

# Dinitroamino benzene derivatives: a class new potential high energy density compounds

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**Abstract** Dinitroamino benzene derivatives are designed and studied in detail with quantum chemistry method. The molecular theory density, heats of formation, bond dissociation energies, impact sensitive and detonation performance are investigated at DFT-B3LYP/6-311G\*\* level. The results of detonation performance indicated most of the compounds have better detonation velocity and pressure than RDX and HMX. The N-N bond can be regard as the trigger bond in explosive reaction, and the bond dissociation energies of trigger bond are almost not affected by the position and number of substituent group. The impact sensitive are calculated by two different theory methods. It is found that the compounds, which can become candidates of high energy materials, have smaller  $H_{50}$  values than RDX and HMX. It is hoped that this work can provide some basis information for further theory and experiment studies of benzene derivatives.

**Keywords** Benzene derivatives · Density function theory · High energy density compounds · Impact sensitive · Quantum chemistry

## Introduction

High-nitrogen-content compounds have attracted significant attention in the area of high-energy-density compounds (HEDCs) research because of their novel properties, such as high density and a high positive heat of formation [1–6], which can be directly attributed to the large number of

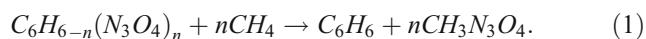
inherently energetic N-N and C-N bonds contained in the molecule [7, 8]. An ideal explosive is considered to be one which achieves high detonation performance, but is insensitive enough to permit safe handling. However, it should not be, at the same time, so insensitive that detonation becomes difficult or impractical [9]. To our best knowledge, nitro is an important group and benzene ring is a significant parent molecule of energetic materials. Some high energetic materials are designed and synthesized based on nitrobenzene. For example, 2,4,6-trinitrobenzene (TNT) [10, 11], 3-dimethyl-2,4,6-trinitrotoluene (TNX), 1,3,5-trimethyl-2,4,6-trinitrobenzene (TNM), triamino-trinitrobenzene (TATB) [12, 13] and pentanitrobenzene are important energetic materials. Especially TNT, which was prepared by Wilbrand in 1863 and was first studied in detail by Beilstein and Kuhlberh in 1870. By 1914, it became the standard explosive for all armies in World War I. And TATB has excellent stability in the range 260–290 and is known as a heat-resistant explosive. However, it is regretful that the detonation performance of these nitrobenzene compounds cannot meet the requirement as HEDCs. So we wish to get some excellent high energetic molecules based on benzene ring via molecule designing to meet the future civil and military requirements. In our present work, the hydrogen atoms of benzene are replaced by dinitroamino group, and obtained a series of dinitroamino-benzene derivatives. The main differences among the dinitroamino group and the nitro group, nitroso group, and the nitrate group are the amount of oxygen present and nitrogen present. The high nitrogen content can lead to high crystal density, which is associated with increased denotation performance. The high oxygen content has an advantage for combustion reaction. For the new compounds, thermodynamic stabilities and detonation properties are studied in detail with quantum chemistry theory.

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## Computational methods

Gaussian 03 program packages [14] have been employed in this study. The hybrid density functional DFT-B3LYP [15] method with the 6-311G\*\* basis set was used. The optimized structures were characterized to the relative energy minimum of the potential surface by frequency calculation. Wiberg bond index has been computed for the optimized geometries of designing molecules by natural bond orbital (NBO) [16] analysis at the same theory level.

The isodesmic reaction [17, 18], which has proved to be reliable, used to derive the HOFs of benzene derivatives at 298 K is as follows:



For the isodesmic reaction, the heat of reaction (HOF)  $\Delta H_{298}$  at 298K can be calculated from the following equation:

$$\Delta H_{298} = \Delta H_{f,p} - \Delta H_{f,R}, \quad (2)$$

where  $\Delta H_{f,p}$  and  $\Delta H_{f,R}$  are the HOFs of the reactants and products at 298 K, respectively. The experimental HOFs of the reference  $CH_4$ ,  $C_6H_6$ , and  $CH_3N_3O_4$  are available, which are obtained from NIST WebBook. Therefore, the HOFs of dinitroamino-benzene derivatives can be determined when the heat of reaction  $\Delta H_{298}$ . Now the most important task is to compute  $\Delta H_{298}$ , which can be calculated using the following expression:

$$\Delta H_{298} = \Delta E + \Delta ZPE + \Delta H_T + \Delta nRT, \quad (3)$$

where  $\Delta E$  is the change in total energy between the reactants and products at 0 K,  $\Delta ZPE$  is the difference between the zero-point energy of reactants and products,  $\Delta H_T$  is the thermal correction from 0 to 298 K, and  $\Delta nRT$  is the work term, which equals zero here.

