ORIGINAL PAPER

Theoretical investigation of a novel high density cage compound 4,8,11,14,15–pentanitro-2,6,9,13–tetraoxa-4,8, 11,14,15-pentaazaheptacyclo[5.5.1.1^{3,11}. 1^{5,9}] pentadecane

He Lin · Shun-guan Zhu · Lin Zhang · Xin-hua Peng · Peng-yuan Chen · Hong-zhen Li

Abstract A novel polynitro cage compound 4,8,11,14,15-pentanitro-2,6,9,13-tetraoxa-4,8,11,14,15–pentaazaheptacyclo [5.5.1.1^{3,11}.1^{5,9}]pentadecane(PNTOPAHP) has been designed and investigated at the DFT-B3LYP/6-31(d) level. Properties, such as electronic structure, IR spectrum, heat of formation, thermodynamic properties and crystal structure have been predicted. This compound is most likely to crystallize in C2/c space group, and the corresponding cell parameters are $Z=8$, $a=29.78$ Å, $b=6.42$ Å, $c=32.69$ Å, $\alpha=90.00°$, $\beta=151.05°$, $\gamma=90.00°$ and $\rho=1.94$ g/cm^3. In addition, the detonation velocity and pressure have also been calculated by the empirical Kamlet-Jacobs equation. As a result, the detonation velocity and pressure of this compound are 9.82 km/s, 44.67 GPa, respectively, a little higher than those of 4,10-dinitro-2,6,8,12–tetraoxa−4,10-diazaisowurtzitane(TEX, 9.28 km/s, 40.72 GPa). This compound has a comparable chemical stability to TEX, based on the N-NO$_2$ trigger bond length analysis. The bond dissociation energy ranges from 153.09 kJ mol^{-1} to 186.04 kJ mol^{-1}, which indicates that this compound meets the thermal stability requirement as an exploitable HEDM.

Keywords Cage compound · Crystal structure · Detonation performance · DFT · Polynitro · Stability · Thermodynamic properties

H. Lin · S.-g. Zhu (✉) · L. Zhang · X.-h. Peng · P.-y. Chen
School of chemical engineering,
Nan Jing University of Science and Technology,
Jiangsu, Nanjng 210094, China
e-mail: zhusguan@yahoo.com

H.-z. Li
Insititute of Chemical Materials,
Chinese Academy of Engineering Physic,
Sichuan, Mianyang 621900, China

Introduction

Energetic materials are widely used for military and civil applications. However, current energetic materials can not meet the increased requirements, where propellants must transport more payloads, explosive must be more powerful, and pyrotechnics demands a greater range and purity of spectral emissions [1]. Thus, exploring novel high energy density materials (HEDMs) becomes more and more urgent and active in the field of energetic materials, especially for the insensitive high energy density materials (IHEDMs) [2–5]. In order to search the novel HEDMs, numerous researches works are focused on HEDMs with compact structure and high nitrogen content. As a result, it is found that polynitro cage compounds have a positive heat of formation(HOF), high density, high detonation velocity, detonation pressure and high thermal stability [6–9], such as tetranitroadamantane (TNA), 1,3,5,7-tetranitro-2,4,6,8-tetraazacubane (TNTAC) [10], octanitrocubane (ONC), 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazaisowurtzitane (TEX, Fig. 1 right) and 2,4,6,,8,10,12-hexanitro-2,4,6,8,10,12-hexazaisowurtzitane (CL-20).

