

Computational Investigation and Screening of High-Energy-Density Materials: Based on Nitrogen-Rich 1,2,4,5-tetrazine Energetic Derivatives

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Abstract: In the present work, the geometric structures, the frontier molecular orbitals and the enthalpy of formation (*HOF*) of thirty six 1, 2, 4, 5-tetrazine derivatives (FTT) were systematically studied by using the B3LYP/6-311+G* method of density functional theory. Meanwhile, we also predicted the stability, detonation properties and thermodynamic properties of all FTT compounds. Results showed that all compounds have superior enthalpy of formation far exceeding that of common explosives RDX and HMX, ranging from 859kJ·mol⁻¹-1532kJ·mol⁻¹. In addition, the detonation performance ($Q = 1426\text{cal}\cdot\text{g}^{-1}$ -1804cal·g⁻¹; $P = 29.54\text{GPa}$ - 41.84GPa; $D = 8.02\text{km}\cdot\text{s}^{-1}$ - 9.53km·s⁻¹), which is superior to TATB and TNT. It is also concluded that the introduction of coordination oxygen on the tetrazine ring can improve the *HOF*, density and detonation performance of the title compound, and -NH-NH- bridge and -NHNO₂ group are also the perfect combination to increase these values. In view of stability, because of the fascinating performance of D3 ($\rho = 1.89\text{g}\cdot\text{cm}^{-3}$; $D = 9.38\text{km}\cdot\text{s}^{-1}$; $P = 40.13\text{GPa}$), E3 ($\rho = 1.87\text{g}\cdot\text{cm}^{-3}$; $D = 9.19\text{km}\cdot\text{s}^{-1}$; $P = 38.35\text{GPa}$), F1 ($\rho = 1.87\text{g}\cdot\text{cm}^{-3}$; $D = 9.42\text{km}\cdot\text{s}^{-1}$; $P = 40.23\text{GPa}$) and F3 ($\rho = 1.92\text{g}\cdot\text{cm}^{-3}$; $D = 9.53\text{km}\cdot\text{s}^{-1}$; $P = 41.84\text{GPa}$), makes them very attractive to be chosen as HEDMs.

KEYWORDS: 1,2,4,5-tetrazine derivatives, Detonation property, Enthalpies of formation, Thermodynamic property

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1 | Introduction

Nitrogen-rich compounds are a type of novel high-energy density materials (HEDMs) that have attracted much attention in recent years.^[1, 2] Its energy mainly comes from high heat of formation. Meanwhile, its characteristics of high nitrogen and low hydrocarbon content make it have the dual effect of not only increasing the material density, but also achieving better oxygen balance easily.^[3, 4] Among them, the nitrogen content of tetrazine compounds reached 68.3% is a very effective structural unit in the design of high-energy insensitive energy-containing materials, tetrazine compounds have high thermal stability, high positive *HOF* and low sensitivity, because of their powerful N-N and C-N bonds.^[5-8] With the increase of oxygen atoms coordinated with tetrazine, the density and properties of the molecule are improved, and the whole molecule tends to be stable.^[9-13] In general, the density and other properties of the compound become better as the number of coordinated oxygen increases. The structure and properties of several different tetrazine oxides are shown in Figure 1.

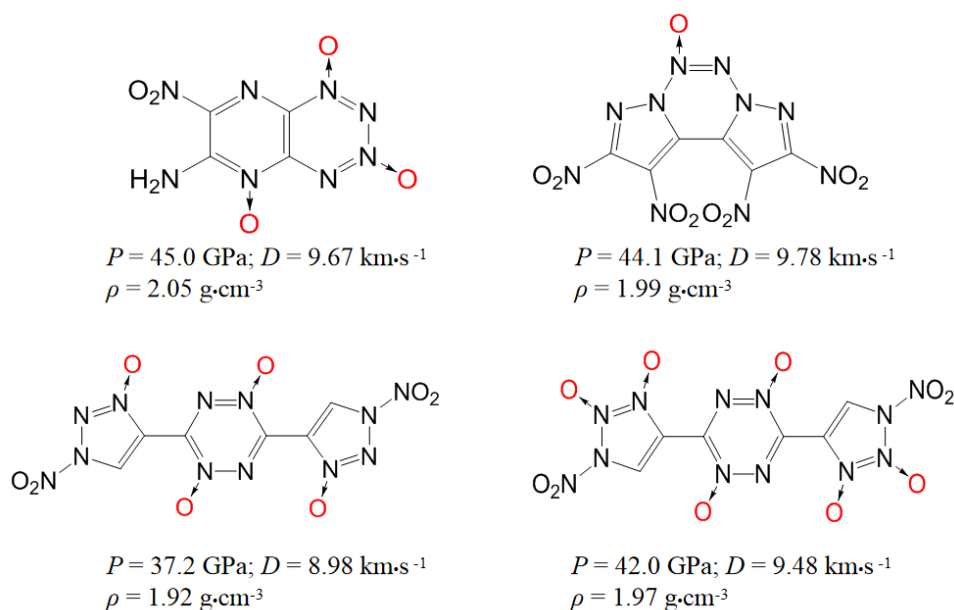


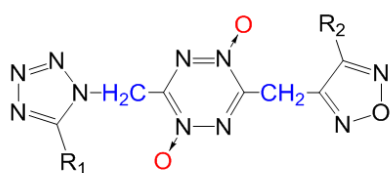
FIGURE 1 The structure and properties of several different tetrazine oxides

The furazan is also an efficient building block in the design and synthesis of new HEDMs.^[14-17] The parent structure of furazan compound is a five-membered nitrogen-oxygen heterocyclic ring, and the furazan ring contains an active oxygen atom, which will form a hidden nitro structure in the ring.^[18] Due to its high electronegativity of nitrogen and oxygen atoms, its nitrogen

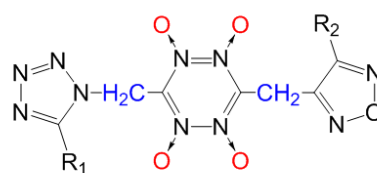
heterocyclic ring system can form large π bond like benzene structure, so they have good planeness, high thermal stability, high density, which is also insensitive. According to favorable evidence, the detonation density and detonation velocity will increase about $0.06\text{--}0.08\text{ g}\cdot\text{cm}^{-3}$ and $300\text{ m}\cdot\text{s}^{-1}$ after furazan replaces the nitrogen group.^[18]

Tetrazole derivatives are typical compounds of nitrogen-rich explosives.^[19, 20] It is a structural unit with the highest nitrogen content that can exist stably at present. The molecular structure of this kind of nitrogen-rich compound contains a large number of N-N, C-N, N=N, C-N bonds, so that the enthalpy of formation of the compound is mostly positive value, which is also beneficial to improve the molecular explosion heat.^[21-23]

In this paper, 1,2,4,5-tetrazine oxide rings with high energy were selected as the basic skeleton, and thirty six 1,2,4,5-tetrazine derivatives were designed with different Bridges ($-\text{CH}_2-$, $-\text{NH}-$, $-\text{NH}-\text{NH}-$) to connect tetrazole ring and furazan ring (Figure 2). The theoretical calculation of these compounds was carried out at the level of DFT-B3LYP/6-311+G*, the density of the compound is predicted, and the enthalpy of formation is obtained using the atomization scheme. On this basis, the detonation performance is estimated to select a new type of HEDMs.