Since the condensed phases of most energetic compounds are solid, calculating detonation properties requires knowledge of the solid-phase heat of formation ( $\Delta H_{f,solid}$ ). According to Hess's law of constant heat summation. The gas-phase heat of formation ( $\Delta H_{f,gas}$ ) and heat of sublimation ( $\Delta H_{sub}$ ) can be used to evaluate the solid-phase heats of formation:

$$\Delta H_f(s) = \Delta H_f(g) - \Delta H_{sub}, \quad (4)$$

where  $\Delta H_{sub}$  is the sublimation enthalpy evaluated using Eq. (5) suggested by Rice and Politzer et al. [19–21].

$$\Delta H_{sub} = \alpha_1(SA)^2 + \beta_1(\nu\sigma_{tot}^2)^{0.5} + \lambda_1, \quad (5)$$

where SA is the area of the isosurface of 0.001e Bohr<sup>-3</sup> electron density of a molecule. The values of coefficient  $\alpha_1$ ,  $\beta_1$ , and  $\lambda_1$  are taken from ref. [19].

The empirical Kamlet-Jacobs equations were employed to estimate the values of D and P for the high-energy materials containing C, H, O, and N [22]:

$$D = 1.01 \left( N\bar{M}^{1/2} Q^{1/2} \right)^{1/2} (1 + 1.30\rho_0). \quad (6)$$

$$P = 1.558\rho_0^2 N\bar{M}^{1/2} Q^{1/2} \quad (7)$$

D is the detonation velocity (km s<sup>-1</sup>), P is the detonation pressure (GPa). N is the moles of gas produced per gram of explosive, and  $\bar{M}$  is the mean molecular weight of the gaseous detonation products. Q is the heats of detonation (cal g<sup>-1</sup>).  $\rho$  is molecular theory density (g cm<sup>-3</sup>), which was calculated from the molar weight (M) divided by the average value molar volume (V), which was gained from the arithmetic average value of 100 single point molar volumes, defined as the volume of 0.001 electrons Bohr<sup>-3</sup> electron density envelope and computed by Monte Carlo integration, but the procedure used to estimate densities can lead to significant errors. Peter Politzer and coworker considered that the solid density can be corrected by the electrostatic potential [23, 24]. The method is shown by Eqs. (8)–(12):

$$\text{Crystal density}(\rho_0) = \alpha(M/Vm) + \beta(\nu\sigma_{tot}^2) + \gamma \quad (8)$$

$$\begin{aligned} \sigma_{tot}^2 = \sigma_+^2 + \sigma_-^2 = & \frac{1}{m} \sum_{i=1}^m [V^+(r_i) - \bar{V}_s^+]^2 \\ & + \frac{1}{n} \sum_{j=1}^n [V^-(r_j) - \bar{V}_s^-]^2 \end{aligned} \quad (9)$$

$$\nu = \sigma_+^2 \sigma_-^2 / |\sigma_{tot}^2|^2 \quad (10)$$

$$V_s^+ = \frac{1}{m} \sum_{i=1}^m V^+(r_i) \quad (11)$$

$$V_s^- = \frac{1}{n} \sum_{j=1}^n V^-(r_j), \quad (12)$$

where  $\nu$  is balance parameter, V(r) is electrostatic potential, V(r<sub>i</sub>) is the value of V(r) at any point r<sub>i</sub> on the surface,  $V_s^+(r_i)$  and  $V_s^-(r_j)$  represent the positive and negative value of V(r) on the surface.  $\bar{V}_s^+$  and  $\bar{V}_s^-$  are their averages,  $\sigma_{tot}^2$  is the total variance, in this paper, these parameter of the title compounds were obtained at B3LYP/6-311G\*\* level.

