Design of Energetic Materials Based on Asymmetric Oxadiazole

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A new family of asymmetric oxadiazole based energetic compounds were designed. Their electronic structures, heats of formation, detonation properties and stabilities were investigated by density functional theory. The results show that all the designed compounds have high positive heats of formation ranging from 115.4 to 2122.2 kJ mol⁻¹. −N=N= bridge−/−N=N groups played an important role in improving heats of formation while −O= bridge−/−NF₂ group made more contributions to the densities of the designed compounds. Detonation properties show that some compounds have equal or higher detonation velocities than RDX, while some other have higher detonation pressures than RDX. All the designed compounds have better impact sensitivities than those of RDX and HMX and meet the criterion of thermal stability. Finally, some of the compounds were screened as the candidates of high energy density compounds with superior detonation properties and stabilities to that of HMX and their electronic properties were investigated.

1. Introduction

High energy density compounds (HEDCs, encompassing propellants, explosives and pyrotechnics) as a type of special energy material have attracted significant attention owing to their wide applications in military and civilian. Nowadays, many works have been done in designing and synthesizing novel organic HEDCs with high densities, positive heats of formation, favorable insensitivities, excellent detonation properties, good thermal stabilities, and environmental acceptability.[1-5] One concept to design new HEDCs is to select proper parent skeletons and extra energetic substituent groups which can increase the heats of formation (ΔHf) and densities. This is because the detonation properties were mainly depended on these two parameters. Previous research have demonstrated that −NF₂ can enhance the density while −N=N group can improve the heats of formation apparently.[6,7] Besides, −NF₂ group can also acted as incendiary and oxidizing agent during the decomposition process of an explosive. Then the next work is to select proper backbone which possesses acceptable density and heat of formation.

Recently, many oxadiazole (especially 1,2,5-oxadiazole or bridged 1,2,5-oxadiazole) based energetic materials have been reported and most of the compounds presented excellent energetic properties, thermal stabilities and sensitivities.[8-12] Generally speaking, there are four oxadiazole isomers: 1,2,4-oxadiazole, 1,2,5-oxadiazole, 1,3,4-oxadiazole, and 1,2,3-oxadiazole. Among these isomers, 1,2,5-oxadiazole has the highest heat of formation while 1,2,3-oxadiazole is unstable and reverts to the diazoketone tautomer.[13] On the other hand, a series of asymmetric 1,2,4-oxadiazole and 1,2,5-oxadiazole based energetic were synthesized and investigated by Shreeve et al.[14] Then it led to the idea that how will the energetic properties change if −NF₂ and −N=N groups were introduced into the asymmetric 1,2,5-oxadiazole and 1,3,4-oxadiazole rings?

In attempts to meet the continuing need for improved energetic materials, 24 new asymmetric oxadiazole based energetic compounds were designed (Scheme 2) based on the above-mentioned statements. Their geometrical and electronic structures, heats of formation, detonation properties, impact sensitivities, thermal stabilities and electronic structures were systematically investigated. The present research may shine lights on the further experimental study of these high density energetic compounds including their synthesis and performance testing.

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Scheme 1. Different isomers of oxadiazole.

Scheme 2. The designed energetic molecules.
1.1. Computational Methods

All the calculations and simulation of the designed compounds were performed on Gaussian 03 program\cite{15} combined with density functional theory (DFT) method at B3LYP/6-311G(d,p) level. The optimized structures were checked via vibrational analysis to ensure that they were local energy minimum on the potential energy surface. Then all the calculations (frontier molecular orbitals, heats of formation, energetic properties and bond dissociation energies) were done based on these optimized structures. The accurate gas-phase heats of formation ($\Delta H_{f,gas}$) of the title molecules were predicted by designing isodesmic reactions in which the calculation errors of $\Delta H_{f,gas}$ will decrease greatly.\cite{16-21} The isodesmic reactions (Scheme 3) and equations (equations 1 and 2) were designed as follows:

$$\Delta H_{298K} = \sum \Delta H_{f,p} - \sum \Delta H_{f,R} \quad (1)$$

$$\Delta H_{298K} = \Delta E_{298K} + \Delta (PV) = \Delta E_0 + \Delta ZPE + \Delta H_f + \Delta nRT \quad (2)$$

Where $\Delta H_f$ and $\Delta H_{f,R}$ were $\Delta H_f$ of the products and reactants; $\Delta E_0$ were energy changes between products and reactants; $\Delta ZPE$ were difference between the zero-point energy (ZPE) of products and reactants; $\Delta H_f$ were thermal correction from 0 to 298 K; $n$ was the number of the energetic groups; $\Delta (PV)$ equals to $\Delta nRT$.