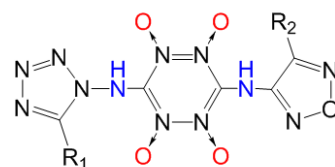
- A1: R1= R2: $-\text{NO}_2$
A2: R1= R2: $-\text{CH}(\text{NO}_2)_2$
A3: R1= R2: $-\text{NHNO}_2$
A4: R1= $-\text{NO}_2$, R2= $-\text{CH}(\text{NO}_2)_2$
A5: R1= $-\text{H}$, R2= $-\text{CH}(\text{NO}_2)_2$
A6: R1= $-\text{CH}(\text{NO}_2)_2$, R2= $-\text{H}$



- B1: R1= R2: $-\text{NO}_2$
B2: R1= R2: $-\text{CH}(\text{NO}_2)_2$
B3: R1= R2: $-\text{NHNO}_2$
B4: R1= $-\text{NO}_2$, R2= $-\text{CH}(\text{NO}_2)_2$
B5: R1= $-\text{H}$, R2= $-\text{CH}(\text{NO}_2)_2$
B6: R1= $-\text{CH}(\text{NO}_2)_2$, R2= $-\text{H}$



- C1: R1= R2: $-\text{NO}_2$
C2: R1= R2: $-\text{CH}(\text{NO}_2)_2$
C3: R1= R2: $-\text{NHNO}_2$
C4: R1= $-\text{NO}_2$, R2= $-\text{CH}(\text{NO}_2)_2$
C5: R1= $-\text{H}$, R2= $-\text{CH}(\text{NO}_2)_2$
C6: R1= $-\text{CH}(\text{NO}_2)_2$, R2= $-\text{H}$



- D1: R1= R2: $-\text{NO}_2$
D2: R1= R2: $-\text{CH}(\text{NO}_2)_2$
D3: R1= R2: $-\text{NHNO}_2$
D4: R1= $-\text{NO}_2$, R2= $-\text{CH}(\text{NO}_2)_2$
D5: R1= $-\text{H}$, R2= $-\text{CH}(\text{NO}_2)_2$
D6: R1= $-\text{CH}(\text{NO}_2)_2$, R2= $-\text{H}$

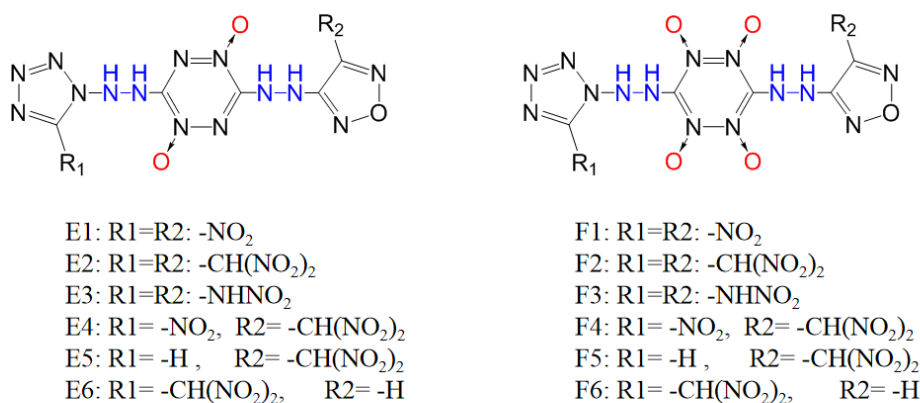


FIGURE 2 Molecular structures of 1, 2, 4, 5-tetrazine derivatives

2 | Computational methods

All calculations involved in this work were performed using the Gaussian 09^[24] suite of programs. In order to select the suitable basis set we used , the geometries optimization and HOFs of three tetrazine compounds, 1,2,4,5-tetrazine, 3,6-diamino-1,2,4,5-tetrazine and 3,6-dihydrazinyl -1,2,4,5- tetrazine were calculated using B3LYP/(6-31G*, 6-311G*, 6-311+G*, 6-311G**). The results favorably show that the calculated geometries and *HOFs* are the closest to the experimental results under the condition of 6-311+G* optimization. On this basis, the geometrical structure and *HOFs* of the above compounds were calculated by the combination of the basis set of 6-311+G* and different methods (B3PW91 , M05, M06, wB97), so as to select the optimal method. The results are listed in Supporting Information. B3LYP/6-311+G* was considered to be the best method for the theoretical study of the designed 1,2,4,5-tetrazine derivatives compounds.

Heat of formation reflects the basic thermodynamic properties of energetic compounds. The atomic equivalent scheme used to convert the quantum mechanical energy of atoms into the heat of formation of molecules as shown in **Eq.(1)**^[25] According to the Multiwfn^[26] software to predict the electrostatic potential of molecules, the enthalpy of sublimation or vaporization can be expressed as:

$$HOF(g) = E(g) - \sum n_i x_i \quad (1)$$

The density of energetic compounds is one of the important parameters affecting detonation performance. Politzer^[27] believes that the correction of the electrostatic interaction can improve the crystal structure and effectively predict the density as **Eq.(2)**. where $V(0.001)$ is the volume of the

isolated gas molecule ($\text{cm}^3 \cdot \text{mol}^{-1}$), which is encompassed by the 0.001 a.u. contour of the electronic density, M is the molecular mass ($\text{g} \cdot \text{mol}^{-1}$), $v\sigma_{tot}^2$ is taken from the molecular ESP calculation, And α , β , and γ are the density distribution coefficients of the series design compounds.

$$\rho = \alpha \left(\frac{M}{V(0.001)} \right) + \beta (v\sigma_{tot}^2) + \gamma \quad (2)$$

The famous semi-empirical Kamlet-Jacobs^[28-30] formula proposed in 1968 was used to estimate the detonation pressure and detonation velocity s in terms of **Eq.(3)** and **Eq.(4)**

$$D = 1.01(N\overline{M}^{1/2}Q^{1/2})^{1/2}(1 + 1.30\rho) \quad (3)$$

$$P = 1.558\rho^2 N\overline{M}^{1/2}Q^{1/2} \quad (4)$$

Among them, the meaning of each item in the above formula is as follows: P , the detonation pressure (GPa); D , the detonation velocity ($\text{km} \cdot \text{s}^{-1}$); \overline{M} , the average molecular weight of these gases; N , the moles of detonation gases per gram explosive; Q , the heat of explosion ($\text{cal} \cdot \text{g}^{-1}$), defined as the difference of the *HOFs* between products and reactants; and ρ , replaced by the theoretical density ($\text{g} \cdot \text{cm}^{-3}$). ;

The stability of energetic compounds plays a vital role in its practical application, and the bond dissociation energy (BDE) provides very useful information for judging the stability of energetic compounds.^[31-33] The energy required for bond homolysis at 298 K and 1 atm corresponds to the enthalpy of reaction $A-B (g) = A(g) + B(g)$, which is the bond dissociation enthalpy of the molecule $A-B$ by definition.^[34, 35] The bond dissociation energy of all titled compounds was calculated by formula 6 at the PUB3LYP / 6-31G * level.

$$BDE_0(A-B) = E_0(A\cdot) + E_0(B\cdot) - E_0(A-B) \quad (5)$$

The BDE with ZPE correction can be calculated by **Eq.(6)**:

$$BDE(A-B)_{ZPE} = BDE_0(A-B) + \Delta E_{ZPE} \quad (6)$$

where ΔE_{ZPE} is the difference between the ZPEs of the products and the reactants.