The strength of bonding, which can be evaluated by BDE, is fundamental to understanding chemical processes [25]. The homolysis reaction of A-B is used to calculate the BDEs [26]:



$$BDE_{(A-B)} = [E_{A^\bullet} + E_{B^\bullet}] - E_{(A-B)}. \quad (14)$$

The bond dissociation energy with zero-point energy (ZPE) correction can be calculated by Eq. (8):

$$BDE_{(A-B)ZPE} = [E_{A^\bullet} + E_{B^\bullet}] - E_{(A-B)} + \Delta ZPE \quad (15)$$

$BDE_{(A-B)}$  is the BDE of the bond A-B,  $E_{(A-B)}$ ,  $E_{A^\bullet}$  and  $E_{B^\bullet}$  are the total energies of parent molecule and the corresponding radicals, respectively.

The impact sensitivity, usually expressed as the impact sensitivity index (i.e., characteristic height- $H_{50}$ ), is one of the qualities to scale the reliable performance of energetic materials. It is usually measured by drop-weight impact tests. The characteristic height was estimated using the Eq. (16) suggested by Cao [27]:

$$H_{50} = 0.1926 + 98.64Q_{NO_2}^2 - 0.03405OB_{100} \quad (16)$$

$Q_{NO_2}$  is nitro net charge.  $OB_{100}$  is oxygen balances.

Another method obtained characteristic height was proposed by Pospil et al. [28–30].

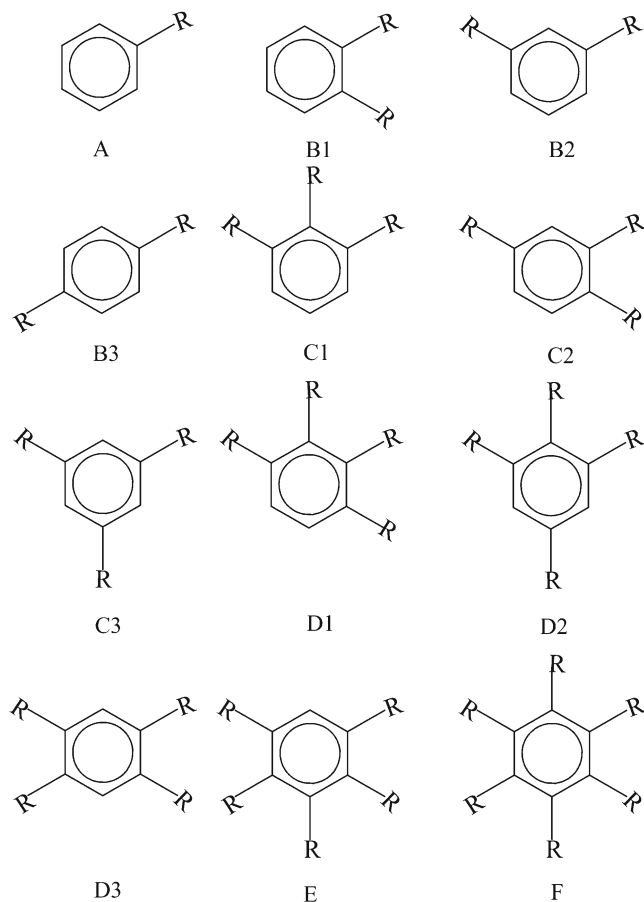
$$H_{50} = \alpha_2\sigma_+^2 + \beta_2\gamma + \lambda_2, \quad (17)$$

where the values of coefficients are taken from ref. [28].

## Results and discussion

### Heats of formation

Before discussing the results on dinitroamino benzene derivatives, all molecular structures are presented in Fig. 1. Heat of formation reflects the energy content of a compound. High positive HOF is usually required for an effective energetic material. Previous studies indicated that the calculated values of HOF by applying the isodesmic reactions agree well with experiments when appropriate reference compounds have been chosen. Table 1 lists the relevant data of reference compounds. The HOF(g) and HOF(s) of the title compounds are listed in Table 2. Evidently, all the derivatives of benzene have quite large positive HOF(s), which is favorable for high energy density materials. In addition, all HOF(s) values decline comparison HOF(g) values, and there is a good linear relationship between HOF(s) and the number of substituent groups (n):  $HOF = 100.6n + 1280.0$  ( $n = 1 - 6$ ,  $R = 0.999$ ). It should be pointed out that the average values are used for the isomers. We



**Fig. 1** Illustration of the molecular structures of the derivatives of benzene { $R=N(NO_2)_2$ }

also note that the HOF(s) of the benzene derivatives are not satisfactory with the relationship of simple group addition rule. In addition, differences can be found between the HOF(s) of the isomers, revealing that the HOF(s) is also affected by the special relative position of the substituted groups. Generally speaking, the closer the substituted groups, the more the repulsion energy, thus the higher the HOF(s), but there is a slight difference of HOF(s) for isomers in dinitroaminobenzenes.