From the isodesmic reactions, it is found that the $\Delta H_f$ of all the related molecules were known except for CH$_4$NHNH$_3$, CH$_2$NHNCH$_3$, 1,2,5-oxadiazole and 1,3,4-oxadiazole. Therefore, atomization reactions C$_n$H$_m$N$_f$F$_g$→aC(g) + bH(g) + cN(g) + dF(g) were employed to calculated the $\Delta H_{f,gas}$ of these unknown compounds at CBS-Q level.\cite{22-23} The calculated total energies ($E_0$), zero-point energies (ZPE), thermal corrections ($H_f$) and gas-phase heats of formation ($\Delta H_{f,gas}$) of the reference compounds were summarized in Table 1.

The accurate solid-phase heats of formation ($\Delta H_{f,solid}$) were also calculated according to Hess’s law since energetic materials were mostly in condensed phase (equation 3).\cite{24}

$$\Delta H_{f,solid} = \Delta H_{f,gas} - \Delta H_{sub} \quad (3)$$

where, $\Delta H_{sub}$ is the heat of sublimation. $\Delta H_{sub}$ is the sublimation enthalpy and can be calculated by the following empirical expression (equation 4).\cite{20}

$$\Delta H_{sub} = aA^2 + b(\nu r^2)^{0.5} + c \quad (4)$$

where, $a$, $b$ and $c$ were coefficients according to the reference.\cite{20} $A$ was the surface area of the 0.001 e bohr$^{-3}$ isosurface of electronic density of the molecule; $\nu$ was the

\[\text{T able 1. Calculated total energies ($E_0$), zero-point energies (ZPE), thermal corrections ($H_f$) and heats of formation ($\Delta H_f$) of the reference compounds.}

| Compound | $E_0$ (a.u.$^\dagger$) | ZPE (kJ mol$^{-1}$)$^\ddagger$ | $H_f$ (kJ mol$^{-1}$)$^\ddagger$ | $\Delta H_{f,gas}$ (kJ mol$^{-1}$)$^\ddagger$ |
|----------|------------------------|------------------|------------------|------------------|
| CH$_4$   | $-40.533748$           | 117.0            | 10.0             | $-74.6^\ddagger$ |
| CH$_3$NF | $-294.298331$          | 122.8            | 13.6             | $-98.4^\ddagger$ |
| CH$_3$N  | $-204.148401$          | 131.7            | 14.2             | 289.9            |
| CH$_2$CH | $-79.856261$           | 195.3            | 11.6             | 84.0$^\ddagger$  |
| CH$_3$CH$_2$ | $-119.180686$          | 270.4            | 14.4             | $-104.7^\ddagger$ |
| CH$_3$NHCH$_3$ | $-135.695161$          | 254.5            | 14.9             | $-19.0^\ddagger$ |
| CH$_3$OCH | $-155.071921$          | 208.2            | 13.8             | $-184.1^\ddagger$ |
| CH$_3$CH$_2$CH$_2$ | $-158.504982$          | 345.1            | 17.7             | $-125.6^\ddagger$ |
| CH$_3$NNHCN | $-190.535853$          | 286.9            | 17.1             | 109.3$^3$        |
| CH$_3$NNHNCN | $-262.161719$          | 121.4            | 11.5             | 65.4$^4$        |
| CH$_3$NNHNCN | $-262.112125$          | 119.6            | 11.6             | 197.4$^4$        |

$^\dagger$ calculated at B3LYP/ 6-311G (d,p) level; $^\ddagger$ obtained from http://webbook.nist.gov; $c$, calculated values were calculated at the CBS-Q level.

Scheme 3. The designed isodesmic reactions.
Table 2. Calculated HOMO and LUMO energies (eV) and energy gaps ($\Delta E_{\text{LUMO-HOMO}}$) of the designed compounds.

| Compd. | A1 | A2 | A3 | A4 | B1 | B2 | B3 | B4 |
|--------|----|----|----|----|----|----|----|----|
| HOMO   | −7.44 | −8.69 | −7.75 | −8.10 | −7.29 | −8.59 | −7.03 | −7.34 |
| LUMO   | −2.71 | −3.37 | −3.00 | −3.08 | −2.15 | −2.55 | −2.34 | −2.19 |
| $\Delta E_{\text{LUMO-HOMO}}$ | 4.73 | 5.32 | 4.75 | 5.02 | 5.14 | 6.04 | 6.49 | 5.15 |
| Compd. | C1 | C2 | C3 | C4 | D1 | D2 | D3 | D4 |
| HOMO   | −6.94 | −7.87 | −7.02 | −7.56 | −7.42 | −8.57 | −7.57 | −8.14 |
| LUMO   | −2.14 | −2.65 | −2.52 | −2.37 | −2.38 | −2.90 | −2.63 | −2.60 |
| $\Delta E_{\text{LUMO-HOMO}}$ | 4.80 | 5.22 | 4.50 | 5.19 | 5.04 | 5.67 | 4.94 | 5.54 |
| Compd. | E1 | E2 | E3 | E4 | F1 | F2 | F3 | F4 |
| HOMO   | −7.36 | −8.46 | −7.44 | −7.86 | −6.85 | −7.72 | −7.01 | −7.39 |
| LUMO   | −2.14 | −2.55 | −2.42 | −2.22 | −1.97 | −2.39 | −2.22 | −2.13 |
| $\Delta E_{\text{LUMO-HOMO}}$ | 5.22 | 5.91 | 5.02 | 5.59 | 4.88 | 5.33 | 4.79 | 5.26 |

degree of balance between positive and negative potential on the isosurface. $\sigma_{\text{tot}}^2$ was the measure of variability of the electrostatic potential on the molecular surface (by Multwf program).[28]

