cleavage reaction follows:



Its dissociation energy can be described by

$$\text{BDE}_{(\text{RA}-\text{BR}')} = [E_{\text{RA}\cdot} + E_{\text{R}'\text{B}\cdot}] - E_{(\text{RA}-\text{BR}')}$$

In which $\text{RA}-\text{BR}'$ is reactant, and $\text{RA}\cdot$ and $\text{R}'\text{B}\cdot$ are product radical. Therefore, the bond dissociation energy are calculated based on these equations and the results are listed in Table 3

The detonation velocity (D) and detonation pressure (P) are very important factors for HEDCs. The Kamlet-Jacobs approach has been proved to be reliable [27]. The equation is shown as:

$$\begin{aligned} D &= 1.01(N\bar{M}^{1/2}Q)^{1/2} (1 + 1.30\rho) \\ P &= 1.558\rho^2 N\bar{M}^{1/2}Q^{1/2} \end{aligned}$$

N is the moles of gas produced by per gram of explosive, and \bar{M} is the mean molecular weight of the gaseous detonation products. Q is the heat of detonation. For $\text{C}_a\text{H}_b\text{O}_c\text{N}_d$ explosives, N , \bar{M} and Q are calculated according to Table 4.

Results and discussion

Heats of formation

The heat of formation is the performance that is considered when the high energy density compounds are designed. From Table 2, we can conclude that the derivatives of purine have high positive heats of formation, consistent with previous reports that energetic high-nitrogen heterocycles have high positive heat of formation value and can increase with the number of nitro growing. From A1 to A6, we found the heat of formation values of A1, A3, and A4 are smaller than A2, A5, and A6. The result shows that the higher heat of formation, the smaller the distance between nitro groups.

Fig. 1 The schemed structures of the isomers of nitro- and amino-substituted purine obtained at B3LYP/6-31 G** level