3 | Results and Discussions

3.1 | The determination of the two different calculation methods on the derivatives of furazans and tetrazoles

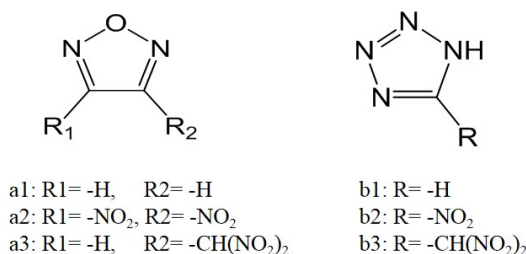


FIGURE 3 Molecular structures of furazan and tetrazole derivatives

In order to verify whether the screened method is a good choice for furazan and tetrazole derivatives, this paper used B3LYP/6-311+G* and wB97/6-311 +G* to optimize the structure of the compound shown in Figure 3. Table 1 lists the E_0 , E_{ZPE} , H_T and $HOFs$ values of a series of compounds. The values calculated by the two methods are very similar, especially the total energy(E_0), the correlation coefficient is equal to 1 (Figure 4). The gap of $HOFs$ is also less than 50kJ·mol⁻¹, and the correlation coefficient R is as high as 0.9850. Therefore, B3LY/P6-311+G* can also perfectly calculate furazan and tetrazole compounds. At the same time, we can also conclude that the introduction of nitro is a good way to improve HOF_s .

TABLE 1 Calculated E_0 , H_T , E_{ZPE} and $HOFs$ of furazan and tetrazoles derivatives at two levels

Compd.	B3LYP/6-311+G*				wB97/6-311+G*			
	E_0	E_{ZPE}	H_T	$HOFs$	E_0	E_{ZPE}	H_T	$HOFs$
a1	-262.0193	0.0455	0.0044	253.67	-262.0336	0.0470	0.0043	216.30
a2	-670.9536	0.0498	0.0096	366.16	-670.9706	0.0527	0.0093	321.48
a3	-710.2522	0.0785	0.0109	384.64	-710.2564	0.0821	0.0105	373.62
b1	-258.2127	0.0468	0.0044	410.34	-258.2335	0.0484	0.0044	355.75
b2	-462.6829	0.0491	0.0068	458.58	-462.6959	0.0513	0.0067	424.51
b3	-706.4562	0.0799	0.0109	513.46	-706.4745	0.0835	0.0105	465.43

Note: The unit of E_0 , E_{ZPE} and H_T are Hartree, the unit of $HOFs$ is kJ·mol⁻¹.

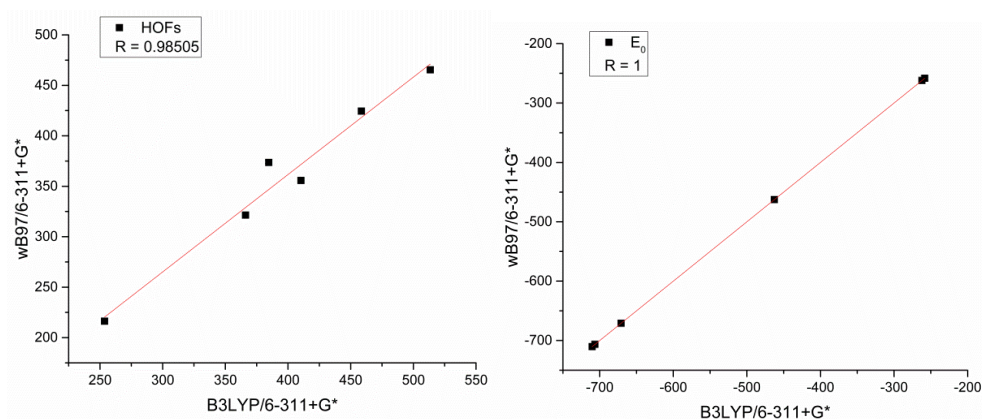


FIGURE 4 The linear fit of $HOFs$ and E_0 calculated by two different methods of furazan and tetrazole derivatives

3.2 | The optimized geometries

All designed compounds were geometrically optimized by using the hybrid DFT-B3LYP method with the 6-311+G* basis set. Table 2 clearly shows the bond lengths, bond angles and dihedral angles of some compounds. When the hydrogen on the tetrazine ring with four coordination oxygens is replaced by different bridges, all the bond lengths (C-N, N-N) in the ring are increased, but the N-N bond grows more. Among them, the introduction of -NH-NH- has the greatest impact, the increase of C-N bond is between 0.0013nm-0.0033nm, and the increase of N-N bond is between 0.0106nm-0.0123nm. The impact on C-N is much greater than the N-N bond when there are only two coordination oxygens exist on the tetrazine ring. The length of C-N bonds formed by N directly connected to the coordination oxygen increased slightly (0.1349nm-0.1390nm), while the rest of the C-N bonds decreased (0.1307nm-0.1327nm). The difference with four coordination is that the introduction of -CH₂- has more obvious influence on it. The C-N and N-N bond lengths of all design molecules are between single bond and double bond. All the design molecules have C-N, N-N bond lengths that are perfectly intermediate between single and double bonds.

The value of the bond Angle in the tetrazine ring associated with different bridges has decreased, while the remaining bond angles increase slightly, but all of them accord with the range of the ring bond. The dihedral angles N5C4N17C12 and N6C1N18N7 of compound C1, D1 are 31.49° and 149.44°, 128.21° and 149.44°, respectively, and the dihedral angles C4N17N21C12 and C1N18N20C7 of E3, F3 are -52.63° and -51.56°, 114.25° and 136.33°, respectively. Undoubtedly, the results show that the coplanarity of tetrazine, tetrazole and furazan ring is not

good when there are linkage groups.

TABLE 2 The optimized bond length (nm), bond Angle (°), and dihedral Angle (°) of some selected title