Detonation velocity ($D$) and detonation pressure ($P$) were two important indicators to evaluate the explosive performances of energetic materials. These parameters can be predicted by Kamlet-Jacobs equations (equation 5 and 6):[29]

$$D = 1.01(\text{M}^{1.05} \text{Q}^{0.5})(1 + 1.3\rho)$$  \hspace{1cm} (5)

$$P = 1.558\rho^2 \text{M}^{1.05} \text{Q}^{0.5}$$  \hspace{1cm} (6)

where $D$ was detonation velocity (km s$^{-1}$); $P$ was detonation pressure (GPa); $N$ was the mole of detonation gases per-gram explosive (mol g$^{-1}$). $\text{M}$ was average molecular weight of these gases (g mol$^{-1}$). $Q$ was heat of detonation (cal g$^{-1}$) and $\rho$ was the density which can be modified by equation 7 proposed by Politzer et al.[29]

$$\rho = \beta_1 \left( \frac{M}{V} \right) + \beta_2 (\nu\sigma_{\text{tot}}^2) + \beta_3$$  \hspace{1cm} (7)

where $\beta_1$, $\beta_2$ and $\beta_3$ were coefficients according to the reference, $M$ was the molecular mass (g mol$^{-1}$), $V$ was the volume of a molecule (m$^3$ mol$^{-1}$).

Bond dissociation energies (BDEs) of the title compounds were presented to predict the strength of bonding and the way of bond cleavage. The accurate BDEs were given in terms of equation (8) and (9).

$$\text{BDE}_A(\text{A} - \text{B}) = E_0(\text{A}^*) + E_0(\text{B}^*) - E_0(\text{A} - \text{B})$$  \hspace{1cm} (8)

$$\text{BDE}(\text{A} - \text{B})_{\text{ZPE}} = \text{BDE}_A(\text{A} - \text{B}) + \Delta E_{\text{ZPE}}$$  \hspace{1cm} (9)

where $E_0(\text{A}^*)$, $E_0(\text{B}^*)$ and $E_0(\text{A} - \text{B})$ were the energy of A*, B* and A-B; $\Delta E_{\text{ZPE}}$ was the difference between the ZPEs of the products and the reactants.

Finally, impact sensitivity ($h_{\text{sa}}$) was calculated according to equation 10 since it can reflect the stability of an energetic material during the storage or handling process.[30]

$$h_{\text{sa}} = a\sigma_0^2 + b\frac{\sigma_0^2\sigma^2}{(\sigma_0^2 + \sigma^2)^2} + c$$  \hspace{1cm} (10)

where $a$, $b$ and $c$ were constants; $\sigma_0^2$, $\sigma^2$ were indicators of the strengths and variabilities of the positive and negative surface potentials.

2. Results and Discussion

2.1. Frontier Molecular Orbitals

Frontier molecular orbitals, which contain the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), will provide useful information in kinetic stability, chemical reactivity and optical polarizability of a molecule.[31] Table 2 presented the energy of HOMO ($E_{\text{HOMO}}$), the energy of LUMO ($E_{\text{LUMO}}$) and the energy gap ($\Delta E_{\text{LUMO-HOMO}}$) of every compound. It is found that values of $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ were from −8.69 eV (compound A2) to −6.85 eV (compound F1) and from −3.37 eV (compound A2) to −1.97 eV (compound F1), respectively. Obviously, compound A2 has the lowest HOMO/LUMO energy while compound F1 has the highest values of HOMO/LUMO energy. On the other hand, compound B2 has the highest $\Delta E_{\text{LUMO-HOMO}}$ (6.04 eV) while compound C3 has the smallest $\Delta E_{\text{LUMO-HOMO}}$ (4.50 eV). It indicates that compound C3 will be more chemical reactive compared to compound B2.