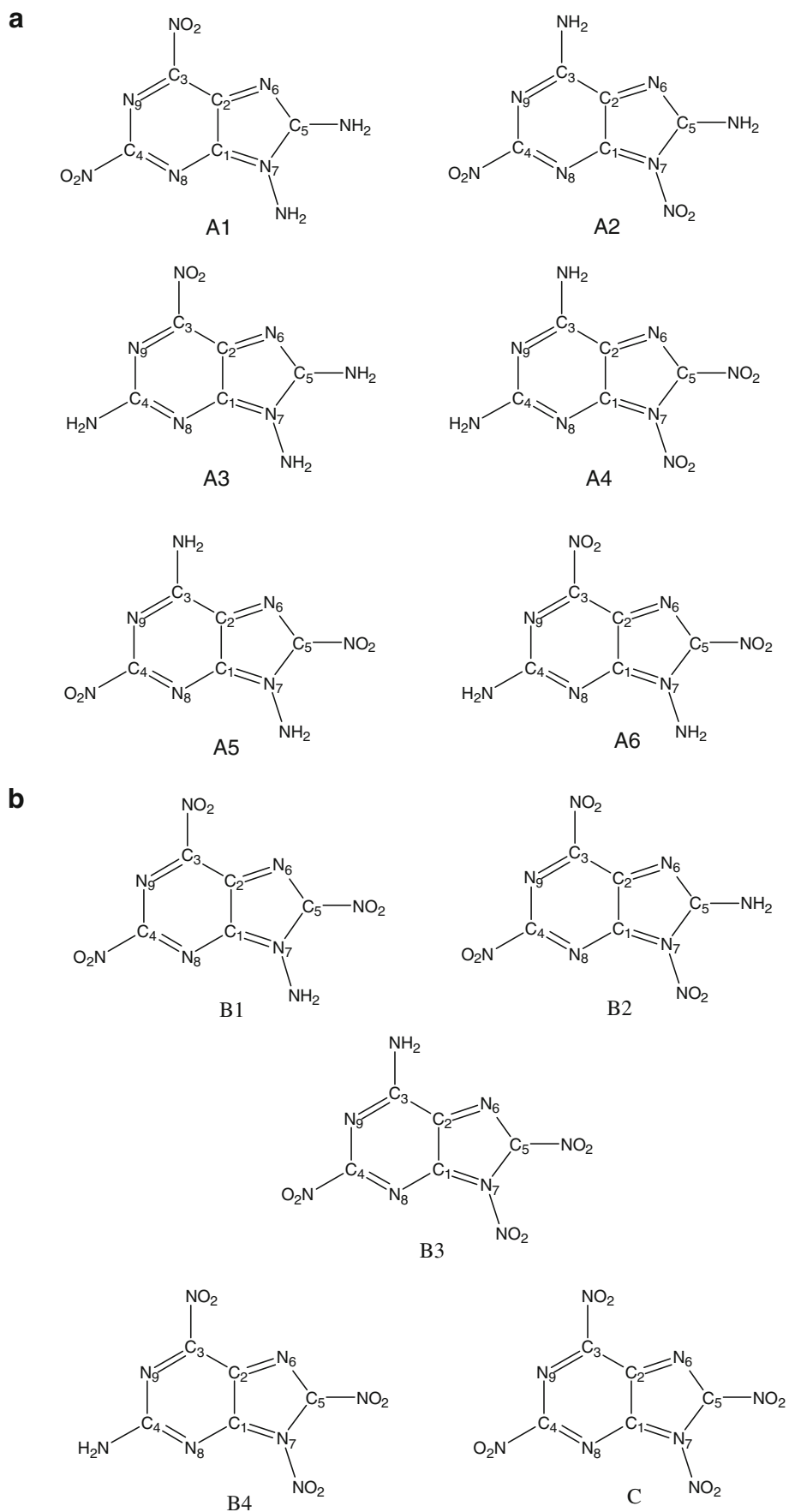


Table 1 Total energies (E_0), zero point energies (ZPE), thermal correction values (H_T), and the experimental heats of formation (HOFs) of reference molecules used in paper

Compound	E_0 /(a.u)	ZEP/(a.u)	H_T /(a.u)	HOF/(KJ·mol ⁻¹)
CH ₃ NH ₂	-95.87856	0.06424	0.00433	-23.0
CH ₃ NO ₂	-245.07755	0.04995	0.00529	-74.7
C ₅ H ₄ N ₄	-412.04627	0.09493	0.00664	18.0
CH ₄	-40.52794	0.04484	0.00381	-74.8

The heat of formation value of B1 is biggest in B1 to B4. These compounds, in which hydrogen atoms on nitrogen are replaced by amino, have small heat of formation values. This is because the conjugation role between amino and purine ring is weaker than nitro and purine ring.

Bond dissociation energies

The sensitivity and stability of the energetic compounds are directly relevant to the bond strength, which is commonly described by BDE. Generally speaking, the stronger the weakest bonds are, the more stable the energetic materials are. From Table 3, we found that C-NO₂ or N-NO₂ has the lowest bond order, so they are easier to break than other bonds according to the principle of the smallest bond order [28]. The BDE after zero point corrections is 17.3–26.2 kJ·mol⁻¹ lower than that without zero point energy corrections. However, the order of the BDE and pyrolysis mechanism is not affected by the zero-point energies. A4, B3, B4, and C have smaller BDE values than other derivatives. The fact results from close distance and strong space

Table 2 Total energies (E_0), zero point energies (ZPE), thermal correction values (H_T), heat of formation (HOF) of the derivatives of purine at the B3LYP/6-31 G** level

Compound	E_0 /(a.u)	ZEP/(a.u)	H_T /(a.u)	HOF/(KJ·mol ⁻¹)
A1	-931.62494	0.13235	0.01628	73.9
A2	-931.64520	0.13186	0.01519	16.7
A3	-931.64126	0.13181	0.01506	26.3
A4	-931.63878	0.13176	0.01534	36.1
A5	-931.62567	0.13295	0.01500	70.6
A6	-931.61738	0.13228	0.01535	91.4
B1	-1080.71968	0.11758	0.01627	945.6
B2	-1080.74946	0.11686	0.01628	826.6
B3	-1080.74397	0.11714	0.01634	842.1
B4	-1080.73907	0.11684	0.01641	854.1
C	-1229.83486	0.10158	0.01773	1071.6

Table 3 Calculated bond dissociation energies, trigger bond, and bond order of the purine derivatives at the B3LYP/6-31 G** level

Compound	BDE (KJ·mol ⁻¹)	BDE _{zpe} (KJ·mol ⁻¹)	Trigger bond	Bond order
A1	276.7	259.1	C ₄ -NO ₂	0.8563
A2	275.9	258.0	C ₄ -NO ₂	0.8460
A3	263.8	246.5	C ₃ -NO ₂	0.8786
A4	139.1	120.2	N ₇ -NO ₂	0.8714
A5	269.9	252.5	C ₄ -NO ₂	0.8387
A6	249.9	232.6	C ₃ -NO ₂	0.8636
B1	262.2	245.2	C ₄ -NO ₂	0.8470
B2	268.0	250.4	C ₄ -NO ₂	0.8523
B3	166.3	140.4	N ₇ -NO ₂	0.8278
B4	158.3	134.3	N ₇ -NO ₂	0.8544
C	213.3	187.5	N ₇ -NO ₂	0.8053