Parameters	molecules					
	A2	C1	D1	E3	F3	s-tetrazine
<i>R</i> (1,2)	0.1378	0.1379	0.1349	0.1367	0.1349	0.1336
<i>R</i> (2,3)	0.1342	0.1331	0.1430	0.1337	0.1436	0.1313
<i>R</i> (3,4)	0.1309	0.1314	0.1357	0.1307	0.1356	0.1336
<i>R</i> (4,5)	0.1390	0.1385	0.1358	0.1403	0.1369	0.1336
<i>R</i> (5,6)	0.1339	0.1327	0.1416	0.1315	0.1419	0.1313
<i>R</i> (6,1)	0.1310	0.1310	0.1355	0.1327	0.1366	0.1336
<i>R</i> (7,8)	0.1359	0.1349	0.1350	0.1343	0.1340	
<i>R</i> (8,9)	0.1282	0.1288	0.1287	0.1293	0.1295	
<i>R</i> (9,10)	0.1354	0.1359	0.1361	0.1353	0.1351	
<i>R</i> (10,11)	0.1313	0.1300	0.1299	0.1313	0.1314	
<i>R</i> (11,7)	0.1358	0.1362	0.1364	0.1368	0.1369	
<i>R</i> (12,13)	0.1440	0.1431	0.1431	0.1435	0.1437	
<i>R</i> (13,14)	0.1304	0.1298	0.1299	0.1303	0.1304	
<i>R</i> (14,15)	0.1353	0.1350	0.1349	0.1350	0.1348	
<i>R</i> (15,16)	0.1363	0.1378	0.1375	0.1385	0.1387	
<i>R</i> (16,12)	0.1305	0.1307	0.1306	0.1301	0.1301	
<i>R</i> (1,18)		0.1386	0.1380	0.1382	0.1370	
<i>R</i> (4,17)		0.1371	0.1361	0.1359	0.1370	
<i>R</i> (5,19)	0.1245	0.1254	0.1245	0.1251	0.1241	
<i>R</i> (18,20)				0.1408	0.1409	
<i>R</i> (17,21)				0.1389	0.1407	
<i>R</i> (22,23)				0.1423	0.1419	
<i>R</i> (1,24)	0.1503					
<i>R</i> (1,25)	0.1494					
<i>A</i> (1,2,3)	119.02	117.98	117.72	119.73	118.99	116.98
<i>A</i> (2,3,4)	118.59	118.97	119.33	117.87	117.85	116.98
<i>A</i> (3,4,5)	121.97	122.64	121.65	122.42	121.20	126.04
<i>A</i> (4,5,6)	119.34	118.29	118.00	118.93	119.25	116.98
<i>A</i> (5,6,1)	118.45	118.78	119.21	118.44	118.62	116.98
<i>A</i> (6,1,2)	122.60	123.26	122.64	122.37	121.27	126.04
<i>A</i> (7,8,9)	107.26	106.72	106.70	106.22	106.15	
<i>A</i> (8,9,10)	110.98	111.44	111.50	111.56	111.49	
<i>A</i> (9,10,11)	106.28	105.47	105.47	106.26	106.45	

<i>A</i> (10,11,7)	108.63	109.47	109.44	108.22	107.45
<i>A</i> (12,13,14)	108.44	109.76	109.61	108.46	108.18
<i>A</i> (13,14,15)	106.31	105.21	105.21	105.93	106.27
<i>A</i> (14,15,16)	111.23	112.09	112.20	111.96	111.81
<i>A</i> (15,16,12)	106.64	105.38	105.38	104.81	104.84
<i>A</i> (16,12,13)		107.46	107.59	108.83	108.89
<i>A</i> (16,12,24)	117.52				
<i>A</i> (16,12,25)	117.74				
<i>A</i> (6,5,19)	119.77	120.43	117.91	118.73	117.64
<i>A</i> (6,1,18)		115.87	114.82	123.18	117.18
<i>A</i> (5,4,17)		119.47	121.52	119.80	119.25
<i>A</i> (7,20,18)				114.05	113.67
<i>A</i> (12,21,17)				116.64	115.55
<i>D</i> (1,6,5,19)	-178.66	178.77	176.64	-177.98	-176.17
<i>D</i> (18,7,8,9)		179.16	178.52		
<i>D</i> (5,4,17,12)		31.49	149.44		
<i>D</i> (6,1,18,7)		128.21	149.44		
<i>D</i> (6,1,24,7)	118.33				
<i>D</i> (24,1,7,8)	174.39				
<i>D</i> (2,3,4,17)		-176.09	177.89	-179.05	174.86
<i>D</i> (2,3,4,25)	178.80				
<i>D</i> (4,17,21,12)				-52.63	-51.56
<i>D</i> (1,18,20,7)				114.25	136.33
<i>D</i> (5,4,17,21)				167.33	126.05
<i>D</i> (6,1,18,20)				140.45	143.09
<i>D</i> (17,21,13,14)				-56.78	-39.44
<i>D</i> (17,21,16,15)				129.45	145.17
<i>D</i> (18,20,7,8)				-72.09	-68.14

3.3 | The frontier orbital energy

The frontier molecular orbitals play a pivotal role in analyzing the substantial electronic structure of compounds, The energy gap (ΔE) between HOMO and LUMO usually determines the chemical reactivity and kinetic stability of molecules.^[36, 37] The E_{HOMO} , E_{LUMO} and ΔE values are depicted in Table 3 , The HOMO and LUMO orbitals are shown in Figure S4. The energy gap values of compound A1 (3.32 eV), B1 (3.32 eV), C1 (3.01 eV), D1 (3.11 eV), E1 (3.14 eV) and F1 (3.21 eV) are almost the lowest in their series, indicating that the introduction of -NO₂ is not

conductive to improving the stability of 1,2,4,5-tetrazine derivatives. However, the energy gap values of A2 (3.49 eV), B2 (3.24 eV), C5 (3.24 eV), D2 (3.30 eV), E2 (3.22 eV), and F4 (3.23 eV) containing the substituent $-\text{CH}(\text{NO}_2)_2$ are the largest in its series, indicating that $-\text{CH}(\text{NO}_2)_2$ is beneficial to improve the stability of 1,2,4,5-tetrazine derivatives. The regularities of the presence of different bridges are as follows:

(1) For $-\text{CH}_2-$, the energy gap value decreases with the increase of coordinated oxygen, so it is unfavorable for the stability of the compound. Among them, series A has the lowest chemical reaction activity and the highest stability among all FTT compounds.

(2) For $-\text{NH}-$ and $-\text{NH}-\text{NH}-$, the ΔE of four-coordinate oxygen compounds is significantly higher than that of the two-coordinate oxygen compounds. At the same time, the energy gap values of series D and F are larger than series C and E, respectively, indicating that $-\text{NH}-\text{NH}-$ is beneficial to the improvement of the stability of 1,2,4,5-tetrazine derivatives.

TABLE 3 Values of E_{HOMO} and E_{LUMO} and energy gaps ΔE (eV)

Compd.	E_{HOMO}	E_{LUMO}	ΔE	Compd.	E_{HOMO}	E_{LUMO}	ΔE
A1	-7.61	-4.28	3.32	D1	-7.66	-4.55	3.11
A2	-8.25	-4.88	3.37	D2	-7.99	-4.69	3.29
A3	-7.46	-3.99	3.47	D3	-7.39	-4.12	3.27
A4	-8.00	-4.51	3.49	D4	-7.83	-4.64	3.19
A5	-7.52	-4.09	3.43	D5	-7.80	-4.58	3.22
A6	-7.93	-4.53	3.39	D6	-7.77	-4.48	3.29
B1	-7.42	-4.34	3.08	E1	-7.38	-4.24	3.14
B2	-7.72	-4.48	3.24	E2	-7.71	-4.48	3.22
B3	-7.25	-4.04	3.21	E3	-7.67	-4.49	3.18
B4	-7.67	-4.50	3.18	E4	-7.33	-4.19	3.14
B5	-7.35	-4.15	3.20	E5	-7.63	-4.45	3.18
B6	-7.74	-4.54	3.20	E6	-7.46	-4.34	3.12
C1	-7.45	-4.43	3.01	F1	-7.56	-4.35	3.21
C2	-7.81	-4.72	3.08	F2	-8.00	-4.74	3.25
C3	-7.07	-3.91	3.16	F3	-8.04	-4.82	3.23
C4	-7.60	-4.56	3.04	F4	-7.77	-4.53	3.23
C5	-7.61	-4.45	3.17	F5	-7.88	-4.65	3.23
C6	-7.52	-4.43	3.08	F6	-7.72	-4.48	3.24

3.4 | The enthalpy of formation

The enthalpy of formation is an important indicator to measure the energy level of energy-

containing materials,^[38] so accurate calculation of enthalpy of formation is of great significance for screening new HEDM.^[39] The values of E_0 , E_{ZPE} , H_T , nitrogen content (N%) and HOF of thirty six FTT compounds optimized at the B3LYP/6-311+G* level were summarized in Table 4. The HOF values of all compounds, which are much higher than the traditional compounds RDX(79kJ·mol⁻¹) and TNT(63.12kJ·mol⁻¹), have high positive formation.