### Detonation performances

For each title compound, explosive reaction is designed in terms of the maximal exothermal principle, that is, all the N

**Table 1** The relevant data of the reference compounds at B3LYP/6-311G\*\* level

Compounds	E(a.u)	ZPE(a.u)	HT(a.u)	HOF(kJ mol <sup>-1</sup> )
CH <sub>4</sub>	-40.53375	0.04484	0.00381	-74.9
C <sub>6</sub> H <sub>6</sub>	-232.30854	0.10017	0.00534	82.9
CH <sub>3</sub> N(NO <sub>2</sub> ) <sub>2</sub>	-504.94238	0.06819	0.00859	43.1

**Table 2** Calculated heats of formation and related parameters

Compounds	E (a.u)	ZPE (a.u)	H <sub>T</sub> (a.u)	HOF(g) (kJ mol <sup>-1</sup> )	ΔH <sub>sub</sub> (kJ mol <sup>-1</sup> )	HOF(s) (kJ mol <sup>-1</sup> )
A	-696.71897	0.11997	0.01181	1490.91	115.08	1375.83
B1	-1161.12293	0.13972	0.01827	1616.13	149.10	1467.03
B2	-1161.12389	0.13936	0.01852	1613.32	112.97	1500.36
B3	-1161.12381	0.13928	0.01854	1613.38	111.25	1502.12
C1	-1625.52266	0.15916	0.02483	1751.91	148.56	1603.35
C2	-1625.52412	0.15879	0.02510	1747.81	161.29	1586.52
C3	-1625.52462	0.15846	0.02537	1746.34	172.83	1573.51
D1	-2089.91956	0.17838	0.03147	1894.75	203.25	1691.49
D2	-2089.92089	0.17799	0.03178	1891.04	220.63	1670.42
D3	-2089.92089	0.17789	0.03189	1891.07	222.57	1668.50
E	-2554.31312	0.19737	0.03821	2046.01	270.48	1775.53
F	-3018.70113	0.21672	0.04447	2211.53	320.19	1891.34

atoms turn into N<sub>2</sub>, the O atoms react with H atoms to give H<sub>2</sub>O at first, and then form CO<sub>2</sub> with the C atom. If the number of O atoms is more than what is needed to oxidize H and C atoms, redundant O atoms will convert into O<sub>2</sub>. If the number of atoms is not enough to satisfy full oxidation of the H and C atoms, the remaining H atoms will convert into H<sub>2</sub>O, and the C atoms will exist as solid-state C. The Kamlet-Jacobs Eqs. (6) and (7) show that density is a key factor to influence D and P. Thus, density is one of the most important physical properties of all energetic materials. In the present study, single-point molecular volume calculations at B3LYP/6-311G\*\* level are performed based on geometry optimized structures, and a reliable correction method is used. The calculation datum is listed in Table 3. Detonation velocity and detonation pressure are two important performance parameters for an energetic material, and which are calculated according to molecular density and heat of detonation. Table 3 lists some important detonation performances. For a comparison, the detonation performance of HMX and RDX [31], which are applied widely at present, are also listed in Table 3. To our surprise, most benzene derivatives have large molecule density except A, the largest value and the smallest one are 2.02 and 1.65 g/cm<sup>3</sup>, respectively. From A to F, it is clear that an increase in density is observed with an increase in the number of dinitroamino group. In addition, it is also found that the closer the distance of substituent groups, the larger the molecule density is for isomers. Furthermore, an abnormal trend is found that the detonation heat values become smaller as the number of dinitroamino groups is increased, which indicates that increasing the number of dinitroamino groups does not necessarily increase the heat of detonation, nor the detonation properties [19]. The detonation velocity and detonation pressure of the title compounds are close or over than that of HMX and RDX. In other words, except A,

all compounds can become a candidate of the high energy compounds if they can be synthesized.

