

Theoretical studies on the thermodynamic properties, densities, detonation properties, and pyrolysis mechanisms of trinitromethyl-substituted aminotetrazole compounds

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Abstract Trinitromethyl-substituted aminotetrazoles with $-NH_2$, $-NO_2$, $-N_3$, and $-NHC(NO_2)_3$ groups were investigated at the B3LYP/6-31G(d) level of density functional theory. Their sublimation enthalpies, thermodynamic properties, and heats of formation were calculated. The thermodynamic properties of these compounds increase with temperature as well as with the number of nitro groups attached to the tetrazole ring. In addition, the detonation velocities and detonation pressures of these compounds were successfully predicted using the Kamlet–Jacobs equations. It was found that these compounds exhibit good detonation properties, and that compound G ($D = 9.2$ km/s, $P = 38.8$ GPa) has the most powerful detonation properties, which are similar to those of the well-known explosive HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocine). Finally, the electronic structures and bond dissociation energies of these compounds were calculated. The BDEs of their C–NO₂ bonds were found to range from 101.9 to 125.8 kJ/mol⁻¹. All of these results should provide useful fundamental information for the design of novel HEDMs.

Keywords Trinitromethyl-substituted tetrazole · Detonation properties · Thermodynamic properties · Bond dissociation energy · Density functional theory

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Introduction

High energy density materials (HEDMs) have been used extensively for military and civil purposes. However, there are always demands for new, improved HEDMs, as propellants must transport ever-heavier payloads, more powerful explosives are needed, and a wider range of pyrotechnics that exhibit less noise in their spectral emissions are desirable [1]. This means that research into novel HEDMs is becoming increasingly urgent. Previous studies [2–5] have shown that tetrazole derivatives are highly promising potential candidates for HEDMs due to their positive heats of formation (HOFs), high thermal stabilities, good detonation performances, and their insensitivities. The most striking feature of this family of compounds is that their energies are mainly derived from their N–N or C–N bonds rather than carbon backbone oxidation or cage strain [6], which reduces the amount of environmentally unfriendly gases (NO_x gas) produced during the explosion. In addition, the trinitromethyl group, which is stabilized by intramolecular interactions [7, 8], is a useful HEDM component as it can improve the oxygen balance of a tetrazole derivative, and the detonation energy is closely related to the oxygen balance. The oxygen balance is zero (optimal) if there is just enough oxygen in the molecule to enable the HEDM to be fully oxidized; otherwise, if there is insufficient oxygen in the HEDM to achieve this, the oxygen balance is negative, and if there is excess oxygen (i.e., some is not needed for HEDM oxidation), the oxygen balance is positive. Therefore, tetrazole derivatives containing a trinitromethyl group can show good detonation performances.

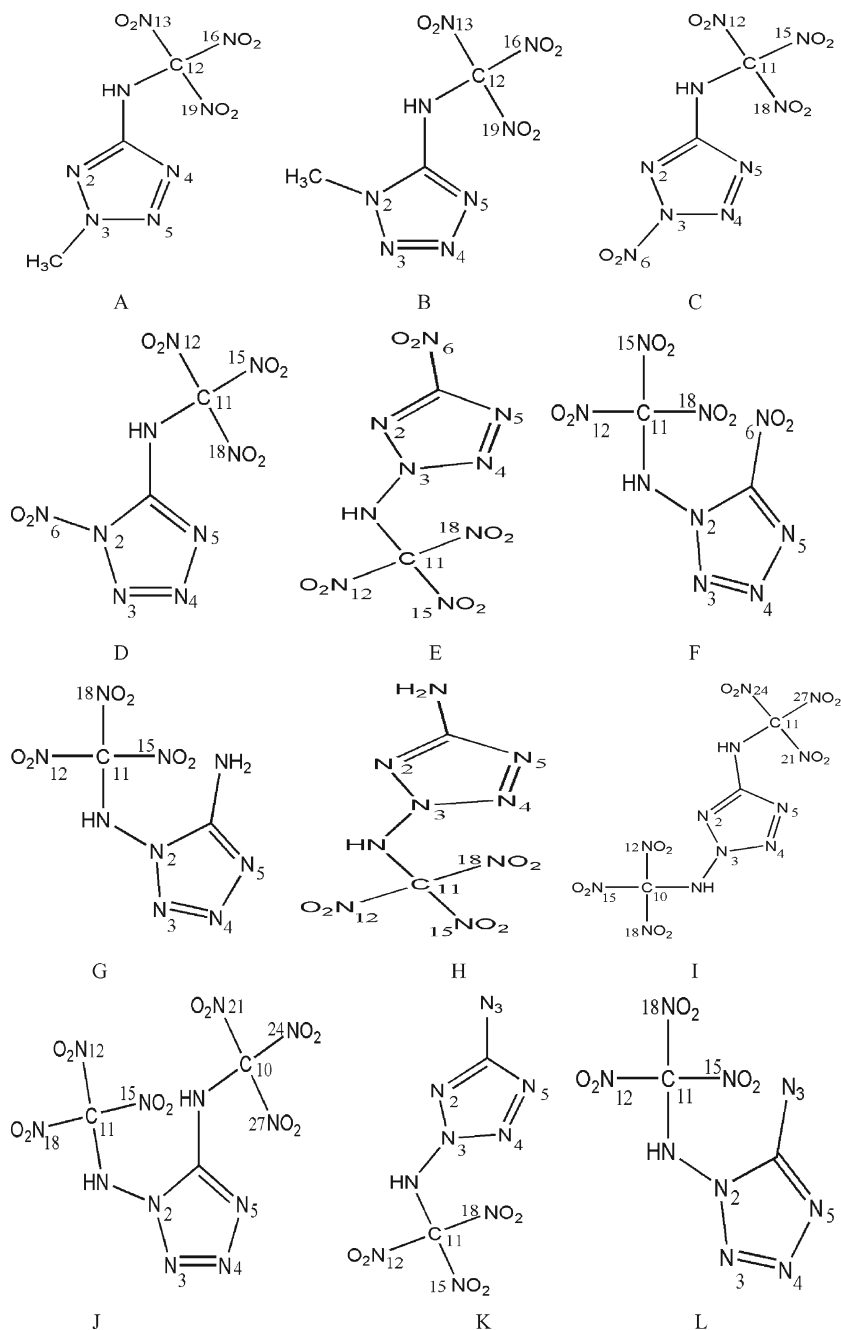
Despite growing interest in trinitromethyl-substituted tetrazoles [9] and trinitromethyl-substituted triazoles [10, 11], the experimentally determined detonation properties and thermodynamic properties of such