TABLE 4 Calculated total energies (E_0), zero-point energies (E_{ZPE}), temperature correction (H_T), and HOF for FTT compounds

Compd.	formular	E_0	E_{ZPE}	H_T	N/%	HOF
A1	C ₇ H ₄ N ₁₂ O ₇	-1452.1610	0.1742	0.0216	45.65	917
A2	C ₉ H ₆ N ₁₄ O ₁₁	-1939.7716	0.2354	0.0297	40.33	859
A3	C ₇ H ₆ N ₁₄ O ₇	-1562.8610	0.2089	0.0238	45.58	1002
A4	C ₈ H ₅ N ₁₃ O ₉	-1695.9667	0.2052	0.0256	42.62	887
A5	C ₈ H ₆ N ₁₂ O ₇	-1491.4905	0.2029	0.0232	43.98	855
A6	C ₈ H ₆ N ₁₃ O ₇	-1491.4875	0.2026	0.0231	43.98	863
B1	C ₇ H ₄ N ₁₂ O ₉	-1602.4600	0.1807	0.0240	42.00	958
B2	C ₉ H ₆ N ₁₄ O ₁₃	-2090.0713	0.2426	0.0322	37.84	898
B3	C ₇ H ₆ N ₁₄ O ₉	-1713.1597	0.2153	0.0263	45.58	1044
B4	C ₈ H ₅ N ₁₃ O ₁₁	-1846.2582	0.2395	0.0280	39.65	948
B5	C ₈ H ₆ N ₁₂ O ₉	-1641.7928	0.2094	0.0256	40.58	887
B6	C ₈ H ₆ N ₁₃ O ₉	-1641.7894	0.2091	0.0256	40.58	896
C1	C ₅ H ₂ N ₁₄ O ₇	-1484.1913	0.1502	0.0215	52.98	1155
C2	C ₇ H ₄ N ₁₆ O ₁₁	-1971.8153	0.2120	0.0295	45.90	1062
C3	C ₅ H ₄ N ₁₆ O ₇	-1594.9060	0.1853	0.0236	56.00	1201
C4	C ₆ H ₃ N ₁₅ O ₉	-1728.0091	0.1812	0.0255	48.95	1093
C5	C ₆ H ₄ N ₁₄ O ₇	-1523.5159	0.1789	0.0230	51.04	1105
C6	C ₆ H ₄ N ₁₅ O ₇	-1523.5374	0.1792	0.0229	51.04	1049
D1	C ₅ H ₂ N ₁₄ O ₉	-1745.1218	0.1569	0.0238	48.76	1219
D2	C ₇ H ₄ N ₁₆ O ₁₃	-2232.7430	0.2182	0.0318	43.08	1173
D3	C ₅ H ₄ N ₁₆ O ₉	-1855.8269	0.1913	0.0261	51.85	1308
D4	C ₆ H ₃ N ₁₅ O ₁₁	-1988.9309	0.1879	0.0277	45.56	1202
D5	C ₆ H ₄ N ₁₄ O ₉	-1784.4620	0.1849	0.0255	47.12	1171
D6	C ₆ H ₄ N ₁₅ O ₉	-1784.4587	0.1851	0.0253	47.12	1167
E1	C ₅ H ₄ N ₁₆ O ₇	-1594.8434	0.1851	0.0236	56.00	1365
E2	C ₇ H ₆ N ₁₈ O ₁₁	-2082.4584	0.2464	0.0315	48.65	1296
E3	C ₅ H ₅ N ₁₈ O ₇	-1705.5403	0.2191	0.0275	58.60	1333

E4	C ₆ H ₅ N ₁₇ O ₉	-1838.6499	0.2157	0.0251	51.85	1299
E5	C ₆ H ₆ N ₁₁ O ₇	-1634.1744	0.2138	0.0252	54.10	1318
E6	C ₆ H ₆ N ₁₂ O ₇	-1634.1674	0.2132	0.0259	54.10	1458
F1	C ₅ H ₄ N ₁₆ O ₉	-1745.1218	0.1906	0.0263	51.85	1461
F2	C ₇ H ₆ N ₁₈ O ₁₃	-2232.7430	0.2529	0.0338	45.82	1375
F3	C ₅ H ₅ N ₁₈ O ₉	-1855.8269	0.2256	0.0282	52.94	1532
F4	C ₆ H ₅ N ₁₇ O ₁₁	-1988.9309	0.2217	0.0301	48.47	1422
F5	C ₆ H ₆ N ₁₁ O ₉	-1784.4620	0.2203	0.0273	50.22	1370
F6	C ₆ H ₆ N ₁₂ O ₉	-1784.4587	0.2198	0.0273	50.22	1379
RDX	C ₃ H ₆ N ₆ O ₆	/			37.81	79 ^[40]
TNT	C ₇ H ₅ N ₃ O ₆	/			18.49	-63.12 ^[40]
TATB	C ₆ H ₆ N ₆ O ₆	/			32.54	-74.61 ^[40]

Note: The unit of E_0 , E_{ZPE} and H_f are Hartree, the unit of HOF s is $\text{kJ}\cdot\text{mol}^{-1}$.

Figure 5 compares the effects of different numbers of coordinated oxygens on the tetrazine ring on HOF . It is worth mentioning that variational trend of two series of HOF were consistent with each other, the results show that increasing the number of coordination oxygen is a favorable way to improve HOF . Moreover, the introduction of $-\text{NHNO}_2$ on furazan and tetrazole ring can further enhance the HOF of FTT compounds. All compounds 5 and 6 of series A-F that only have the same substituent $-\text{CH}(\text{NO}_2)_2$ in different positions have very close HOF values, indicating that the same substituent has the same influence on enthalpy of formation whether on the furazan and tetrazole ring. The influence order of different substituents on HOF is as follows: $-\text{NHNO}_2 > \text{NO}_2 > -\text{CH}(\text{NO}_2)_2$. So we can assume that the value of HOF is not necessarily proportional to the amount of nitro, such as A2($857\text{kJ}\cdot\text{mol}^{-1}$), B2($898\text{kJ}\cdot\text{mol}^{-1}$). The effect of different bridges on HOF was in the order of $-\text{NH}-\text{NH}- > -\text{NH}- > -\text{CH}_2-$. It is also found that the values of HOF will be significantly improved as the number of N atoms increases. In the same series, the compound with the most N content must correspond to the maximum HOF , but the HOF of the compound with the lowest N content is not necessarily the smallest. In summary, the substituent $-\text{NHNO}_2$ and coordination oxygen are good medicines to increase the HOF of the designed compound. Moreover, the $-\text{NHNO}_2$ group and $-\text{NH}-\text{NH}-$ bridges are the best combination to enhance the HOF of FTT compound.

