



DFT Investigation of a High Energy Density Polynitro Compound, 2,2'-Bis(trinitromethyl)-5,5'-azo-1,2,3,4-tetrazole

He LIN¹, Shun-Guan ZHU^{1*}, Peng-Yuan CHEN¹, Kun LI¹,
Hong-Zhen LI² and Xin-Hua PENG^{1*}

¹*School of Chemical Engineering, Nanjing University of Science and Technology, Nanjing, Jiangsu, 210094, China*

²*Institute of Chemical Materials, Chinese Academy of Engineering Physics, Mianyang, Sichuan, 621900, China*
E-mail: zhuguan@yahoo.com; xinhpeng@mail.njust.edu.cn

Abstract: A novel polynitro compound, 2,2'-bis(trinitromethyl)-5,5'-azo-1,2,3,4-tetrazole, was designed and investigated at the DFT-B3LYP/6-31G(d) level. Its properties, such as electronic structure, IR spectrum, heat of formation, thermodynamic properties and crystal structure, were predicted. This compound is most likely to crystallize in the $P2_1$ space group, and the corresponding cell parameters are $Z = 2$, $a = 5.46 \text{ \AA}$, $b = 9.72 \text{ \AA}$, $c = 14.05 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$. In addition, the detonation velocity and pressure were also estimated by using the empirical Kamlet-Jacobs equations, and were predicted to be 8.28 km/s and 31.61 GPa respectively. The oxygen balance of this compound is +13.79%, which indicates that it could serve as an oxidizer. Bond dissociation energy calculations show that the C(13)-N(21)O₂ and C(14)-N(30)O₂ bonds are the locations of thermal decomposition and that this compound meets the thermal stability requirements as an exploitable explosive.

Keywords: polynitro, electronic structure, thermodynamic properties, crystal structure, detonation performance, stability

Introduction

As high energy density materials (HEDMs) are widely used for both military and civilian purposes, they have attracted considerable interest in the

recent years [1-5]. However, the current HEDMs cannot meet the increasingly high requirements. Therefore, there is an urgent need to explore novel HEDMs possessing significant advantages over the current HEDMs. Compared with traditional HEDMs, for example TNT, RDX, HMX and CL-20, azole-based HEDMs possess a higher nitrogen content, relatively higher densities, better thermal stability and lower sensitivity [6-8]. Moreover, the trinitromethyl group is an attractive unit in HEMD design, due to its high heat of formation, and good oxygen balance [9]. Thus, trinitromethyl-substituted, azole-based energetic materials may exhibit desirable detonation performance. Recently, Jean'ne M. Shreeve *et al.* have synthesized various trinitroethyl triazole compounds and found that these compounds exhibit good physical and energetic properties [10, 11]. In addition, Shun-guan Zhu *et al.* have theoretically investigated trimethyl substituted tetrazoles as potential HEDMs [12]. However, to the best of our knowledge, trinitromethyl substituted bistetrazoles have not been studied.