^a BDE_{zpe} denotes the bond dissociation energies including zero-point energy corrections

repulsion between two adjacent nitro, which lead to thermodynamics stability declining. It is interesting to note that A1, A2, A5, and A6 have relatively lower bond order but higher BDE values. However, the A4 has higher bond order but lower BDE value compared to A1, A2, A5, and A6. This result shows that to judge the thermal stability of purine derivatives is not by the bond order simply. The BDE values of B1, B2, in which hydrogen bond exist, are bigger than B3, B4, in which the distance of between amino and nitro is too distant to form hydrogen bond. Hence, steric hindrance and hydrogen bond play an important role in increasing thermodynamics stability aspects. The BDE values of all molecules that were designed by us are over 120KJ·mol⁻¹, which meets the requirements as HEDCs. Compared to the BDE value of HMX (166.4 KJ·mol⁻¹) at the same theoretical level, the derivatives of purine designed by us are all more stable except for A4, B3, and B4, which means they are promising well-behaved HEDCs.

Explosive performance

In these derivatives, the theoretical density could replace the loading density. The theoretical density was obtained from the molecular weight divided by the average molecular volume. The volume was defined as inside a contour of 0.001 electrons·bohr⁻³ density that was evaluated using a Monte Carlo integration. This method has been successfully applied to high-nitrogen compounds [29]. Basis of the molecule density values, explosive performances of these derivations are obtained and listed in Table 5. For a comparison, the experimental detonation performances of two known explosives RDX and HMX are also listed in this table. From Table 5, we found that the detonation performance of purine

Table 4 For the $C_aH_bO_cN_d$ explosives, the values of N, M, Q, are calculated following the formula

Parameters	Explosives components conditions		
	$C \geq 2a+b/2$	$2a+b/2 > c \geq b/2$	$b/2 > c$
N	$b+2c+2d/4M$	$b+2c+2d/4M$	$b+d/2M$
M	$4M/b+2c+2d$	$56d+88c-8b/b+2c+2d$	$2b+28d+32c/b+d$
$Q \cdot 10^{-3}$	$28.9b+94.05a+0.239\Delta H_f^0/M$	$28.9b+94.05(c/2-b/4)+0.239\Delta H_f^0/M$	$57.8c+0.239\Delta H_f^0/M$

M is the molecular weight of the title compound ($\text{g}\cdot\text{mol}^{-1}$)

derivatives will enhance with nitro number increasing. Tetranitropurine have best detonation performance ($\rho=2.00 \text{ g}\cdot\text{cm}^{-3}$, $D=9.90 \text{ km}\cdot\text{s}^{-1}$, $P=46.37\text{Gpa}$) in all molecules that are designed by us. B1, B2, C have better molecule density, detonation velocity, and detonation pressure than HMX and RDX, and meet the requirements as HEDCs ($\rho \approx 1.9 \text{ g}\cdot\text{cm}^{-3}$, $D \approx 9.0 \text{ km}\cdot\text{s}^{-1}$ and $P \approx 40\text{Gpa}$) [30]. This is because conjugate action and intramolecular hydrogen bonds exist in the system. In addition, the high nitrogen contents also play an important role in improving detonation performance.

Conclusions

In this paper, the properties of the derivatives of purine have been studied theoretically. The stable geometries of the 11 compounds were optimized at B3LYP/6-31 G** level. The heats of formation, bond dissociation energies, and explosive performance are calculated at the same level. The results are listed as follows:

- (1) All purine derivatives have high positive heats of formation which can increase with the number of nitro

Table 5 Detonation properties of the derivatives of purine at B3LYP/6-31 G** level together with HMX and RDX

Compound	$\rho(\text{g}\cdot\text{cm}^{-3})$	$Q(\text{KJ}\cdot\text{g}^{-1})$	P(Gpa)	D($\text{km}\cdot\text{s}^{-1}$)
A1	1.75	947.13	22.28	7.15
A2	1.81	890.17	23.12	7.21
A3	1.83	899.73	23.79	7.29
A4	1.93	909.49	26.58	7.58
A5	1.67	943.85	20.29	6.92
A6	1.90	964.56	26.53	7.61
B1	2.01	1921.89	43.40	9.58
B2	2.10	1816.58	46.05	9.75
B3	1.89	1830.27	37.44	9.06
B4	1.75	1840.92	32.19	8.59
C	2.00	2107.89	46.37	9.90
HMX ^b	1.91	1633.9	39.00	1.82
RDX ^b	1.82	1591.03	34.00	1.91

^b Experimental value from ref [33]

- (2) The bond dissociation energies values of all derivatives are over $120\text{KJ}\cdot\text{mol}^{-1}$, which is a standard to estimate high energy density compounds, which shows that the all derivatives are very stable. In addition, this result also shows that to judge the thermal stability of purine derivatives is not by the bond order simply.
- (3) The explosive performance of B1, B2, and C are over HMX and RDX, especially C, the detonation performance ($\rho=2.00 \text{ g}\cdot\text{cm}^{-3}$, $D=9.90 \text{ km}\cdot\text{s}^{-1}$, $P=46.37\text{Gpa}$) would range up with CL-20(2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane) [31].