compounds are still unavailable, so a systematic study of trinitromethyl-substituted tetrazoles is needed. In the work described in the present paper, the gas-phase HOFs, solid-phase HOFs, thermodynamic properties, densities, detonation properties, and pyrolysis mechanisms of trinitromethyl-substituted aminotetrazoles with different groups ($-\text{NHC}(\text{NO}_2)_3$, $-\text{NH}_2$, $-\text{NO}_2$, $-\text{N}_3$, $-\text{CH}_3$) were investigated theoretically using density functional theory (Fig. 1). The main purpose of this work was to provide information that should prove useful when synthesizing these compounds and developing novel HEDMs.

Computational method

Geometry optimization and calculations of the thermodynamic properties, heats of formation, and relative properties of these compounds were performed in the Gaussian 03 package [12]. The DFT-B3LYP method [13] with the 6-31G(d) basis set, which has been extensively employed to predict the structures and detonation properties of energetic compounds [14–17], was adopted to investigate these compounds. We checked that the local minima were real (i.e., no imaginary frequencies). Additionally, vibrational analysis was performed to collect thermodynamic data.

Fig. 1 Illustration of the molecular structures of the trinitromethyl-substituted tetrazoles studied in the present work



Detonation velocities and detonation pressures—two important parameters of energetic materials—were evaluated using the empirical Kamlet–Jacobs equations [18]. These can be written as follows:

$$D = 1.01(NM^{1/2}Q^{1/2})^{1/2}(1 + 1.30\rho) \tag{1}$$

$$P = 1.558\rho^2NM^{1/2}Q^{1/2}, \tag{2}$$

where D is the detonation velocity (km/s), P is the detonation pressure (GPa), ρ is the density of the explosive (g/cm³), N is the amount (mol⁻¹) of gaseous detonation products per gram of explosive, M is the average molecular weight of the gaseous products, and Q is the chemical energy of the detonation reaction (cal/g). Since Q and ρ are unknown for these unsynthesized compounds, use of the modified Kamlet–Jacobs equations (based on the results of quantum calculations) is recommended in order to predict detonation performance [19–22]. The density ρ of an explosive can be calculated using the following equation, as suggested by Politzer et al. [23]:

$$\rho = \alpha_1 \left[\frac{M_1}{V(0.001)} \right] + \beta_1(\nu\sigma_{\text{tot}}^2) + \gamma_1, \tag{3}$$

where M_1 is the molecular mass (g/molecule) and $V(0.001)$ is the volume (Å³/molecule) defined as the space inside a counter of electron density of 0.001 e/Bohr^3 . α_1 , β_1 , and γ_1 are regression coefficients, and their values were taken from [23]. ν is the degree of balance between positive and negative potential on the molecular surface, while σ_{tot}^2 is a measure of the variability of the electrostatic potential.