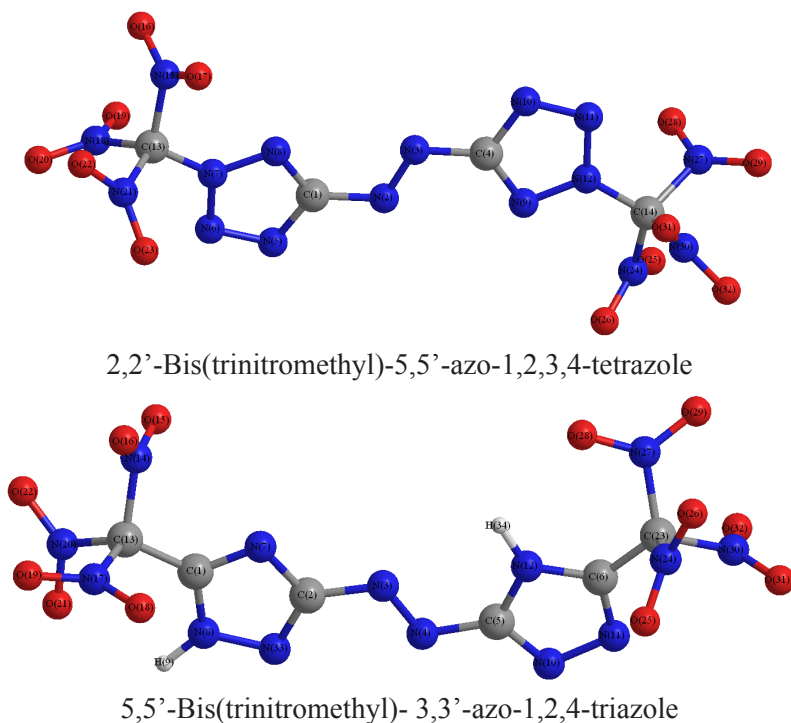


Figure 1. Optimized structures of 2,2'-bis(trinitromethyl)-5,5'-azo-1,2,3,4-tetrazole (compound **1**) and 5,5'-bis(trinitromethyl)- 3,3'-azo-1,2,4-triazole (compound **2**) at B3LYP/6-31G(d) level.

Herein, we proposed a novel polynitro tetrazole-based compound 2,2'-bis (trinitromethyl)-5,5'-azo-1,2,3,4-tetrazole (compound 1, Figure 1) as a potential HEDM and investigated its structural and energetic properties by using density functional theory. Its electronic structure, heat of formation (HOF), IR spectrum, thermodynamic properties, molecular packing, detonation performance, mechanism of pyrolytic decomposition, and thermal stability were estimated. Theoretical investigation of this designed compound will help us to understand this system better and to explore its potential as a novel HEDM.

Computational methods

Geometry optimization, the vibrational spectrum, and related properties of this compound were performed in the Gaussian03 [13] and Materials Studio 4.4 Package [14]. The DFT-B3LYP method with 6-31G(d) basis set, which has proven to be a reliable approach for the evaluation of the structural and energetic properties of energetic materials [15-17], was adopted for the investigation of this compound. A local minimum was verified without any imaginary frequency. In addition, we performed vibrational analysis and natural bond orbital (NBO) analysis at the same level. A frequency scaled factor of 0.96 was employed for the vibrational analysis, because the DFT-calculated harmonic vibrational frequencies are usually larger than those observed experimentally [18].

The empirical Kamlet-Jacobs equations [19], which are widely employed to evaluate the energy performance of HEDMs, were adopted to estimate its detonation velocity and detonation pressure. The Kamlet-Jacobs equations can be written as follows:

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

$$P = 1.558\rho^2NM^{1/2}Q^{1/2} \quad (2)$$

where D is the detonation velocity (km/s); P is the detonation pressure (GPa); ρ is the crystal density of the explosive (g/cm³); N is the moles of gaseous detonation products per gram of explosive; M is the average molecular weight of the detonation products; Q is the detonation energy (cal/g, $Q = -\Delta H_D$).

A bond dissociation energy (BDE) investigation, the difference between the energies of the parent molecule and the corresponding radicals in a unimolecular bond dissociation reaction, was carried out to evaluate its mechanism of pyrolytic decomposition and its thermal stability. In the present work, at 0 K, the BDEs of the initial bonds were calculated in terms of the following equation:

$$BDE_0(A-B) = E_0(A) + E_0(B) - E_0(A-B) \quad (3)$$

The BDE with zero point energy (ZPE) correction can be calculated by the

following equation:

$$BDE(A - B)_{ZPE} = BDE_0(A - B) + \Delta E_{ZPE} \quad (4)$$

where $E_0(A - B)$, $E_0(A)$ and $E_0(B)$ represent the energies of the parent compound and the corresponding radicals, respectively. ΔE_{ZPE} is the difference between the ZPEs of the parent compound and the corresponding radicals.