Therefore, the derivatives of purine may become a viable candidate for a new high energy density compound, if they can be synthesized easier. For example, they can be synthesized via substitution reactions [32]. This paper may provide some basis information of physical chemistry and explosive properties for people interested in these compounds.

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References

1. Sewell TD, Menikoff R, Bedrov D, Smith GD (2003) J Chem Phys 119:7417–7426
2. Shalashilin DV, Thompson DL (1997) J Phys Chem A 101:961–966
3. Nielsen AT, Chafin AP, Christian SL, Moore DW, Nadler MP, Nissan RA, Vanderah DJ, Gilardi RD, George CF, Flippen-Anderson JL (1998) Tetrahedron 54:11793–11812
4. Wang GX, Gong XD, Du HC (2011) Liu Y, Xiao HM. J Phys Chem A 115:795–804
5. Liu Y, Gong XD, Wang L, Wang GX, Xiao HM (2011) J Phys Chem A 115:1754–1762
6. Jadhav HS, Talawar MB, Sivabalan R, Dhavale DD, Asthana SN, Krishnamurthy VN (2007) J Hazard Mater 143:192–197

7. Jin RCGC, Kwang JK, Jeong KK (2000) *Insensitive Munitions & Energetic Materials Technology Symposium*, p 393
8. Nurullah S (2007) *Tetrahedron* 63:4199–4236
9. Wade LG (2009) *Organic Chemistry*, 6th edn. Higher Education Press, China
10. Rosemeyer H (2007) *Chem Biodivers* 1:361–401
11. Hirschi JS, Arora K, Brooks CL 3rd, Schramm VL (2010) *J Phys Chem B* 114:16263–16272
12. Lecka J, Molski S, Komoszynski M (2010) *Nucleos Nucleot Nucl* 29:647–657
13. Sharma S, Das M, Kumar A, Marwaha V, Shankar S, Singh P, Raghu P, Aneja R, Grover R, Arya V, Dhir V, Gupta R, Kumar U, Juyal RC, Thelma BK (2009) *Pharmacogn Genom* 19:823–828
14. Zhao HL, Zhou LX (2011) *Comput Theor Chem*. doi:10.1016/j.comptc.2011.10.010
15. Verga D, Nadai M, Doria F, Percivalle C, Di Antonio M, Palumbo M, Richter SN, Freccero M (2010) *J Am Chem Soc* 132:14625–14637
16. Frisch MJ, Trucks GW, Schlegel BH et al (2004) *Gaussian 03, Revision C02*. Gaussian Inc, Wallingford, CT
17. Parr RG, Yang W (1989) *Density Functional Theory of Atoms and Molecules*[M]. Oxford University Press, New York
18. Hahre WJ, Ditchfield R, Pople JA (1972) *J Chem Phys* 56:2257
19. Woon DE, Dunning TH (1993) *J Chem Phys* 98:1358–1371
20. Xu XJ, Xiao HM, Ju XH et al (2006) *J Phys Chem A* 110:5929–5933
21. Chen ZX, Xiao JM, Xiao HM et al (1999) *J Phys Chem A* 103:8062–8066
22. Wei T, Zhu WH, Zhang JJ, Xiao HM (2010) *J Hazard Mater* 179:581–590
23. Nathanael SG, Soojin K, Peter GS (1997) *Tetrahedron Lett* 38:1161–1164
24. Owens FJ (1996) *J Mol Struct (THEOCHEM)* 370:11–16
25. Blanksby SJ, Ellison CB (2003) *Acc Chem Res* 36:255–263
26. Fan JF, Xiao HM (1996) *J Mol Struct (THEOCHEM)* 365:225–229
27. Kamlet M, Jacobs SJ (1968) *J Chem Phys* 48:23–35
28. Zhang JY, Du HC, Wang F, Gong XD, Huang YS (2011) *J Phys Chem A* 115:6617–6621
29. Wang GX, Shi CH, Gong XD, Xiao HM (2009) *J Phys Chem A* 113:1318–1326
30. Xiao HM, Xu XJ, Qiu L (2008) *Theoretical design of high energy density materials*. Science Press, Beijing
31. Ghule VD, Jadhav PM, Patil RS, Radhakrishanan S, Soman T (2010) *J Phys Chem A* 114:498–503
32. Rodenko B, Koch M, van der Burg AM, Wanner MJ, Koomen GJ (2005) *J Am Chem Soc* 127:5957–5963
33. Talawar MB, Sivabalan R, Mukundan T, Muthurajan H, Sikder AK, Gandhe BR, Subhananda Rao A (2009) *J Hazard Mater* 161:589–607