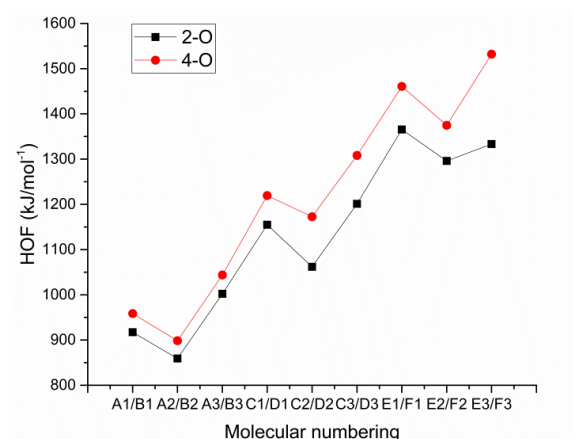


FIGURE 5 Compared the *HOF* of FTT compounds with different coordination oxygens

3.5 | The detonation properties

Table 5 shows the density (ρ), heat of detonation (Q), detonation velocity (D), detonation pressure (P), and oxygen balance (OB) of the title energetic compounds and two common explosives TNT and TATB in detail, providing a reference for further understanding of the designed compound.

TABLE 5 Detonation parameters of 1, 2, 4, 5-tetrazine derivatives(FTT)

Compd.	ρ	Q	D	P	OB^a
A1	1.77	1548	8.26	29.99	-39
A2	1.79	1553	8.40	31.16	-33
A3	1.75	1509	8.26	29.76	-37
A4	1.75	1550	8.23	29.54	-36
A5	1.75	1480	8.02	28.05	-50
A6	1.71	1426	8.41	31.72	-50
B1	1.73	1684	8.43	30.79	-28
B2	1.82	1656	8.74	34.12	-25
B3	1.83	1639	8.80	34.71	-30
B4	1.83	1679	8.76	34.38	-26
B5	1.86	1612	8.67	33.99	-39
B6	1.76	1617	8.36	30.63	-39
C1	1.85	1664	8.96	36.16	-17
C2	1.82	1624	8.82	34.70	-16
C3	1.80	1594	8.79	34.30	-18
C4	1.83	1632	8.85	35.04	-26
C5	1.81	1601	8.65	33.30	-29
C6	1.77	1566	8.48	31.57	-21

D1	1.88	1804	9.36	39.96	-8
D2	1.86	1755	9.22	38.46	-9
D3	1.89	1753	9.38	40.13	-11
D4	1.87	1780	9.27	39.03	-9
D5	1.84	1741	9.05	36.85	-19
D6	1.85	1739	9.06	36.99	-19
E1	1.81	1692	8.95	35.58	-20
E2	1.85	1658	9.02	36.65	-19
E3	1.87	1650	9.19	38.35	-20
E4	1.84	1674	9.01	36.43	-28
E5	1.80	1622	8.73	33.77	-31
E6	1.78	1633	8.68	33.20	-23
F1	1.87	1837	9.42	40.23	-11
F2	1.83	1767	9.17	37.68	-12
F3	1.92	1726	9.53	41.84	-13
F4	1.81	1800	9.17	37.51	-11
F5	1.84	1755	9.14	37.60	-22
F6	1.81	1759	9.05	36.44	-22
RDX ^[41]	1.80	1591	8.75	34.00	-21.62
TNT ^[41]	1.64	1295	6.95	19.00	-73.97
TATB ^[41]	1.93	1149	7.86	31.50	-55.81

Note: The units of ρ , Q , D and P are $\text{g}\cdot\text{cm}^{-3}$, $\text{cal}\cdot\text{g}^{-1}$, $\text{km}\cdot\text{s}^{-1}$ and GPa.

^aOxygen balance for $\text{C}_a\text{H}_b\text{O}_c$, $OB/\% [1600(c - 2a - b/2)/MW]$ (MW, molecular weight).

It can be seen from Table 6 that the introduction of N-O bond on the tetrazine ring can provide a higher density to the FTT compound, which may be because the addition of coordination oxygen makes the entire molecular structure table compound more compact. Among them, the density of compound 5 in the same series was higher than that of compound 6, indicating that the substituent on furazan ring was more favorable to ρ . From D3($1.89\text{g}\cdot\text{cm}^{-3}$), E3($1.87\text{g}\cdot\text{cm}^{-3}$) and F3($1.92\text{g}\cdot\text{cm}^{-3}$), which is superior to RDX ($1.8\text{g}\cdot\text{cm}^{-3}$) density, we can found that $-\text{NHNO}_2$ group can significantly improve the density of 1, 2, 4, 5-tetrazine derivatives. On the contrary, the greater the number of $-\text{CH}(\text{NO}_2)_2$ groups, the lower the density. Looking at all the density values, we can easily find that the contribution of $-\text{CH}_2-$ to the density is much smaller than $-\text{NH}_2-$ and $-\text{NH}-\text{NH}-$.

oxygen balance(OB) represents the degree to which explosives can be oxidized. According to previous reports, it is known that the ideal OB value is equal to zero, and the OB value of all FTT compounds ranges from -50% to -8%, which is closer to 0 than the traditional compounds TNT (-

56%) and TATB (-74%) Oxygen balance, providing better performance.

Detonation velocity (D) and detonation pressure (P) are two important indexes of energetic materials. According to the comparison of detonation performance of 1,2,4,5-tetrazine derivatives with RDX, TNT and TATB as shown in Figure 6: We can conclude that the ideal Q (1426-1800 cal·g⁻¹), D (8.02-9.36 km·s⁻¹), P (28.05-41.84 GPa) of FTT compound are higher than ordinary compounds TNT and TATB. We also found that the Q , D , and P values are relatively low when the -CH₂- is possessed, while the addition of coordinated oxygen and -NO₂ has a higher Q value, and that compounds with higher ρ and Q values have Higher D and P values.

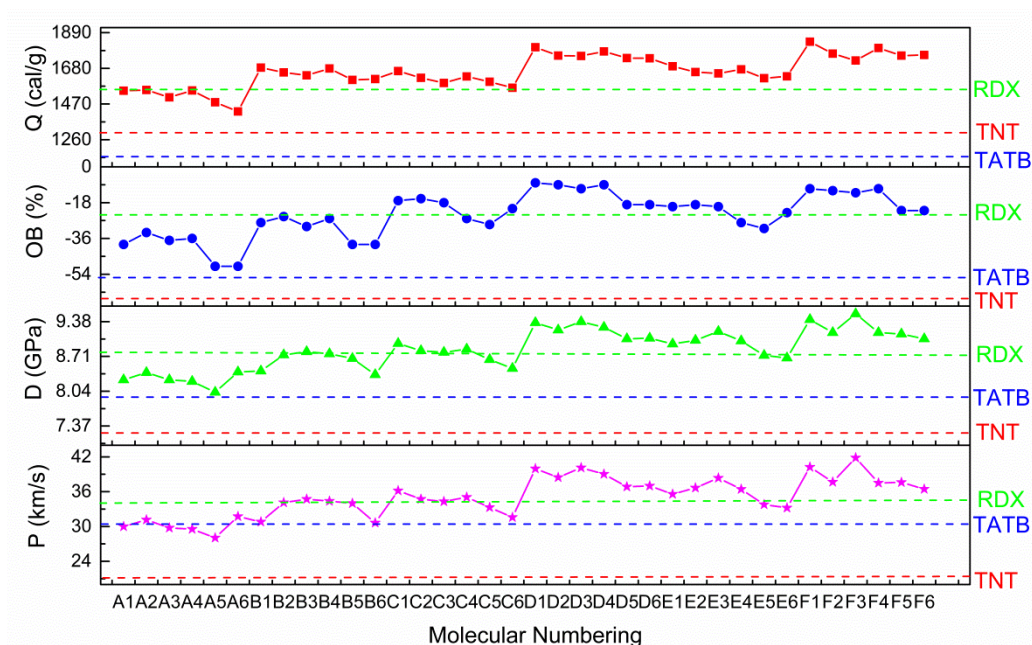


FIGURE 6 Calculated OB , P , Q and D of FTT compounds together with common explosives