#### Bond dissociation energies and pyrolysis mechanism

Stability of the energetic compounds is the prime importance for the practical interest of the explosive material. In general, N(C)-NO<sub>2</sub> bond is the weakest in the energetic molecules and its cleavages is the common primary fission step of energetic materials under heat, impact, and electric spark stimulation [32]. In the present work, the BDEs of C-NO<sub>2</sub> and N-NO<sub>2</sub> are calculated at UB3LYP/6-311G\*\* level. The bond order is a measure of the overall bond strength

**Table 3** Predicted densities and detonation properties of the title compounds

Compounds	ρ <sup>a</sup> (g cm <sup>-3</sup> )	ρ <sub>0</sub> <sup>b</sup> (g cm <sup>-3</sup> )	Q (cal g <sup>-1</sup> )	D (m s <sup>-1</sup> )	P (GPa)
A	1.59	1.65	2971.92	8.5	30.1
B1	1.82	1.83	2598.51	9.7	41.7
B2	1.77	1.75	2626.17	9.4	38.4
B3	1.77	1.74	2627.42	9.4	38.1
C1	1.92	1.87	2452.07	10.0	45.5
C2	1.90	1.84	2441.83	9.9	43.8
C3	1.88	1.81	2433.92	9.8	42.4
D1	2.02	1.93	2060.98	9.9	44.8
D2	2.00	1.91	2050.86	9.7	43.6
D3	2.01	1.92	2050.86	9.8	44.1
E	2.02	1.91	1687.48	9.3	39.7
F	2.14	2.02	1435.49	9.4	41.9
RDX	1.82		1591.03	8.8	34.0
HMX	1.91		1633.90	9.1	39.0

<sup>a</sup> values are obtained with the following equation:  $\rho = M/V$

<sup>b</sup> values have been corrected

between two atoms [33]. A high value for the bond order indicates a covalent bond, while a low value shows an ionic nature. A smaller Wiberg bond index (WBI) generally indicates a weaker bond. It should be pointed out that, among bonds of the same type, the weakest bond was selected as the breaking bond, according to the principle of the smallest bond order. However, we also must aware that the mechanism for the pyrolysis of compounds is linked to their molecular structure, and is not estimated by bond order simply in practice. Table 4 lists the Wiberg bond index and BDEs of C-NO<sub>2</sub> and N-NO<sub>2</sub>. Inspecting the values from Table 4, it is found that the bond index of C-N bond is larger than that of N-N bond. The calculated BDEs agree with the change trend of bond index, which shows that N-N bond can be considered as the trigger bond in explosive reaction. Nonetheless, it is a pity that BDEs of the title compounds are smaller than that of RDX and HMX. It is noteworthy that the calculated BDE values of N-N bonds are not affected by the position and the number of substituent group.

#### Impact sensitive

To predict the impact sensitivity of HEDCs is a very important step for developing new high energy compounds. Impact sensitivity is usually characterized through a drop hammer test. It is measured by the height H<sub>50</sub> from which a given weight falling upon the compound has a 50 % probability of producing an explosion. In the present work, the H<sub>50</sub> is calculated by two difference methods. Table 5

**Table 4** Calculated bond order and bond dissociation energies (kJ mol<sup>-1</sup>) of the trigger bonds at UB3LYP/6-311G\*\* level

Compounds	B <sub>C-N</sub>	BDE	BDE <sub>ZPE</sub>	B <sub>N-N</sub>	BDE	BDE <sub>ZPE</sub>
A	0.97	412.91	393.54	0.83	117.39	100.19
B1	0.98	402.96	383.45	0.74	111.16	93.88
B2	0.97	403.51	385.10	0.82	119.38	102.11
B3	0.97	402.46	384.34	0.83	117.10	99.84
C1	0.98	405.64	386.68	0.74	116.31	98.81
C2	0.98	394.90	377.16	0.73	113.40	96.12
C3	0.98	394.88	377.22	0.81	119.04	101.99
D1	0.98	401.75	383.16	0.73	116.55	98.85
D2	0.98	388.92	371.76	0.73	117.39	99.90
D3	0.98	386.21	367.93	0.72	109.56	92.19
E	0.98	398.16	379.95	0.72	113.37	95.81
F	1.00	384.03	365.02	0.72	118.31	99.72
RDX						145.62
HMX						160.41

BDE<sub>ZPE</sub> denotes the bond dissociation energies including zero-point energy corrections