Figure 1 displays the variation trends of $E_{\text{HOMO}}$, $E_{\text{LUMO}}$ and $\Delta E_{\text{LUMO-HOMO}}$ of the title compounds. For the derivatives with the same bridges and different substituents, it is seen that series 2 have the lowest $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$ while series 1 possess the highest values (except for compounds B1 and B2). This is because the electron-withdrawing capacity of -NF$_2$ group is more stronger than that of -N$_2$ group. Compared to series 3 and 4, value of $E_{\text{HOMO}}$ were found to be different from each other while values of $E_{\text{LUMO}}$ were very close to each other. It indicates that the influence of different positions of the substituent groups on $E_{\text{HOMO}}$ was apparent and the variation trend of $E_{\text{HOMO}}$ was more obvious than $E_{\text{LUMO}}$. In view of the $\Delta E_{\text{LUMO-HOMO}}$, the variation trends of $\Delta E_{\text{LUMO-HOMO}}$ of series B and E
2.2. Heat of Formation and Density

Calculated total energies ($E_f$), thermal corrections ($H_t$), zero point energies (ZPE), molecular properties ($A$, $v$ and $\alpha_{tot}^2$), heats of formation ($\Delta H_f$) and densities ($\rho$) of the title compounds were summarized in Table 3. Obviously, the variation trends of the gas-phase heats of formation ($\Delta H_{f,gas}$) and solid-phase heats of formation ($\Delta H_{f,solid}$) were similar to each other. High positive solid-phase heats of formation ($\Delta H_{f,solid}$) were found for all the designed compounds range from 115.4 (compound D2) to 2122.2 kJ mol$^{-1}$ (compound C1). This result meets the concept for designing energetic materials since high positive $\Delta H_f$ plays an important role in improving the detonation properties of an explosive. On the other hand, the densities of the title compounds were from 1.60 (compound E1) to 2.06 g cm$^{-3}$ (compound D2). For a comparison, all the compounds possess higher $\Delta H_f$ than those of RDX (79.0 kJ mol$^{-1}$) and HMX (102.4 kJ mol$^{-1}$). However, only 14 compounds (A2, A3, A4, B2, C2, C3, C4, D2, D3, D4, E2, F2, F3 and F4) have higher densities than that of RDX (1.82 g cm$^{-3}$) while 6 compounds (A2, B2, C2, D2, D3 and F2) possess equal or higher densities to that of HMX (1.91 g cm$^{-3}$).

Figure 2 illustrates the variation trends of the solid-phase heats of formation and densities of the title compounds. For the derivatives with the same bridges and different substituents, it is found that double $-N_2$ group substituted molecules have the highest $\Delta H_{f,solid}$ while the double $-NF_2$ group substituted molecules have the highest $\rho$. It can be concluded that $-N_2$ group was more effective in improving the $\Delta H_{f,solid}$ while $-NF_2$ group was more effective in improving values of $\rho$. Besides, similar $\Delta H_{f,solid}$ and $\rho$ were found when both of $-N_2$ and $-NF_2$ groups were introduced to the oxadiazole rings at the same time. For the derivatives with the same substituents and different bridges, the $-NH-$ bridged compounds were found to have the highest $\Delta H_{f,solid}$ while the $-O-$ bridged ones have the highest $\rho$. This phenomenon shows that the $-NH-$ was the most effective bridge in improving $\Delta H_{f,solid}$ while the $-O-$ bridge

![Figure 1. Variation trends of $E_{f,gas}$, $E_{f,solid}$ and $\Delta E_{f,solid}$](image)