Results and Discussion

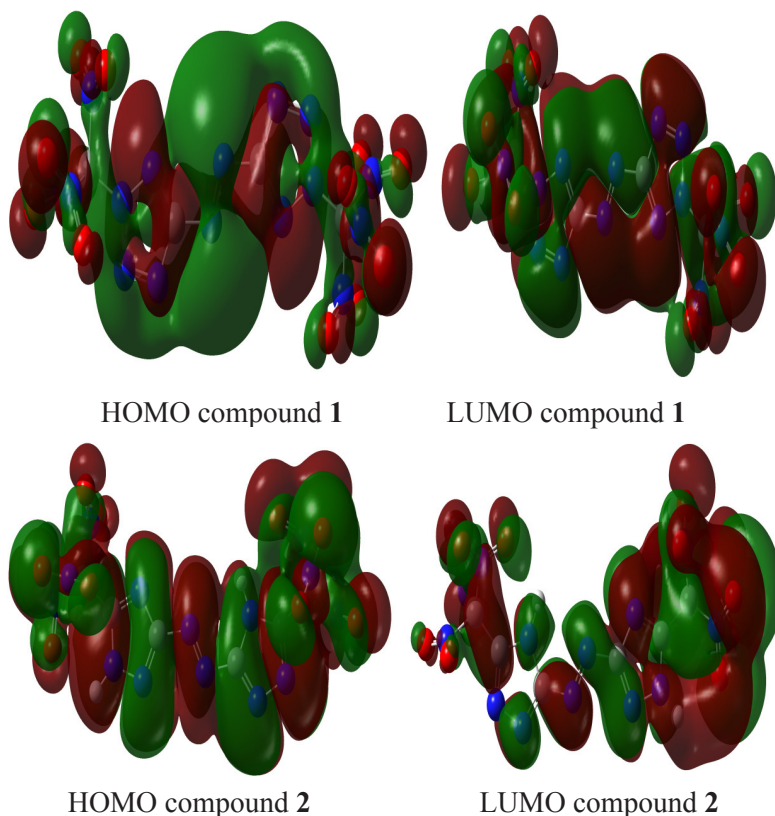
Molecular geometry and electronic structure

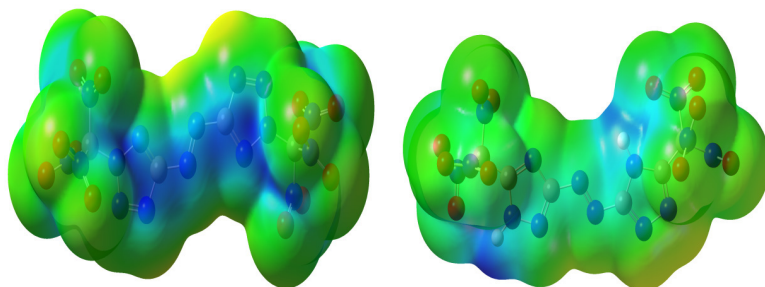
Selected bond parameters of this compound are listed in Table 1. For comparison, the corresponding geometrical parameters of 5,5'-bis(trinitromethyl)-3,3'-azo-1,2,4-triazole (compound 2, Figure 1) are also listed. Clearly, the C-N bond lengths in this compound (1.329-1.372 Å) are a little longer than those in compound 2 (1.318 to 1.361 Å). The N-N bond lengths in compound 1 are also longer than those in compound 2. This may result from the large influence of the trinitroethyl group on the tetrazole ring. Additionally, compared with those in compound 2, the C-NO₂ bonds are also slightly longer. Although there are some differences between the corresponding geometrical parameters of compound 1 and compound 2, they are not significant. Both experimental and theoretical investigations have verified that the trigger bond of polynitro compounds is usually the C-NO₂ bond [20-22]. The chemical bond strength is closely related to the bond length. Thus, based on a trigger bond length analysis between compound 1 and compound 2, we can deduce that compound 1 is also stable and can withstand external stimuli to a certain extent.