The chemical energy of the detonation reaction Q can be derived from the HOFs of the products and reactants. The gas-phase HOFs of these compounds were evaluated using atom-equivalent energies and the following equation [22]:

$$\Delta H_f(g) = E(g) - \sum_i n_i x_i, \tag{4}$$

where $E(g)$ is the energy of the molecule at 0 K, n_i is the number of atoms of element i , and x_i is its atom-equivalent energy. Atom-equivalent energies were taken from [24].

However, it is reported that the detonation properties of energetic materials are usually poorly estimated using gas-phase HOFs [25]. Thus, the solid-phase HOFs of these compounds were employed to determine detonation properties. These can be calculated using the following equation:

$$\Delta_f H(s) = \Delta_f H(g) - \Delta H_{\text{sub}}, \tag{5}$$

where ΔH_{sub} is the sublimation enthalpy, which can be evaluated using the following equation suggested by Rice and Politzer et al. [26, 27]:

$$\Delta H_{\text{sub}} = \alpha_2(\text{SA})^2 + \beta_2(\nu\sigma_{\text{tot}}^2)^{0.5} + \gamma_2, \tag{6}$$

where SA is the surface area of an electron density isosurface of 0.001 e/Bohr^3 for the molecule. The coefficients α_2 , β_2 , and γ_2 were taken from [26].

The bond dissociation energy (BDE)—the difference between the energy of a molecule and those of the radicals produced when one of the bonds of this molecule is broken—was employed to investigate the pyrolysis mechanisms of these compounds. Furthermore, it is very important to understand the pyrolysis mechanism [28–30]. In the present work, the BDE of the trigger bond C–NO₂ was evaluated using the following equation:

$$\text{BDE}(A - B) = [\Delta_f H(A_{(g)}) + \Delta_f H(B_{(g)})] - \Delta_f H(A - B_{(g)}), \tag{7}$$

where A–B is the (HEDM) molecule and A and B are the radicals produced when the trigger bond is broken.

Results and discussion

HOF

The heat of formation is a good indicator of the energy content of a compound. A highly positive HOF is usually required for an effective HEDM. Therefore, the HOFs of these compounds were calculated using Eq. 4. $\Delta_f H(g)$ values, $\Delta_f H(s)$ values, and related data for these compounds are shown in Table 1.

As seen in Table 1, the HOFs of these compounds are quite large, ranging from 222.56 to 712 kJ/mol⁻¹. These highly positive HOFs are favorable from the perspective of detonation properties. In addition, the HOFs of these compounds are much larger than those of RDX (1,3,5-trinitro-hexahydro-*s*-triazine, $\Delta H_f(s) = 191.63$ kJ/mol⁻¹) and HMX (1,3,5,7-tetranitro-1,3,5,7-tetrazocine, $\Delta H_f(g) = 258.15$ kJ/mol⁻¹ [31]), which may be due to the contributions of the tetrazole ring and the trinitromethyl group. The relationship between structure and HOF is plotted in Fig. 2. It is clear that different substituent groups have different impacts on the HOF, and that compounds K and L have rather high HOFs. Upon comparing different substituents, their contributions to the HOF can be summarized as follows: –N₃> –NHC(NO₂)₃> –NH₂ ≈ –NO₂> –CH₃. Strikingly, the HOF of compound F is higher than those of the other compounds except for K and L. On the other hand, there is little difference in the HOFs calculated for different isomers with –N₃, –NHC(NO₂)₃, –NH₂, or –CH₃, indicating that the HOF is

Table 1 Calculated heats of formation and related parameters

Compound	SA (Å ²)	ν	σ_{tot}^2 ((kJ/mol ¹) ²)	ΔH_{sub} (kJ/mol ¹)	$\Delta H_{\text{f}}(\text{g})$ (kJ/mol ¹)	$\Delta H_{\text{f}}(\text{s})$ (kJ/mol ¹)
A	224.9	0.17	2729.4	104.20	326.76	222.56
B	223.4	0.17	5337.0	117.20	361.30	244.10
C	232.5	0.07	3487.9	98.00	469.07	371.07
D	229.0	0.10	3777.5	103.49	478.62	375.13
E	232.8	0.13	4514.0	112.43	524.61	412.18
F	225.7	0.12	3185.2	101.77	542.64	440.87
G	215.8	0.16	6771.7	118.43	516.78	398.35
H	218.8	0.12	4425.9	104.76	506.14	401.38
I	311.6	0.06	4264.6	147.29	564.77	417.48
J	306.0	0.10	4593.9	153.25	574.10	420.85
K	238.7	0.08	3181.6	102.20	814.24	712.04
L	235.8	0.17	3470.6	114.92	819.71	704.49
RDX						191.63 ^a
HMX					258.15 ^a	