3.6 | Thermal stabilities

Xiaohong^[42, 43] et al reported that R-NO₂ bond (R= C, N or O) is the weakest bond in high-energy cyclic molecules, therefore, the dissociation energy of R-NO₂ bonds of all title compounds was calculated at the PUB31YP/6-31G* level shown in Table 6. R_{g1} stands for Tetrazole ring; R_{g2} stands for furazan ring.

TABLE 6 The Wiberg bond order (BO, a. u.) and bond dissociation energy (BDE, kJ·mol⁻¹) of the relatively weak bond of 1, 2, 4, 5-tetrazine derivatives (FTT)

Compd.	R _{g1} -NO ₂		R _{g2} -NO ₂		-NH-NO ₂ (R _{g1})		-NH-NO ₂ (R _{g2})		-CH-NO ₂ (R _{g1})		-CH-NO ₂ (R _{g2})		BDE
	BO	BDE	BO	BDE	BO	BDE	BO	BDE	BO	BDE	BO	BDE	
A1	0.97	260.22	0.98	265.51									260.22
A2									0.92	132.24	0.92	110.58	110.58
A3					1.12	106.21	1.12	108.40					106.21
A4	0.92	260.61									0.91	100.57	100.57
A5											0.92	124.57	124.57
A6									0.92	107.93			107.93
B1	1.72	255.64	0.98	261.65									255.64
B2									0.92	115.08	0.92	114.68	114.68
B3					1.12	114.91	1.14	114.91					114.91
B4	0.97	255.95									0.93	136.18	136.18
B5											0.92	125.07	125.07
B6									0.92	136.58			136.58
C1	0.97	261.23	0.97	260.18									260.18
C2									0.91	124.84	0.92	135.68	124.84
C3					1.11	109.48	1.15	117.69					109.48
C4	0.96	253.34									0.92	136.18	136.18
C5											0.92	134.60	134.60
C6									0.91	125.28			125.28
D1	0.97	261.09	0.97	260.07									260.07
D2									0.92	133.58	0.91	106.12	106.12
D3					1.12	101.98	1.13	106.85					101.98
D4	0.97	260.56									0.93	107.20	107.20
D5											0.92	133.12	133.12
D6									0.92	132.92			132.92
E1	0.97	267.22	0.97	260.62									260.62
E2									0.91	137.95	0.91	118.12	118.12
E3					1.12	99.25	1.15	124.89					99.25
E4	0.98	262.19									0.92	130.54	130.54
E5											0.92	136.95	136.95
E6									0.91	136.29			136.29
F1	0.96	245.59	0.97	246.15									245.59
F2									0.91	142.03	0.92	137.85	137.85
F3					1.12	115.25	1.16	113.79					113.79
F4	0.96	246.33									0.92	128.49	128.49
F5											0.92	127.54	127.54
F6									0.91	138.33			138.33

From the data in the table, we can draw the following inferences: (1) the BDE of different bridges has little change, while the increase of coordination oxygen will reduce the stability of the compound, but the influence is small. (2) The BDE values of different substituents are arranged in the following order: $-\text{NO}_2 > -\text{CH}(\text{NO}_2)_2 > -\text{NHNO}_2$, the BDE value is inversely proportional to the number of substituents, which can be attributed to the effect of steric hindrance. (3) We also found an interesting phenomenon of the $-\text{NHNO}_2$ group, that is, its adverse effect on the stability of the compound increases when it is applied to furazan ring.

Figure 7 shows the variation trend of BO and BDE for relatively weak bonds. Through comparison, it can be seen that their change trends are not completely consistent. So we need to combine the results of BO and BDE to measure the stability of the heading compound. Xiao Heming^[44] believes that $\text{BDE} > 80 \text{ kJ} \cdot \text{mol}^{-1}$ is the entry point for the stable existence of energetic materials; If $\text{BDE} > 120 \text{ kJ} \cdot \text{mol}^{-1}$, it is considered to satisfy the stability requirements of excellent HEDC. As shown in the figure, all title compounds meet the basic requirement of stable existence. Among them, there were 23 species higher than $120 \text{ kJ} \cdot \text{mol}^{-1}$. In particular, A1 ($260.22 \text{ kJ} \cdot \text{mol}^{-1}$), B1 ($255.64 \text{ kJ} \cdot \text{mol}^{-1}$) and C1 ($260.18 \text{ kJ} \cdot \text{mol}^{-1}$) etc. fully satisfy the stability requirements of excellent HEDC.

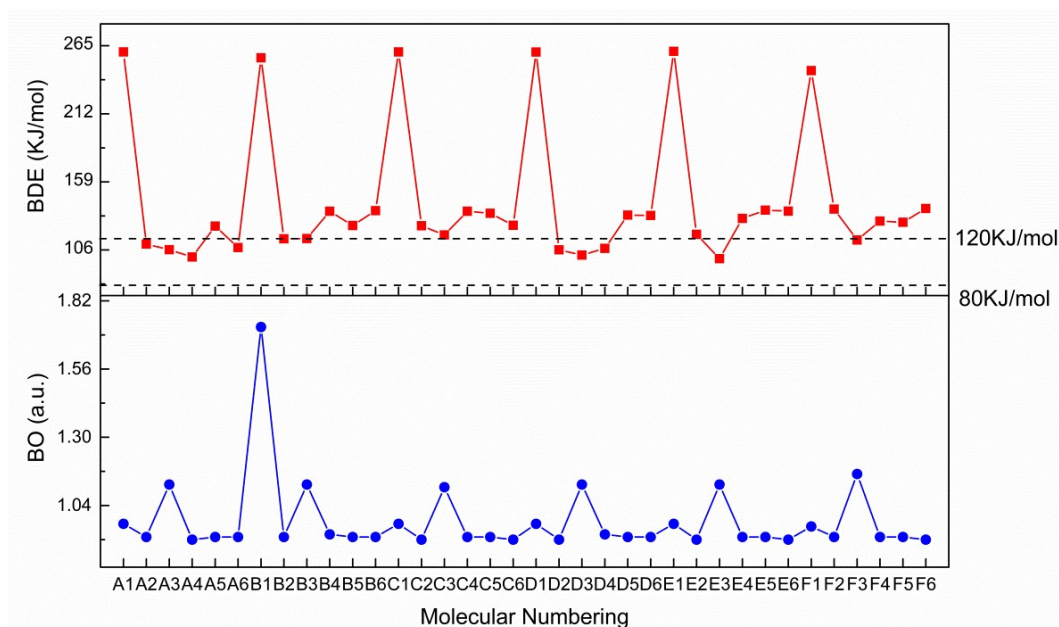


FIGURE 7 Comparison of BO and BDE with relatively weak bonds of 1, 2, 4, 5-tetrazine derivatives (FTT)