Table 1. Selected bond lengths (Å) of compounds **1** and **2**

Bond	Compound 1	Bond	Compound 2
N(2)-N(3)	1.259	N(3)-N(4)	1.264
C(1)-N(8)	1.329	C(2)-N(7)	1.361
N(8)-N(7)	1.329	N(7)-C(1)	1.318
N(7)-N(6)	1.368	C(1)-N(8)	1.360
N(6)-N(5)	1.284	N(8)-N(33)	1.333
N(5)-C(1)	1.372	N(33)-N(2)	1.341
C(13)-N(15)O ₂	1.553	C(13)-N(14)O ₂	1.544
C(13)-N(18)O ₂	1.563	C(13)-N(17)O ₂	1.571
C(13)-N(21)O ₂	1.559	C(13)-N(20)O ₂	1.535

A molecular orbital analysis can provide much useful information on electronic structures and is widely used in the analysis of chemical reactions [23-25]. The energy gap, the difference between LUMO and HOMO, is an indication of the capability of electronic transitions from occupied orbitals to unoccupied orbitals. Table 2 lists the energies of the HOMO, the LUMO and the energy gap ΔE for both compounds 1 and 2. The energy gap ΔE of compound 1 is smaller than that of compound 2. The HOMO, the LUMO and the molecular electrostatic potentials (MEP) of compounds 1 and 2 are shown in Figure 2. For compounds 1 and 2, the skeleton C-N and N-N orbitals participate in both the HOMO and the LUMO levels, and removal of an electron from the HOMO level or addition of an electron to the LUMO level can weaken the tetra/tri-azole ring. From the MEPs of compounds 1 and 2, it is readily observed that the oxygen atoms are electron rich and the nitrogen atoms are electron deficient. Furthermore, the nitrogen atoms in compound 1 are more electron deficient than those in the compound 2.





Electrostatic potential of compound **1** Electrostatic potential of compound **2**

Figure 2. HOMO, LUMO, and electrostatic potential mapped onto 0.001 electron/bohr³ contour of the electronic density at the B3LYP/6-31G(d) level. Potential colour range from red (negative) to blue (positive).

Table 2. Energies of HOMO (E_H), LUMO (E_L) and their Gap ΔE (eV) of compounds **1** and **2** at the B3LYP/6-31G(d) level

Compound	E_H	E_L	ΔE
1	-8.39	-4.53	3.85
2	-8.10	-4.20	3.90

IR spectrum and heat of formation (HOF)

The IR spectrum is an effective tool for the investigation of the identity and the basic properties of compounds. Moreover, it is closely related to the thermodynamic properties. The simulated IR spectrum of this compound is shown in Figure 3, together with the IR spectrum of compound **2**. Only some characteristic bands are discussed here, due to the complexity of the vibrational modes. Obviously, the IR spectrum of compound **1** is a little different from that of compound **2**, and there are several main characteristic regions. The significant difference between them is the peak appearing at 3620 cm⁻¹, which is from the N-H stretching mode. For compound **1**, two peaks at 1349 and 1410 cm⁻¹ are associated with the C-NO₂ symmetric stretch, while for compound **2** the corresponding peaks are at 1353 and 1421 cm⁻¹. The strongest characteristic peak appears at 1724 cm⁻¹ for compound **1** and 1726 cm⁻¹ for compound **2**, corresponding to the C-NO₂ asymmetric stretch. The weak peaks in the range 600 to 1200 cm⁻¹ are mainly caused by deformation of the azole ring. The strongest peak in this region appears at 848 cm⁻¹ for compound **1** and 807 cm⁻¹ for compound **2**.

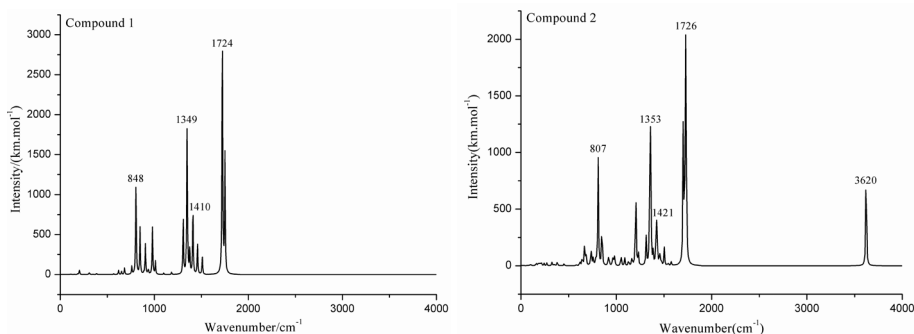
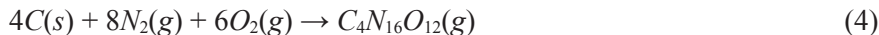


Figure 3. Calculated IR spectra for compounds **1** and **2** at the B3LYP/6-31G(d) level.