^a From [29]

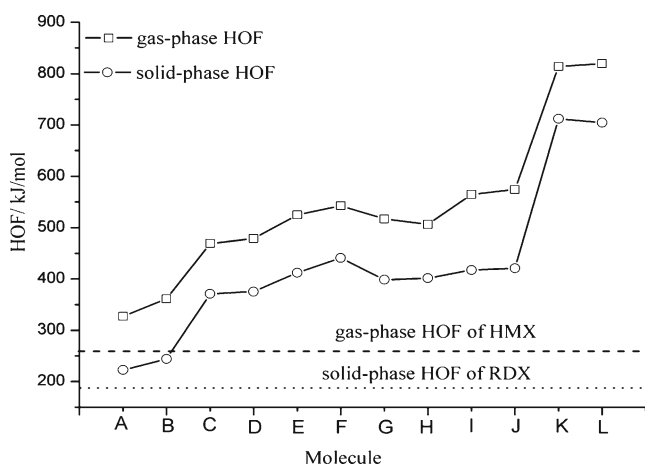
only slightly influenced by the positions of substituent groups on the tetrazole ring.

Thermodynamic properties

Utilizing vibrational analysis and a statistical thermodynamic method, the heat capacities ($C_{\text{p,m}}^0$), entropies (S_{m}^0), and enthalpy corrections (H_{T}^0) in the temperature range 200–800 K were derived and are listed in Table 2. For the vibrational analysis, a frequency scaling factor of 0.960 was adopted, as DFT-calculated harmonic vibrational frequencies are usually larger than those observed experimentally [32]. Obviously, the entropy, heat capacity, and enthalpy correction increase sharply from 200 to 800 K, as molecular translations and rotations contribute to these thermodynamic functions at low temperature, with increasing intense vibrations also contributing at high temperature. As an example, the relationships between the thermodynamic functions of compound F and temperature

are shown in Fig. 3a. As expected, $C_{\text{p,m}}^0$, S_{m}^0 , and H_{T}^0 increase with temperature. However, S_{m}^0 increases more rapidly than $C_{\text{p,m}}^0$ and H_{T}^0 .

In addition, the thermodynamic functions increase with the number of nitro groups in the compound. We can deduce that the thermodynamic functions increase as more nitro groups are attached to the tetrazole ring in the compound. For simplicity, let us take compounds A, F, and I as examples. The relationships between the thermodynamic functions and the number of nitro groups in each compound at 298 K are plotted in Fig. 3b. It is obvious that $C_{\text{p,m}}^0$, H_{T}^0 , and S_{m}^0 all increase as more nitro groups are attached. This indicates that attaching nitro groups to the tetrazole ring can improve the thermodynamic properties of these compounds. It is also clear that the positions of the substituents on the tetrazole ring have little impact on the thermodynamic properties of the compound.

**Fig. 2** Relationship between structure and HOF

Density and oxygen balance

Since detonation properties are significantly dependent on crystal density, a highly accurate approach proposed by Politzer et al. [23] was employed to predict the densities of these compounds. The calculated densities are listed in Table 3: they range from 1.73 to 1.91 g/cm³, indicating that they may exhibit good detonation performance. The density of compound J is the same as that of HMX (1.91 g/cm³) and is much larger than that of RDX (1.82 g/cm³). Moreover, the substituent groups can be listed in order of decreasing contribution to the crystal density as follows: $-\text{NHC}(\text{NO}_2)_3 \approx -\text{NO}_2 \approx -\text{NH}_2 > -\text{N}_3 > -\text{CH}_3$. This order may result from the presence of strong intermolecular interactions, such as dipole...dipole interactions between nitro groups and hydrogen bonds, in the trinitromethyl-substituted amino-tetrazoles containing $-\text{NHC}(\text{NO}_2)_3$, $-\text{NO}_2$, or $-\text{NH}_2$ groups.

Table 2 Thermodynamic properties of the HEDM compounds investigated in this work, calculated for different temperatures