| Compd. | $E_f$ (a.u) | ZPE (kJ mol$^{-1}$) | $H_t$ (kJ mol$^{-1}$) | $\Delta H_{f,gas}$ (kJ mol$^{-1}$) | $\Delta H_{f,solid}$ (kJ mol$^{-1}$) | $\rho$ (g cm$^{-3}$) |
|--------|------------|-----------------|------------------|------------------|----------------------|-----------------|
| A1     | $-850.323859$ | 206.3 | 34.7 | 1127.3 | 219.4 | 0.247 | 146.8 | 107.8 | 1019.5 | 1.74 |
| A2     | $-1030.566190$ | 183.9 | 36.1 | 499.8 | 202.7 | 0.209 | 155.9 | 97.8 | 402.0 | 2.03 |
| A3     | $-940.447866$ | 195.3 | 35.3 | 806.2 | 210.1 | 0.244 | 139.8 | 102.1 | 701.4 | 1.88 |
| A4     | $-940.443436$ | 194.9 | 35.5 | 187.6 | 212.0 | 0.240 | 152.1 | 104.4 | 713.2 | 1.88 |
| B1     | $-889.657677$ | 281.6 | 38.2 | 914.9 | 239.5 | 0.250 | 137.3 | 117.0 | 797.9 | 1.66 |
| B2     | $-1069.909822$ | 259.0 | 39.6 | 277.1 | 221.1 | 0.185 | 175.1 | 106.4 | 170.7 | 1.93 |
| B3     | $-979.782126$ | 270.5 | 38.9 | 592.3 | 229.3 | 0.239 | 155.1 | 113.2 | 479.1 | 1.79 |
| B4     | $-979.785553$ | 270.0 | 39.0 | 601.6 | 232.0 | 0.222 | 152.5 | 112.8 | 488.8 | 1.79 |
| C1     | $-905.943738$ | 251.3 | 37.9 | 2239.8 | 233.3 | 0.233 | 173.7 | 117.6 | 2122.2 | 1.72 |
| C2     | $-1085.949379$ | 228.4 | 39.3 | 1602.2 | 215.0 | 0.145 | 256.7 | 106.2 | 1496.0 | 2.00 |
| C3     | $-995.820112$ | 239.4 | 38.9 | 1913.6 | 225.3 | 0.250 | 235.7 | 122.2 | 1791.4 | 1.86 |
| C4     | $-995.815961$ | 239.6 | 38.7 | 1924.5 | 225.8 | 0.177 | 199.9 | 110.5 | 1814.0 | 1.85 |
| D1     | $-925.545383$ | 218.2 | 37.2 | 843.1 | 230.6 | 0.250 | 116.0 | 109.0 | 734.1 | 1.77 |
| D2     | $-1105.788960$ | 195.6 | 38.5 | 212.0 | 212.3 | 0.206 | 116.4 | 96.6 | 115.4 | 2.06 |
| D3     | $-1015.667381$ | 206.2 | 38.1 | 526.6 | 223.3 | 0.250 | 157.3 | 111.5 | 415.1 | 1.91 |
| D4     | $-1015.665883$ | 206.7 | 38.0 | 530.9 | 222.3 | 0.222 | 115.0 | 102.9 | 428.0 | 1.90 |
| E1     | $-928.987170$ | 356.4 | 41.9 | 880.8 | 260.6 | 0.243 | 121.9 | 125.9 | 754.9 | 1.60 |
| E2     | $-1109.234475$ | 333.9 | 43.4 | 240.2 | 248.2 | 0.218 | 141.1 | 116.6 | 233.6 | 1.84 |
| E3     | $-1019.113356$ | 345.4 | 42.6 | 554.1 | 250.5 | 0.250 | 121.8 | 120.7 | 433.4 | 1.72 |
| E4     | $-1019.108590$ | 344.9 | 42.7 | 566.2 | 253.0 | 0.243 | 124.6 | 122.0 | 444.2 | 1.71 |
| F1     | $-961.031468$ | 295.9 | 41.1 | 1078.0 | 251.6 | 0.239 | 199.9 | 130.9 | 947.1 | 1.70 |
| F2     | $-1141.278583$ | 272.3 | 43.0 | 437.2 | 234.5 | 0.141 | 258.7 | 115.6 | 321.6 | 1.96 |
| F3     | $-1051.156005$ | 284.3 | 42.1 | 753.1 | 242.3 | 0.198 | 213.5 | 122.9 | 630.2 | 1.83 |
| F4     | $-1051.153629$ | 283.7 | 42.3 | 761.1 | 244.0 | 0.184 | 220.5 | 123.0 | 638.1 | 1.83 |
will improve the $\rho$ evidently. The influence order of different bridges on $\Delta H_{\text{coul}}$ and $\rho$ can be written as follows: (1) for $\Delta H_{\text{coul}}$: $\text{NH} \rightarrow$ directly link $\approx -\text{NHNH} \rightarrow -\text{O} \rightarrow -\text{CH}_2 \rightarrow -\text{CH}_3 \rightarrow$; (2) for $\rho$: $-\text{O} \rightarrow$ directly link $\approx -\text{NHNH} \approx -\text{NH} \rightarrow -\text{CH}_2 \rightarrow -\text{CH}_3 \rightarrow$. Overall, variation trends of $\Delta H_{\text{coul}}$ and $\rho$ were similar to each other for each series. All the results reveals that the effects of the bridged links on the $\Delta H_{\text{coul}}$ and $\rho$ were coupled to those of the energetic groups.

2.3. Detonation Properties and Impact Sensitivities

Table 4 shows the heats of detonation ($Q$), detonation velocities ($D$), detonation pressures ($P$), impact sensitivities ($h_{50}$) together with those for the popular explosives RDX and HMX. It is seen that values of $Q$, $D$, $P$ and $h_{50}$ were presented as follows: $Q$ were from 1193.63 (compound A1) to 2725.42 cal g$^{-1}$ (compound C2); $D$ were from 6.88 (compound E1) to 10.67 km s$^{-1}$ (compound C2), $P$ were from 19.5 (compound E1) to 53.6 GPa (compound C2) and $h_{50}$ were from 29.3 (compound F2) to 56.5 cm (compound B1), respectively. It is interesting to found that compound C2 have the highest $Q$, $D$ and $P$ values while compound E1 have the lowest $Q$, $D$ and $P$ values. It indicates that $Q$ was critical to $D$ and $P$. Consequently, molecules with higher values of $Q$ will possess higher values of $D$ and $P$.