The heat of formation (HOF), one of the most useful parameters, is usually taken as an indicator of the ‘energy content’ of an HEDM. It has been reported that the DFT method is a reliable method for investigating the gas-phase HOF through appropriate reactions [26-28]. In the present work, the gas-phase HOF of compound **1** has been calculated by using the following reaction:



The total energies (E_0) and HOFs of the species involved in the reaction are listed in Table 3. Although the HOF of compound **1** is a little less than that of compound **2**, it still exhibits quite a large positive HOF.

Table 3. Calculated total energies of reaction species

	C(g)	O ₂	N ₂	Compound 1	Compound 2
E_0^a (au)	-37.776009	-150.316414	-109.518754	-1930.065468	-1898.083111
$\Delta_f H_{\text{gas}}$ (kJ/mol)	710.52	0	0	375.25	555.1 ^b

^a E_0 is the total energy after correction of the zero point energy. ^b Reference 10

Thermodynamic properties

On the basis of the vibrational analysis and the statistical thermodynamic method, the thermodynamic properties such as the standard molar heat capacity ($C_{p,m}^0$), the molar thermal entropy (S_m^0) and the thermal correction to the enthalpy (H_T^0) from 200 to 800 K of compound **1** and compound **2** were derived and are listed in Table 4. Obviously, all thermodynamic functions increase sharply with temperature from 200 to 800 K, since the thermodynamic functions involve

contributions from the translation and rotation of molecules at low temperatures and these vibrations become intensified at high temperatures. In addition, the thermodynamic functions of compound **2** increase more sharply than those of compound **1**, which may result from the contribution of the triazole ring. The temperature-dependent relations of the thermodynamic functions in the range of 200-800 K are listed in Table 4. These relationships and data are very important for the further investigation of the energetic performance of compound **1**.

Compound **1**: $C_{p,m}^0=102.755+1.243T-6.820\times 10^{-4}T^2$ ($R^2=0.9996$, $SD=2.2724$)

$S_m^0=376.833+1.734T-6.041\times 10^{-4}T^2$ ($R^2=0.9999$, $SD=2.7136$)

$H_T^0=-24.762+0.261T+2.772\times 10^{-4}T^2$ ($R^2=0.9998$, $SD=1.6242$)

Compound **2**: $C_{p,m}^0=92.134+1.310T-7.092\times 10^{-4}T^2$ ($R^2=0.9997$, $SD=2.2566$)

$S_m^0=360.979+1.750T-5.910\times 10^{-4}T^2$ ($R^2=0.9999$, $SD=2.4102$)

$H_T^0=-25.012+0.257T+2.969\times 10^{-4}T^2$ ($R^2=0.9998$, $SD=1.6933$)

where R^2 and SD are the correction coefficient and the standard deviation, respectively.

Table 4. Thermodynamic properties of compounds **1** and **2** at different temperatures

Compound	T	200	298	300	400	500	600	700	800
1	$C_{p,m}^0$	322.08	413.57	415.16	492.89	554.18	600.92	636.22	662.96
	S_m^0	696.23	842.31	844.88	975.35	1092.21	1197.58	1292.99	1379.77
	H_T^0	40.41	76.62	77.39	122.93	175.42	233.28	295.22	360.24
2	$C_{p,m}^0$	323.79	420.27	421.96	504.58	570.13	620.47	658.81	688.18
	S_m^0	684.53	832.22	834.83	967.94	1087.88	1196.48	1295.14	1385.11
	H_T^0	40.14	76.76	77.54	124.01	177.89	237.53	301.58	368.99