Compound	Function	T (K)							
		200	298	300	400	500	600	700	800
A	$C_{p,m}^0$	183.93	236.63	237.56	284.70	323.63	354.57	378.92	398.22
	S_m^0	461.32	544.76	546.23	621.21	689.08	750.93	807.49	859.40
	H_T^0	23.30	43.98	44.42	70.60	101.08	135.06	171.78	210.67
B	$C_{p,m}^0$	185.77	238.36	239.30	286.22	324.89	355.59	379.77	398.94
	S_m^0	465.02	549.18	550.66	626.11	694.29	756.35	813.06	865.07
	H_T^0	23.59	44.44	44.89	71.23	101.85	135.94	172.76	211.73
C	$C_{p,m}^0$	195.36	250.77	251.73	298.37	335.20	363.51	385.12	401.70
	S_m^0	486.22	574.84	576.40	655.44	726.15	789.88	847.62	900.17
	H_T^0	24.82	46.78	47.25	74.84	106.59	141.59	179.07	218.44
D	$C_{p,m}^0$	194.20	250.36	251.33	298.50	335.57	363.95	385.57	402.13
	S_m^0	479.70	567.99	569.54	648.56	719.33	783.14	840.94	893.56
	H_T^0	24.51	46.40	46.86	74.44	106.22	141.26	178.79	218.21
E	$C_{p,m}^0$	192.01	247.83	248.80	296.16	333.67	362.48	384.43	401.25
	S_m^0	487.31	574.66	576.20	654.49	724.79	788.29	845.89	898.37
	H_T^0	24.49	46.14	46.60	73.93	105.50	140.38	177.77	217.09
F	$C_{p,m}^0$	192.04	248.14	249.11	296.63	334.16	362.95	384.86	401.64
	S_m^0	476.51	563.92	565.46	643.87	714.28	777.86	835.53	888.07
	H_T^0	24.18	45.85	46.31	73.68	105.30	140.22	177.66	217.02
G	$C_{p,m}^0$	182.68	237.43	238.38	284.37	320.76	348.89	370.59	387.53
	S_m^0	459.49	542.94	544.41	619.52	687.05	748.13	803.62	854.26
	H_T^0	22.80	43.49	43.94	70.15	100.49	134.03	170.05	207.99
H	$C_{p,m}^0$	181.52	236.61	237.56	283.68	320.20	348.44	370.23	387.24
	S_m^0	456.07	539.13	540.60	615.50	682.90	743.88	799.30	849.89
	H_T^0	22.53	43.13	43.57	69.71	99.98	133.48	169.46	207.36
I	$C_{p,m}^0$	286.70	367.77	369.16	436.60	489.90	530.74	562.07	586.20
	S_m^0	617.16	747.23	749.51	865.30	968.70	1061.78	1146.06	1222.75
	H_T^0	35.53	67.77	68.46	108.87	155.30	206.42	261.13	318.59
J	$C_{p,m}^0$	284.47	366.62	368.03	436.22	489.76	530.85	562.25	586.42
	S_m^0	609.78	739.15	741.42	857.00	960.35	1053.45	1137.74	1214.47
	H_T^0	35.16	67.23	67.91	108.25	154.67	205.79	260.51	318.00
K	$C_{p,m}^0$	195.59	250.82	251.77	297.90	334.25	362.24	383.69	400.25
	S_m^0	496.41	585.11	586.67	665.66	736.21	799.74	857.26	909.62
	H_T^0	24.96	46.95	47.41	74.98	106.66	141.55	178.90	218.13
L	$C_{p,m}^0$	194.31	250.27	251.23	297.73	334.24	362.28	383.76	400.32
	S_m^0	484.85	573.19	574.74	653.64	724.17	787.70	845.23	897.60
	H_T^0	24.55	46.44	46.91	74.44	106.12	141.01	178.36	217.60

Units: $C_{p,m}^0$ in $J/mol^{-1}/K$; S_m^0 in $J/mol^{-1}/K$; H_T^0 in kJ/mol^{-1}

The oxygen balance also plays an important role in the design of HEDMs. A positive oxygen balance is required for the complete oxidation of all carbon, hydrogen, and other elements in the compound (which are oxidized to form CO_2 , H_2O , etc). As seen in Table 3, all these compounds have a positive oxygen balance except for compounds A and B. Introducing an $-NO_2$ or $NHC(NO_2)_3$ group is a useful way to increase the oxygen balance of the HEDM and to release more energy.

Moreover, any of the compounds C, D, E, F, I, or J can serve as an oxidizer.

Detonation properties

The detonation velocity and detonation pressure are two key parameters of HEDMs. Several empirical methods have been developed to evaluate these two parameters [18, 33–36]. However, the Kamlet–Jacobs equations have been