Figure 3 (a–d) shows the variation trends of $Q$, $D$, $P$ and $h_{50}$ of the title compounds, respectively. From the figure, it is seen that variation trends of $Q$, $D$ and $P$ were approximately the same throughout the series while that of $h_{50}$ shows no regularity. For derivatives with the same bridges and different substituents, it is found that double $-\text{NF}_2$ group substituted compounds have the highest values of $Q$, $D$ and $P$ while the double $-\text{N}_2$ group substituted ones have the lowest values. But for the molecules in which $-\text{N}_3$ and $-\text{NF}_2$ groups were introduced to the oxadiazole rings together, the values of $Q$, $D$ and $P$ were similar to each other. For the derivatives with the same substituents and different bridges, the $-\text{NH}$ bridged compounds were found to have the highest $Q$, $D$ and $P$ values while the $-\text{CH}_2\text{CH}_2$ bridged ones have the lowest values. It can be concluded that $-\text{NH}$ bridge will be more effective in improving $Q$, $D$ and $P$ than any other bridges. For series 1 and 4, the $-\text{NH}$ bridged compounds have the lowest $h_{50}$ values while $-\text{NHNH}$– bridged compounds have the lowest $h_{50}$ values for series 2 and 3. The variation trends of series 2 and 4 were stronger than series 1 and 3 suggesting that the bridges were the most important influence factor for series 2 and 4 while the energetic groups may paly an important role in series 1 and 3. For a comparison, only 7 compounds (A2, A3, A4, C1, C2, C3 and C4) have superior values of $Q$ to those of RDX.

Table 4. Predicted heats of detonation ($Q$), detonation velocities ($D$), detonation pressures ($P$) and $h_{50}$ of the designed compounds.

| Compound | $Q$ (cal g$^{-1}$) | $D$ (km s$^{-1}$) | $P$ (GPa) | $h_{50}$/cm |
|----------|-------------------|-----------------|-----------|-------------|
| A1       | 1535.15           | 8.01            | 27.9      | 55.7        |
| A2       | 1783.87           | 9.62            | 43.9      | 46.4        |
| A3       | 1657.96           | 8.79            | 35.2      | 55.1        |
| A4       | 1660.41           | 8.00            | 35.3      | 53.9        |
| B1       | 1862.32           | 7.27            | 22.3      | 56.5        |
| B2       | 1510.32           | 8.75            | 35.4      | 40.0        |
| B3       | 1386.60           | 7.99            | 28.2      | 53.7        |
| B4       | 1396.10           | 8.00            | 28.3      | 49.5        |
| C1       | 2581.46           | 9.17            | 36.3      | 52.0        |
| C2       | 2725.42           | 10.67           | 53.6      | 30.1        |
| C3       | 2639.11           | 9.90            | 44.3      | 56.2        |
| C4       | 2661.16           | 9.88            | 44.0      | 38.4        |
| D1       | 1413.06           | 8.26            | 30.0      | 56.4        |
| D2       | 1588.50           | 9.53            | 43.5      | 45.8        |
| D3       | 1460.50           | 8.71            | 34.8      | 56.4        |
| D4       | 1473.04           | 8.69            | 34.6      | 49.5        |
| E1       | 1193.63           | 6.88            | 19.5      | 54.8        |
| E2       | 1429.63           | 8.22            | 30.4      | 48.5        |
| E3       | 1310.79           | 7.54            | 24.5      | 56.5        |
| E4       | 1320.79           | 7.53            | 24.4      | 54.7        |
| F1       | 1324.73           | 7.77            | 25.9      | 53.5        |
| F2       | 1554.40           | 9.20            | 39.5      | 29.3        |
| F3       | 1440.17           | 8.48            | 32.2      | 43.3        |
| F4       | 1447.43           | 8.49            | 32.3      | 40.0        |

Data From reference [34], *calculated at B3LYP/6-311G(d,p) level.

Figure 2. Variation trends of the $\Delta H_{\text{coul}}$ and $\rho$ of the title compounds.

Figure 3. Variation trends of $Q$, $D$, $P$ and $h_{50}$ of the title compounds.
(1590.7 cal g⁻¹) and HMX (1633.9 cal g⁻¹). 9 compounds (A2, A3, B2, C1, C2, C3, C4, D2 and F2) have equal or higher values of D to RDX (8.75 km s⁻¹) while 7 compounds (A2, C1, C2, C3, C4, D2 and F2) have higher values of D than HMX (9.10 km s⁻¹). 12 compounds (A2, A3, A4, B2, C1, C2, C3, C4, D2, D3, D4 and F2) have higher values of P than RDX (34.0 GPa) while 6 compounds (A2, C2, C3, C4, D2 and F2) have higher values of P than HMX (39.0 GPa). Again for hₗ₀ all the designed compounds have higher hₗ₀ values than RDX (26 cm) and HMX (29 cm) which reveals that these compounds will be more stable under external impacts.