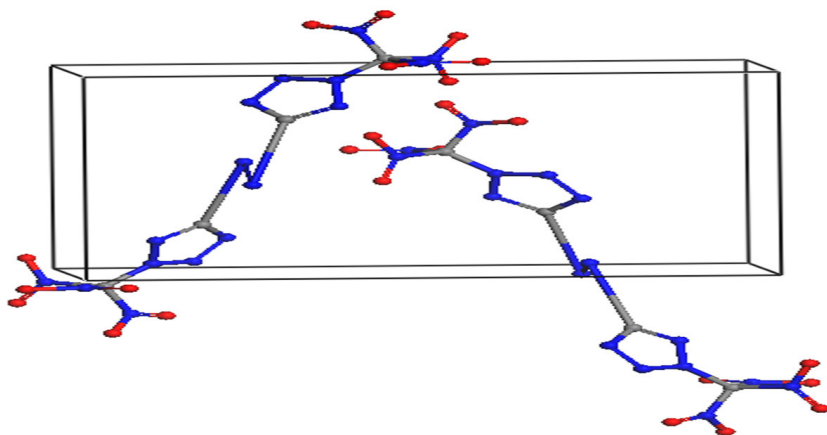
Units: T, K; $C_{p,m}^0$, J/mol/K; S_m^0 , J/mol/K; H_T^0 , kJ/mol.

Crystal structure

Monte Carlo simulation, which is widely used to calculate the crystal structure of energetic materials, was employed to predict the crystal structure of compound **1** [29-31]. Table 5 lists the unit cell parameters of the packing with the lowest energy for the seven most probable space groups [32-36]. It was found that the energies range from -550.21 to -545.57 kJ/mole/cell and that the structure with $P2_1$ symmetry has the lowest energy. Thus, compound **1** is most likely to crystallize in the $P2_1$ space group (Figure 4). The corresponding lattice parameters are $Z = 2$, $a = 5.46 \text{ \AA}$, $b = 9.72 \text{ \AA}$, $c = 14.05 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$ and $\rho = 2.07 \text{ g/cm}^3$. Obviously, this compound has a high density and may exhibit good detonation performance.

Table 5. The crystal structure of compound **1** obtained with the Compass force field in seven of the most probable space groups

Space group	Z	ρ [g/cm ³]	E [kcal/mol/asym.cell]	a [Å]	b [Å]	c [Å]	α [°]	β [°]	γ [°]
<i>P</i> -1	2	2.04	-549.91	5.49	9.94	19.00	111.54	125.25	90.02
<i>P</i> bca	8	1.99	-546.64	35.65	5.50	15.82	90.00	90.00	90.00
<i>P</i> na2 ₁	4	2.04	-547.64	16.32	17.10	5.41	90.00	90.00	90.00
<i>P</i> 2 ₁ / <i>c</i>	4	1.99	-547.97	5.41	17.28	16.51	90.00	89.93	90.00
<i>C</i> 2/ <i>c</i>	8	1.94	-545.57	16.26	5.47	39.48	90.00	115.55	90.00
<i>P</i> 2 ₁	2	2.07	-550.21	5.46	9.72	14.05	90.00	90.00	90.00
<i>P</i> 2 ₁ 2 ₁	4	2.01	-547.07	22.83	5.48	12.27	90.00	90.00	90.00

**Figure 4.** Most probable crystal structure of compound **1**.

Detonation performance

The detonation velocity (D), detonation pressure (P), and detonation energy have been estimated by using the empirical Kamlet-Jacobs equations, involving the following reaction.



Since the crystal density plays a key role in determining the detonation performance, another reliable approach proposed by Polizter *et al.* [37] has been adopted to estimate the crystal density of compound **1**. The detonation parameters are listed in Table 6. Clearly, the detonation velocity, detonation pressure and detonation energy of this compound are comparable to those of compound **2**.

Additionally, compound **1** exhibits a positive oxygen balance (+13.79%), which is much larger than that of compound **2**. This indicates that compound **1** may serve as an oxidizer *e.g.* as an alternative oxidizer to ammonium perchlorate (AP) or ammonium dinitramide (ADN). The detonation performance of compound **1** equals that of RDX and meets the requirements of HEDMs [38].