**Table 5** Calculated characteristic height (H<sub>50</sub>, cm)

Compounds	Q <sub>NO<sub>2</sub></sub> <sup>2</sup>	OB <sub>100</sub>	<sup>a</sup> H <sub>50</sub>	σ <sub>+</sub> <sup>2</sup>	v	<sup>b</sup> H <sub>50</sub>
A	0.001681	-4.81	52.22	55.11	0.2443	55.19
B1	0.000324	-2.78	31.92	95.96	0.1611	34.86
B2	0.000784	-2.78	36.46	109.30	0.1211	25.10
B3	0.000625	-2.78	34.89	113.01	0.1120	22.89
C1	0.000004	-0.76	21.89	139.41	0.0915	17.78
C2	0.000001	-0.76	21.86	144.66	0.0739	13.48
C3	0.000004	-0.76	21.89	156.95	0.0554	8.94
D1	0.000064	0.40	18.53	158.36	0.0544	8.70
D2	0.000064	0.40	18.53	160.60	0.0442	6.22
D3	0.000121	0.40	19.09	141.71	0.0518	8.17
E	0.000019	1.16	15.50	134.39	0.0354	4.25
F	0.000009	1.69	13.59	97.02	0.0296	3.09
RDX						24.0
HMX						26.0

lists H<sub>50</sub> values. <sup>a</sup> H<sub>50</sub> values are calculated by Eq. (16) based on the nitro charge and oxygen balance parameter. The Q<sub>NO<sub>2</sub></sub> is calculated by formula (18):

$$Q_{NO_2} = Q_N + Q_{O1} + Q_{O2}, \quad (18)$$

where Q<sub>N</sub>, Q<sub>O1</sub> and Q<sub>O2</sub> are the net charges on the N and O atoms in the nitro group, respectively. In this case, the Q<sub>NO<sub>2</sub></sub> with the smallest absolute Mulliken net charge value was employed.

The OB<sub>100</sub> [34] is obtained via math (19):

$$OB_{100} = 100(2n_O - n_H - 2n_C - 2n_{COO})/M, \quad (19)$$

where n<sub>O</sub>, n<sub>H</sub>, and n<sub>C</sub> represent the number of O, H, and C atoms, respectively; n<sub>COO</sub> is the number of COO, and here n<sub>COO</sub>=0 for the benzene derivatives; M is the molecular weight. Inspecting the <sup>a</sup> H<sub>50</sub> values, it is found that <sup>a</sup> H<sub>50</sub> values decrease as the number of substituent group increase. However, the difference of <sup>a</sup> H<sub>50</sub> and <sup>b</sup> H<sub>50</sub>, which is calculated by Eq. (17), is inexplicable. Nevertheless, our explanation about difference in the steric affect is neglected in Eq. (16) comparison Eq. (17). So, the <sup>b</sup> H<sub>50</sub> values are discussed in this paper. Compared with the H<sub>50</sub> values of two famous explosives RDX and HMX, it is found that absolutely most of the title compounds are more sensitive except monodinitroaminobenzene. It is noteworthy that the conclusion from H<sub>50</sub> is not very consistent with that from BDE, for example, BDEs of trigger bond are almost not affected by the number of dinitroamino group. However, it is not the case for H<sub>50</sub>, which supports the propose of Politzer [32], that the correlation between bond strength and impact sensitivity is not general but limited within certain classes of molecules.



## Conclusions

The full geometrical optimizations of benzene derivatives are performed using density function theory at B3LYP-6-311G\*\* level, without any symmetry restriction. The HOFs of the title compounds increase with the number of substitution groups added, and there is a good linear relationship between HOF and number of substitution groups. C1 displays the best detonation velocity ( $D=10.0 \text{ m s}^{-1}$ ) and pressure (45.5 GPa) in all compounds. All compounds satisfy the requirements as HEDCs except A if only detonation properties are considered. The bond dissociation energies of C-N and N-N bond are calculated at UB3LYP/6-311G\*\* level, and the N-N bond can be seen as the trigger bond in explosive reaction. Impact sensitive is calculated with two different methods. The results show that most of the compounds may be unstable. Taking all factors into consideration, B1 most likely can become a candidate of HEDCs based on high detonation velocity and pressure, large BDE value and  $H_{50}$  value.

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