2.4. Thermal Stabilities

Bond dissociation energy (BDE) as an important indicator was investigated because it can provide useful information in understanding the thermally stability, elucidating the pyrolysis mechanism and bond cleavage process of an energetic compound. Some research believed that the bridge or energetic groups acted as trigger bond during the decomposition process and thus, BDEs of the possible trigger bonds were selected and investigated: (1) ring-R; (2) C–N (bridge); (3) C–O (bridge); (4) N–N (bridge); (5) C–C (bridge). The weakest bond order (BO) and the corresponding BDEs of the title compounds were summarized in Table 5. From the table, it is seen that the BDEs of ring-R, C–C bridge, C–N bridge, C–O bridge and N–N bridge ranges from 266.4 kJ mol⁻¹ (compound F1), from 237.3 (compound E1) to 518.9 kJ mol⁻¹ (compound A1), from 342.2 (compound F1) to 400.3 kJ mol⁻¹ (compound C3), from 240.6 (compound D3) to 266.1 kJ mol⁻¹ (compound D4) and from 132.4 (compound F1) to 154.6 kJ mol⁻¹ (compound F2), respectively. It is also interesting to note that compound F1 not only has the highest BDEs of ring-R bond, but also possesses the lowest BDEs of N–N bond. The result shows that the effects of the bridged links on the BDEs values of the designed compounds were coupled to those of the substituted energetic groups.

Figure 4 displays the variation trends of BO and BDEs of the designed compounds. For series 2–4, the –O– bridged compounds have the lowest values of BO while the -NHNH- bridged compounds have the highest values of BO. BO of the directly link, –CH₂–, –NH– and –O– bridged compounds were also found to be fluctuated evidently than those of –NHNH– and –CH₂CH₂– bridged ones. It indicates that the types of bridges played an important role in BO for series A–D while energetic groups acted as the main influence factor for series E and F. In

### Table 5. Bond dissociation energies (BDE, kJ mol⁻¹) for the weakest bonds of the designed compounds.

| Compd. | ring-R | C-(Cbridge) | C-(Nbridge) | C-(Obridge) | N–N (bridge) |
|--------|--------|-------------|-------------|-------------|--------------|
|        | BO     | BDE         | BO          | BDE         | BO           |
| A1     | 1.0941 | 358.5       | 1.0635      | 518.9       | –            |
| A2     | 1.0206 | 273.9       | 1.0507      | 514.1       | –            |
| A3     | 1.0268 | 266.4       | 1.0555      | 517.5       | –            |
| A4     | 1.0182 | 275.6       | 1.0613      | 518.8       | –            |
| A1     | 1.0139 | 361.4       | 0.9860      | 372.6       | –            |
| A2     | 1.0160 | 275.5       | 1.0100      | 377.5       | –            |
| B3     | 0.9903 | 272.1       | 0.9846      | 372.6       | –            |
| B4     | 1.0028 | 275.8       | 0.9881      | 375.6       | –            |
| C1     | 1.0900 | 346.8       | –           | –           | 1.0457       |
| C2     | 1.0179 | 275.6       | –           | –           | 1.0525       |
| C3     | 1.0275 | 277.1       | –           | –           | 1.0720       |
| C4     | 1.0178 | 276.4       | –           | –           | 1.0351       |
| D1     | 1.0915 | 353.7       | –           | –           | 0.9366       |
| D2     | 1.0185 | 274.4       | –           | –           | 0.9430       |
| D3     | 1.0277 | 269.0       | –           | –           | 0.9698       |
| D4     | 1.0176 | 275.1       | –           | –           | 0.9271       |
| E1     | 1.0762 | 361.8       | 0.9962      | 237.3       | –            |
| E2     | 1.0150 | 276.4       | 0.9967      | 243.2       | –            |
| E3     | 1.0239 | 275.4       | 0.9964      | 239.7       | –            |
| E4     | 1.0145 | 276.6       | 0.9960      | 241.6       | –            |
| F1     | 1.0763 | 362.6       | –           | 1.0851      | 342.2        |
| F2     | 1.0189 | 276.9       | –           | 1.0930      | 345.0        |
| F3     | 1.0281 | 274.6       | –           | 1.0986      | 344.9        |
| F4     | 1.0189 | 277.4       | –           | 1.0790      | 343.5        |

Figure 4. The variation trends of BO and BDE of the designed compounds.
in view of BDEs, the -NHNH- bridged compounds have the lowest BDE values which suggests that the introduction of -NHNH- bridge may decrease the thermal stability of the designed compounds. For series 1, the BDEs decease sharply when the oxadiazoles were linked by -O-, -NHNH- and -CH₂CH₂- bridges. In addition, the variation trends can be negligible of series for series 2–4 when the bridges were directly link, -NH-, -O-, -CH₂- and -CH₃CH₂-. Finally, compound A₁ has the highest BO (1.0941) while compound D₄ has the lowest BO (0.9271). But on the contrary, compound B₁ has the highest BDE value 361.4 (kJ mol⁻¹) while compound F₁ has the lowest BDE value (132.4 kJ mol⁻¹). The phenomenon reveals that, for different chemical bonds, there exists no inevitable relation between the values of BOs and BDEs.