Table 6. Detonation performance of compounds **1** and **2**

Compound	ρ [g/cm ³]	D [km/s]	P [GPa]	Q [kJ/g]	OB [%]
1	1.92 ^a (2.07 ^b)	8.28 ^a (8.74 ^b)	31.61 ^a (36.74 ^b)	4.20	+13.79
2	1.83 ^b (1.87) ^c	8.96 ^c	36.65 ^c	6.13	-8.6 ^c

^a crystal density calculated using the Politzer approach; ^b crystal density calculated using the Monte Carlo approach; ^c Reference 10.

Mechanism of pyrolytic decomposition and thermal stability

Thermal stability is a fundamental property of energetic materials. It has been reported that the bond dissociation energy (BDE) of the trigger bond is an important parameter for investigating the initial step of the thermal decomposition of HEDMs [39, 40]. Previous research has shown that C-NO₂ and N-NO₂ bonds are the primary trigger bonds in polynitro HEDMs[20-22, 39, 40]. NBO analysis was carried out to find the weakest bond. Since a smaller Wiberg bond index (WBI) generally indicates a weaker bond, C(13)-N(21)O₂ and C(14)-N(30)O₂ were selected and their BDEs were calculated.

Table 7. Wiberg bond index and bond dissociation energy [kJ/mol]

Compound	Bond	WBI	BDE ₀	BDE _{ZPE}
1	C(13)-N(15)O ₂	0.8166		
	C(13)-N(18)O ₂	0.8011		
	C(13)-N(21)O ₂	0.7956	204.46	189.41
	C(14)-N(24)O ₂	0.8166		
	C(14)-N(27)O ₂	0.8011		
	C(14)-N(30)O ₂	0.7956	204.46	189.41
2	C(13)-N(14)O ₂	0.8260		
	C(13)-N(17)O ₂	0.7872	173.74	159.92
	C(13)-N(20)O ₂	0.8372		
	C(23)-N(24)O ₂	0.7852	165.45	151.16
	C(23)-N(27)O ₂	0.8308		
	C(23)-N(30)O ₂	0.8282		

According to the results shown in Table 7, the bond strength of C(13)-N(21)O₂ (BDE₀ = 204.46 kJ/mol, BDE_{ZPE} = 189.41 kJ/mol) is equal to that of C(14)-N(30)

O₂ (BDE₀ = 204.46 kJ/mol, BDE_{ZPE} = 189.41 kJ/mol). Thus, either C(13)-N(21)O₂ or C(14)-N(30)O₂ may be initially cleaved in the pyrolytic process. In contrast to compound **2**, the BDE of the trigger bonds C(13)-N(21)O₂ and C(14)-N(30)O₂ of this compound is much larger and thus compound **1** is more stable. Thus, compound **1** is thermally stable and meets the thermal requirement of HEDMs, which is that the BDE should be larger than 80 kJ/mol, and for an exploitable HEDM, 120 kJ/mol [38].

Conclusions

In the present work, a novel polynitro compound, 2,2'-bis(trinitromethyl)-5,5'-azo-1,2,3,4-tetrazole, compound **1**, has been systematically investigated by using DFT and molecular mechanics methods. The electronic structure, gas-phase HOF, IR spectrum, thermodynamic properties, crystal structure and detonation performance were calculated. The most probable molecular packing belongs to the P2₁ space group. The results also show that the detonation velocity and detonation pressure of compound **1** are 8.28 km/s and 31.61 GPa respectively, comparable to those of RDX. However, compound **1** exhibits a rather high crystal density and a good oxygen balance. On the basis of NBO analysis, C(13)-N(21)O₂ and C(14)-N(30)O₂ were identified as the weakest bonds and their BDEs were calculated. Compound **1** is more thermally stable than 5,5'-bis(trinitromethyl)-3,3'-azo-1,2,4-triazole. All of the calculated results show that compound **1** is a promising potential candidate HEDM and may serve as an oxidiser.

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