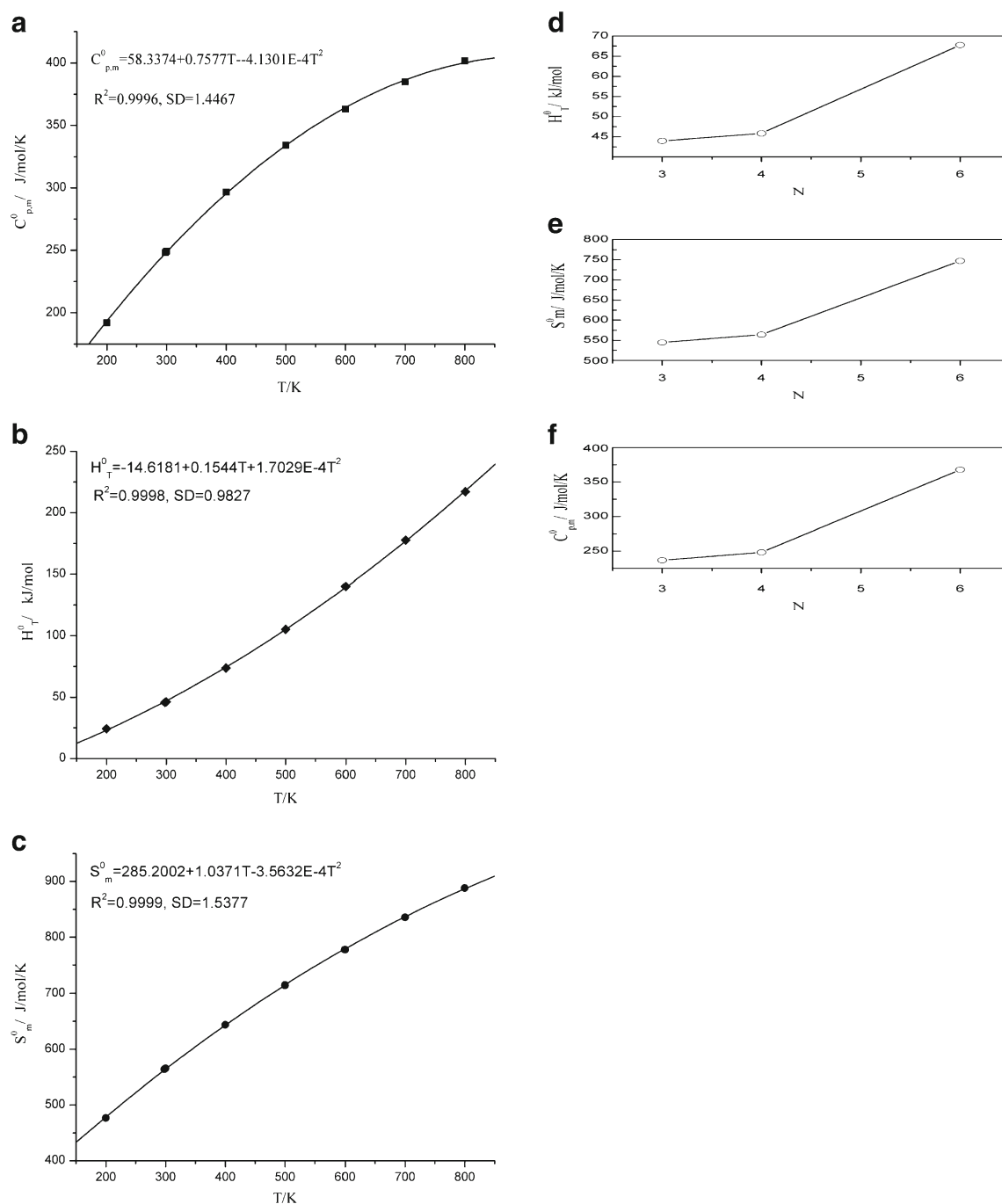


Fig. 3 **a** Relationships between three thermodynamic functions ($C_{p,m}^0$, S_m^0 , H_T^0) of compound F and the temperature (T). **b** Relationships between three thermodynamic functions ($C_{p,m}^0$, S_m^0 , H_T^0) of compounds A, F, and I and the number of nitro groups in the compound (N)

demonstrated to be reliable [14, 37, 38], and were therefore employed in this work. In the calculation of chemical energy, the products of the detonation were assumed to be N_2 , H_2O , CO_2 , and $C_{(s)}$ [25]. The calculated chemical energies, detonation velocities, and detonation pressures are collected in Table 3. For comparison, the experimental detonation parameters of RDX and HMX [31] are also shown in Table 3. Relationships between the detonation properties and molecular structure are exhibited in Fig. 4.