3.7 | Thermodynamic property

Thermodynamic properties can provide valuable knowledge about the reactions and macroscopic properties of energy-containing materials.^[45] In this work, we calculated the thermodynamic properties (including heat capacity (C_p), molar entropy (S_m) and molar enthalpy (H_m) of some compounds in the temperature range of 200 ~ 800 K which based on the principle of statistical thermodynamics by using Gaussian09 are shown in Table S7. Here, F2 is taken as an example, the functional relationship between its thermodynamic properties and T is listed as follows:

$$C_p = 77.7826 + 1.6888T - 8.9156 \times 10^{-4} T^2$$

$$R=0.9998$$

$$H_m = -29.7761 + 0.28609T + 3.9282 \times 10^{-4} T^2$$

$$R=0.9998$$

$$S_m = 357.28975 + 2.0628T - 6.4648 \times 10^{-4} T^2$$

$$R=0.9999$$

The results clearly show that all thermodynamic properties increase significantly with the increase of temperature, and that the rest of the compounds are similar. However, the growth rates of C_p and S_m of the heading compounds decrease gradually with the increase of temperature, while H_m increases. It is seen that both coordinating oxygen and $-NH_2-$ are conducive to the increase of C_p , S_m and H_m . Moreover, all the thermodynamic properties of the compound containing the group $-CH(NO_2)_2$ are the highest in the series, which is consistent with the previous reports^[46] that C_p , S_m and H_m increase with the increase of the steric hindrance occupied by groups.

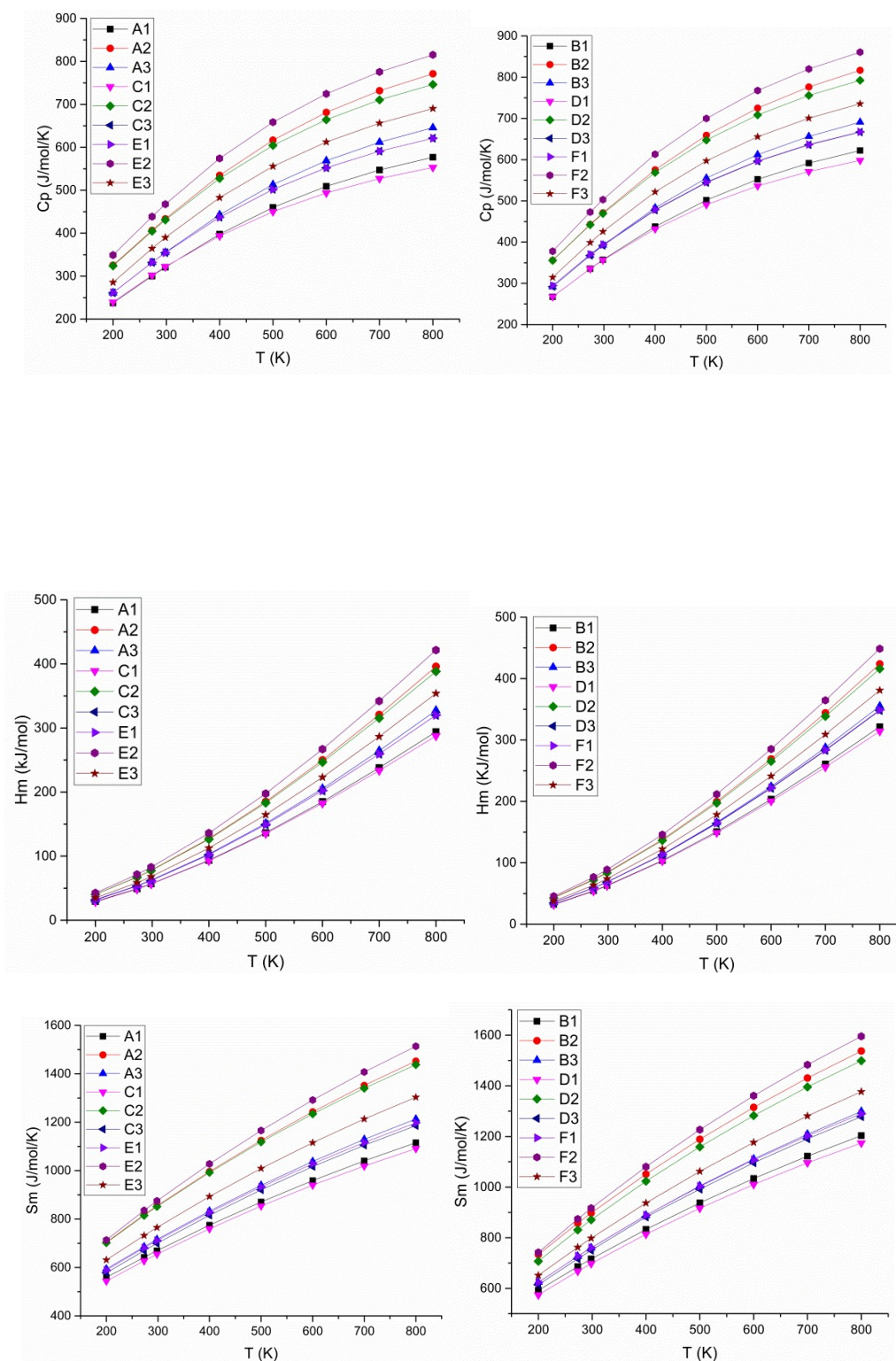


FIGURE 8 The intimate relationship between C_p , S_m , H_m and T of 1, 2, 4, 5-tetrazine derivatives(FTT)

4 | Conclusions

In this study, The thirty six FTT compounds were optimized by using the screened method B3LYP/6-311+G*, On this basis, we studied the HOMO-LUMO orbitals, *HOF*, BDE, detonation

performance and thermodynamic properties. According to the calculation results, the following conclusions can be drawn: (1) The order of influence of different bridges on *HOF* is as follows: -NH-NH- > -NH₂- > -CH₂-, and -NHNO₂ group and coordination oxygen are the best choice to improve *HOF*. (2) The -NHNO₂ group can significantly increase the density of 1, 2, 4, 5-tetrazine derivatives, on the contrary, the density decreases with the increase of -CH(NO₂)₂. (3) The introduction of -NO₂ and coordination oxygen can improve detonation performance. (4) The BDE of all FTT compounds is greater than 80kJ·mol⁻¹, of which 23 have excellent thermal stability, and the -NHNO₂ group is not conducive to improving the stability of the derivatives. (5) All thermodynamic properties including heat capacity (*C_p*), molar entropy (*S_m*) and molar enthalpy (*H_m*) increase with the increase of T, and the thermodynamic properties of compounds with -CH(NO₂)₂ groups are the highest in the series. Considering the thermal stability, compound D3, E3, F1 and F3 are regarded as potential candidates of HEDCs due to its excellent detonation performance.

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