Though TEX is a powerful energetic material, the sensitivity and thermal stability of TEX is comparable to those of another well-known explosive, 1,3,5-triamino-2,4,6-trinitrobenzene (TATB) [11]. Therefore, 4,8,11,14,15-pentanitro-2,6,9,13-tetraoxa−4,8,11,14,15–pentaazaheptacyclo[5.5.1.1^{3,11}.1^{5,9}]pentadecane (PNTOPAHP, Fig. 1 left), a substituted derivative of TEX, has been proposed as a potential high density energy explosive. In this study, density functional theory (DFT) together with molecular mechanics (MM) method has been employed to investigate the structural and energetic properties of this compound, such as the electronic structure, HOF, IR, thermodynamic properties, molecular packing, detonation performance, pyrolysis mechanism and thermal stability.
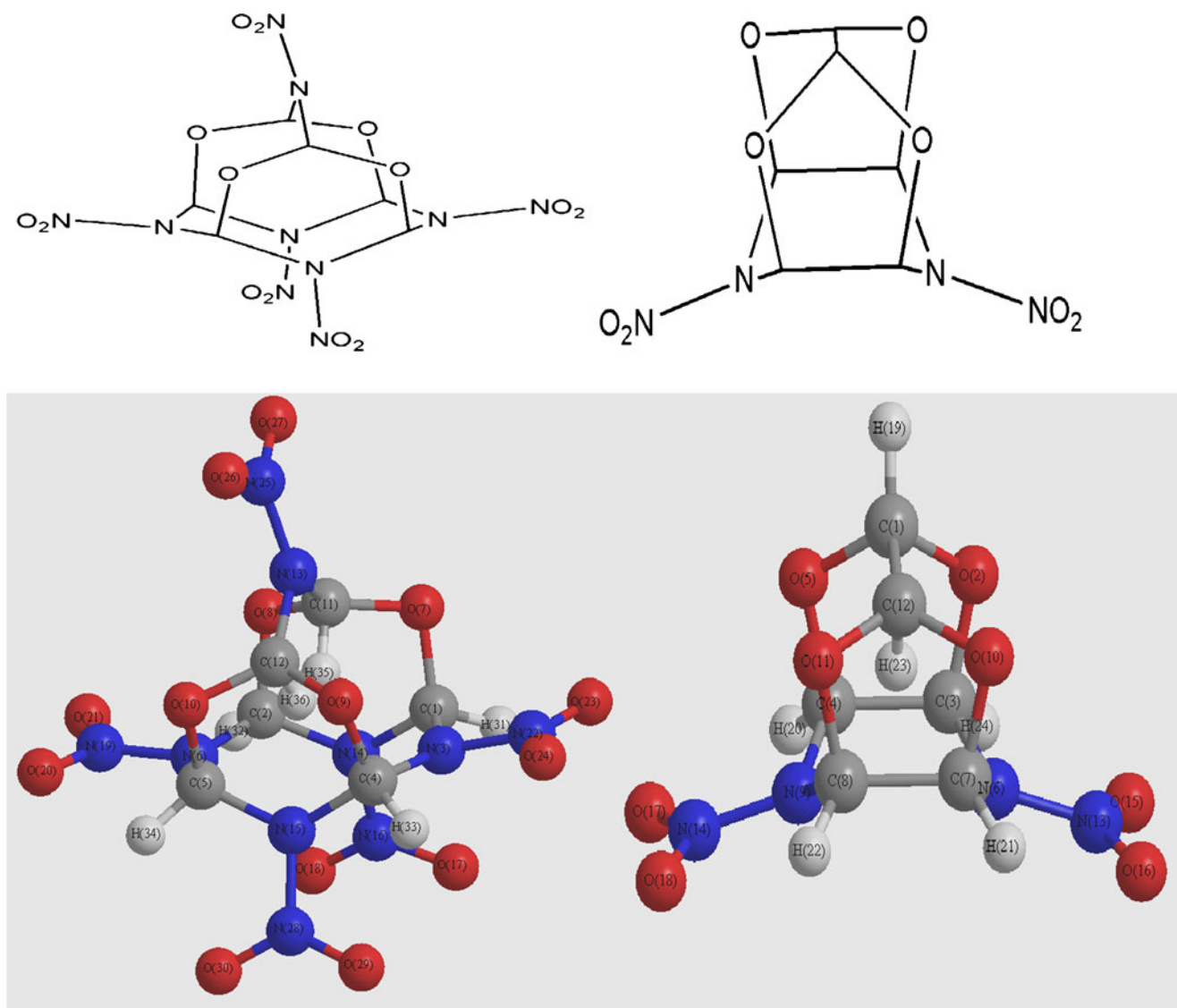
Fig. 1 Optimized structure of 4,8,11,14,15–pentanitro−2,6,9,13–tetraoxa −4,8,11,14,15-pentaazaheptacyclo[5.5.1.1³,¹¹. 1⁵,⁹] pentadecane (PNTO-PAHP, *left*) and TEX (*right*) at B3LYP/6-31G(d) level. Hydrogen atoms are omitted in the above two molecules

Computational methods

Geometry optimization, vibrational spectrum, and related properties of this compound were performed in the Gaussian03 [12] and Materials studio 4.4 Packages [13]. The DFT-B3LYP [14] method with 6-31G(d) basis set, which was extensively used to predict the structures and energetic performances of energetic materials [2, 15–18], was employed to investigate this compound. Local minimum was verified without any imaginary frequency. Meanwhile, thermodynamic data were derived from the vibrational analysis. A frequency scaled factor of 0.96 was adopted for the vibrational analysis, as DFT-calculated harmonic vibrational frequencies were usually larger than those observed experimentally [19].