From Table 3, it is obvious that trinitromethyl-substituted aminotetrazoles with different substituents have a range of detonation velocities (8.3–9.2 km/s) and detonation pressures (31.0–38.8 GPa). $-CH_3$ and $-N_3$ derivatives present higher detonation velocities and detonation pressures than $-NO_2$ and $-NHC(NO_2)_3$ derivatives, while the $-NH_2$ derivatives have the highest detonation velocities and detonation pressures (e.g., 9.2 km/s and 38.8 GPa, respectively, for compound G). This indicates that introducing an $-NH_2$ group

Table 3 Predicted densities, oxygen balances, and detonation properties of these compounds

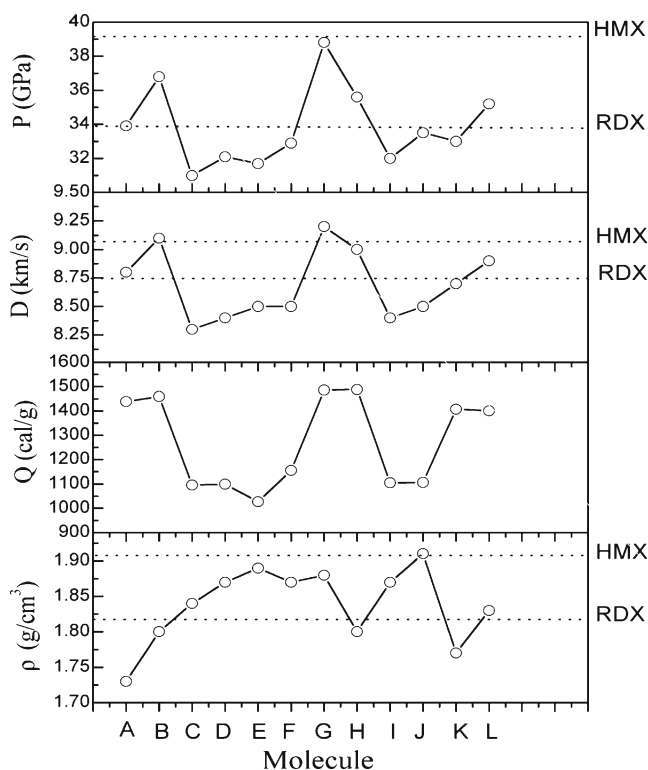
Compound	OB ₁₀₀	V (Å ³ /mol ⁻¹)	ρ (g/cm ³)	Q (cal/g)	D (km/s)	P (GPa)
A	-0.81	226.1	1.73	1439.0	8.8	33.9
B	-0.81	226.2	1.80	1459.8	9.1	36.8
C	1.25	233.6	1.84	1095.6	8.3	31.0
D	1.25	232.7	1.87	1099.1	8.4	32.1
E	1.25	234.1	1.89	1130.9	8.5	31.7
F	1.25	232.6	1.87	1155.4	8.5	32.9
G	0.20	219.9	1.88	1485.9	9.2	38.8
H	0.20	219.7	1.80	1488.8	9.0	35.6
I	1.26	329.0	1.87	1104.8	8.4	32.0
J	1.26	328.0	1.91	1106.8	8.5	33.5
K	0.54	239.3	1.77	1407.9	8.7	33.0
L	0.54	238.7	1.83	1401.4	8.9	35.2
RDX ^a	-21.60		1.82	1343.8	8.75	34.00
HMX ^a	-21.60		1.91	1345.6	9.10	39.00

^a From [29]

can enhance the detonation properties of a trinitromethyl-substituted aminotetrazole. Although $-N_3$ and $-CH_3$ derivatives have large HOFs, their low densities indicate poor detonation properties. On the other hand, while the $-NO_2$ and $-NHC(NO_2)_3$ derivatives have high densities, their chemical energies are too low. Only the $-NH_2$ derivatives have high HOFs and large chemical energies, suggesting that they have outstanding detonation properties. Furthermore, the detonation

properties of isomers (e.g., compounds G and H) are significantly influenced by the positions of the substituents on the tetrazole ring, as the substituent positions affect the density.

Figure 4 shows that compounds A, B, G, H, and L have higher detonation velocities and detonation pressures than the conventional explosive RDX. Strikingly, compounds A, B, H, K, and L show good detonation performances even though their densities are very low. Compound J has a relatively high density but its detonation performance is poor due to its low chemical energy. These results imply that the density is not the dominant influence on the detonation performance—chemical energy also plays an important role. Also, among all of the compounds, I and J contain the most nitro groups, but they do not present good detonation performances. This indicates that adding nitro groups does not greatly increase detonation

**Fig. 4** Densities, chemical energies, detonation velocities, and detonation pressures of the trinitromethyl-substituted aminotetrazoles studied in this work**Table 4** Calculated energies of the HOMO (E_{HOMO} , kJ/mol⁻¹) and LUMO (E_{LUMO} , kJ/mol⁻¹) as well as the energy gap (ΔE , kJ/mol⁻¹) and bond dissociation energy (kJ/mol⁻¹) for each HEDM compound studied in this work