A potential high energy density compound should not only meet the standard of detonation properties (usually compared to those of RDX or HMX), but also should have excellent thermal stabilities. Take both of detonation properties and thermal stabilities into consideration, 6 compounds (A₂, C₂, C₃, C₄, D₂ and F₂) were screened as the candidates of high energy density compounds which possess superior detonation properties and thermal stabilities to that of HMX.

2.5. Electronic Structures

Electronic structures (such as distribution of LUMO and HOMO, electrostatic potential (ESP) and contour line maps) of the selected compounds (A₂, C₂, C₃, C₄, D₂ and F₂) were fully investigated. Figure 5 presents the distribution of LUMO and HOMO of the selected compounds. It is seen that the distribution of HOMO and LUMO of compounds A₂, C₂ and C₃ were mainly localized both on 1,3,4-oxadiazole and 1,2,5-oxadiazole rings while compounds C₄, D₂ and F₂ were on the opposite side. The fact is that LUMOs were mainly distributed on the 1,2,5-oxadiazole ring whereas the HOMO were mainly distributed on the 1,3,4-oxadiazole ring. In addition, the energy gaps of these compounds A₂, C₂, C₃, C₄, D₂ and F₂ were 5.32, 5.22, 4.50, 5.19, 5.04 and 5.33 eV, respectively. It implies that the predicted sequence of stabilities was F₂ > A₂ > C₂ > C₄ > D₂ > C₃ which is also the reverse order of the chemical activities. On the other hand, the HOMO and LUMO distributions agree well with the NBOs that calculated at the same level. Take compound C₂ for example, the NBO charges that distributed on HOMO was about -0.0707 while NBO charges that distributed on LUMO was about 0.0707 (the detailed information on chemical structure and NBO charges of compound C₄ can be found in the supporting information). Obviously, HOMO acted as electron donor while LUMO acted as electron acceptor.

Electrostatic potential (ESP) of the selected compounds were investigated since it is an important part to predict the intermolecular interaction, charge distributions, and chemical reactivity sites on molecular surfaces. 3D plots of ESP and ratios of the positive and negative areas (green color presents the positive potential and red color presents the negative potential) were visualized in Figure 6. For compound A₂, positive potentials were mainly concentrated on the oxadiazole rings while the negative potentials were mainly concentrated on the energetic groups. For compounds C₂-F₂, these potentials were relatively decentralized: positive potentials localized on parts of the oxadiazole rings, bridges and -N₂ groups while negative potentials localized on -NF₂ groups, oxygen and nitrogen atoms of the oxadiazole rings. In addition, the global maxima ESPs of compounds A₂, C₂, C₃, C₄, D₂ and F₂ were calculated as 39.8, 65.2, 60.8, 56.9, 38.9 and 61.6 kcal mol⁻¹ while the global minima ESP were calculated as −25.4, −28.8, −25.8, −43.1, −25.0 and 29.4, respectively.

These sites with the most positive potentials maybe attacked easily by the nucleophile. In view of the surface area of positive and negative potentials, it is found that the area ratio of positive potentials of the selected compounds were larger than the area ratio of negative potentials which indicates that the electrostatic potential is mainly contributed by nuclear charges.
The contour line maps of the electronic densities on compounds A2, C2, C3, C4, D2 and F2 were plotted in Figure 7. It also should be pointed out that high peaks correspond to the nuclear charge of heavy nucleus which will improve the electron aggregation. It is seen that the electron densities around the fluorine atoms were the highest due to its strong electron absorption effects while electron densities around the hydrogen atoms were the lowest. Delocalization was observed in the oxadiazole rings (for example, compound A2, regions α and β) and this phenomenon may improve the stability of the ring skeleton and the molecular structure. Besides, electronic density was also found to be reduced in regions γ (compound C2) and δ (compound C3) which may be caused by the repulsive interactions of heavy atoms (compound C2, N1…F2; compound C3, N1…N2).

3. Conclusions
A series of new energetic materials based on asymmetric oxadiazole were designed and investigated. The results show that all the designed compounds have high positive heats of formation range from 115.4 to 2122.2 kJ mol⁻¹ and −N−bridge/−N− group were the most effective factors in improving heats of formation of the designed compounds. Densities were in the range of 1.60–2.06 g cm⁻³ and −O− bridge/−NF₂ groups make more contributions to densities of the designed compounds. Values of detonation velocities and detonation pressures range from 6.88 to 10.67 km s⁻¹ and from 19.5 to 53.6 GPa, respectively. Besides, all the designed compounds have better impact sensitivities than those of RDX and HMX and meet the criterion of thermal stability. Take both of detonation properties and thermal stabilities into consideration, 6 compounds (A2, C2, C3, C4, D2 and F2) were selected as the candidates of high energy density compounds.

Conflict of Interest
The authors declare no conflict of interest.

Keywords: density functional theory · energetic materials · oxadiazole · detonation properties · heat of formation

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