Compound	E_{HOMO}	E_{LUMO}	ΔE	Bond	BDE
A	-728.8	-332.7	396.1	C(12)-N(16)O ₂	114.6
B	-757.7	-366.0	391.7	C(12)-N(16)O ₂	115.7
C	-800.3	-371.0	429.3	C(11)-N(12)O ₂	119.5
D	-829.9	-394.1	435.8	C(11)-N(15)O ₂	125.8
E	-862.7	-406.2	456.5	C(11)-N(15)O ₂	118.5
F	-875.9	-405.1	470.8	C(11)-N(18)O ₂	122.1
G	-724.6	-369.1	355.5	C(11)-N(15)O ₂	101.9
H	-682.4	-359.7	322.7	C(11)-N(12)O ₂	114.1
I	-791.9	-386.2	405.7	C(11)-N(24)O ₂	118.0
J	-810.5	-431.9	378.6	C(10)-N(27)O ₂	123.3
K	-748.8	-360.7	388.1	C(11)-N(15)O ₂	108.8
L	-778.2	-386.2	392.0	C(11)-N(12)O ₂	111.8

performance. Only compounds B and G exhibit similar detonation properties to another powerful explosive, HMX. Therefore, compounds B and G are the most promising energetic materials among these compounds.

Electronic structure and the pyrolysis mechanism

The energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) as well as the difference in energy between the HOMO and LUMO (the energy gap ΔE) for each compound studied here are shown in Table 4. When an $-\text{NO}_2$ or $-\text{NHC}(\text{NO}_2)_3$ group is introduced onto the tetrazole ring, the energies of both the HOMO and LUMO decrease in comparison to those of the $-\text{CH}_3$, $-\text{N}_3$ and $-\text{NH}_2$ derivatives, and those of the $-\text{NO}_2$ derivatives decrease the most. Additionally, it is interesting to note that the ΔE of compound F ($470.8 \text{ kJ/mol}^{-1}$) is the largest among the compounds, while that of compound H ($322.7 \text{ kJ/mol}^{-1}$) is the smallest. Also, the ΔE values of compounds C, D, E, and F are different, indicating that the energy gaps are significantly influenced by the positions of the substituents on the tetrazole ring. A small energy gap can lead to enhanced reactivity and less stability with respect to chemical and photochemical processes [39–41], so compound F may be the most reactive and compound H the least reactive of these compounds.

The strength of the trigger bond is a fundamental property of HEDMs. The BDE of the trigger bond is usually employed to investigate the initial step of HEDMs [42–45], and the $\text{N}-\text{NO}_2$ bond has been found to be the trigger bond in most nitramine HEDMs [46–48]. However, the $\text{C}-\text{NO}_2$ bond can sometimes serve as the trigger bond in HEDMs. In order to evaluate the $\text{C}-\text{NO}_2$ trigger bonds of the compounds studied here, BDEs were calculated by breaking one of the $\text{C}-\text{NO}_2$ bonds in these compounds. As is evident in Table 4, the BDEs of these compounds are in the range $101.90\text{--}125.82 \text{ kJ/mol}^{-1}$. The BDEs of $-\text{NO}_2$ and $\text{NHC}(\text{NO}_2)_3$ derivatives are larger than those of $-\text{CH}_3$, $-\text{N}_3$, and $-\text{NH}_2$ derivatives, which is in good agreement with the results of HOMO and LUMO analysis. $-\text{NO}_2$ derivatives have the largest BDEs, indicating that introducing nitro groups onto the tetrazole ring increases the sensitivity of the compound.

Conclusions

A systematic theoretical investigation of trinitromethyl aminotetrazole derivatives has been performed at the B3LYP/6-31G(d) level of DFT. The main findings of this work are summarized below:

- (1) These compounds have positive solid-phase HOFs, and different substituent groups on the tetrazole ring have different effects on the HOF. The contributions of the substituents to the HOF decrease in the order: $-\text{N}_3 > -\text{NHC}(\text{NO}_2)_3 > -\text{NH}_2 \approx -\text{NO}_2 > -\text{CH}_3$.
- (2) The thermodynamic functions of these compounds increase with temperature as well as the number of nitro groups attached to the tetrazole ring. Introducing nitro groups onto the tetrazole ring can increase the values of the thermodynamic functions.
- (3) These compounds exhibit high densities, large chemical energies, good oxygen balances, and powerful detonation properties. Compound G has the highest detonation velocity and detonation pressure (9.2 km/s, 38.8 GPa), which are similar to those of a well-known explosive, HMX.
- (4) According to a BDE analysis, the BDEs of these compounds range from 101.9 to $125.8 \text{ kJ/mol}^{-1}$. Introducing nitro groups onto the tetrazole ring increases the sensitivity of the compound.
- (5) Considering the detonation properties of these compounds, some of them (e.g., F, H, and L) may be good potential candidates for HEDMs.

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