The DFT-B3LYP method was successfully employed to calculate the HOFs of many organic systems by the isodesmic reaction with the bond separation reaction (BSR) rules [20–22]. Therefore, the isodesmic reaction was adopted to investigate the HOF of this compound at 298 K with the following reaction:

$$C_6H_6N_{10}O_{14} + 4CH_4 + 4CH_3NH_2 \rightarrow 7CH_3N(NO_2)CH_3. \tag{1}$$
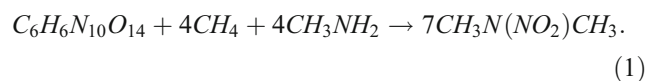
In order to compare with the performance of TEX, the HOF of TEX can also be calculated by the following isodesmic reaction:

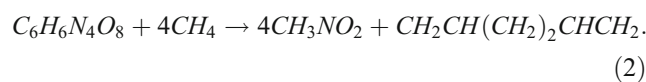$$C_6H_6N_4O_8 + 4CH_4 \rightarrow 4CH_3NO_2 + CH_2CH(CH_2)_2CHCH_2. \tag{2}$$

Table 1 Selected bond lengths (Å) and angles (°) of PNTO-PAHP and TEX at B3LYP/6-31G(d) level

	PNTOPAHP	TEX		PNTOPAHP	TEX
C-O	1.415–1.450	1.428–1.449	C-C		1.576
C-N	1.477–1.525	1.482,1.490	C-O-C	93.50,105.54	99.29,99.81
N-N	1.400–1.434	1.424	C-N-C	104.15–135.31	119.31
N-O	1.219–1.220	1.221,1.222	N-C-O	108.95–123.37	108.47,115.98
C-H	1.022–1.082	1.084,1.085	N/C-C-N[a]	110.68–111.14	108.55,109.29

[a] the angles of N/C-C-N represent the angles of N-C-N and C-C-N for PNTOPAHP and TEX, respectively

For the isodesmic reaction 1 and 2, the HOFs of this compound and TEX can be calculated as the following equation:

$$\Delta H_{298} = \sum \Delta_f H_P - \sum \Delta_f H_R$$
$$= \Delta E_0 + \Delta ZPE + \Delta H_T + \Delta nRT \quad (3)$$

where $\sum \Delta_f H_P$, and $\sum \Delta_f H_R$ are the HOFs of products and reactants at 298 K, respectively. ΔE_0 is the change in total energy between products and reactants. ΔZPE is the difference between zero-point-energy of products and reactants at 0 K. ΔH_T is the thermal correction from 0–298 K. For the isodesmic reaction 1, $\triangle n = -2$, and for the isodesmic reaction 2, $\triangle n = 0$. The gas-phase HOFs of CH_4, CH_3NO_2, CH_3NH_2, $CH_3N(NO_2)CH_3$ and $CH_2CH(CH_2)_2CHCH_2$ are -74.40, -80.80, -22.05, -82.98 84.2 kJ mol^{-1}, respectively [23]. Thus, the HOFs of this compound and TEX can be easily figured out.

The enthalpy of explosion ($\triangle H_D$) of this compound and TEX were calculated based on the following decomposition reaction, according to modified Kistiakowsky-Wilson rules [24]:

$$C_6H_6N_{10}O_{14} \rightarrow 3H_2O + 5CO_2 + CO + 5N_2, \quad (4)$$

$$C_6H_6N_4O_8 \rightarrow 3H_2O + 5CO + C + 2N_2. \quad (5)$$
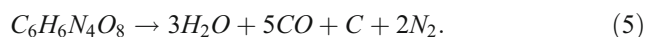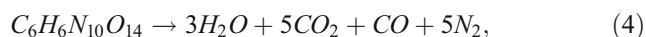
The empirical Kamlet-Jacob equations [25] widely employed to evaluate the energy performance of energetic materials were used to estimate the detonation velocity and pressure of this compound and TEX. Empirical Kamlet-Jacobs equations can be written as follows:

$$V_{det} = 1.01 \left(NM^{1/2}Q^{1/2} \right)^{1/2} (1 + 1.30\rho) \quad (6)$$

$$P_{CJ} = 1.558\rho^2 NM^{1/2}Q^{1/2}, \quad (7)$$

where Vdet is detonation velocity (km/s), PCJ is the detonation pressure (GPa), ρ is the crystal density of explosive (g/cm^3). N is the moles of gaseous detonation products per gram of explosives, M is the average molecular weight of the detonation products. Q is the detonation energy (cal/g; Q=-$\triangle$HD).

Bond dissociation energy (BDE), the difference between the energies of the parent molecule and the corresponding

HOMO PNTOPAHP   LUMO PNTOPAHP

HOMO TEX   LUMO TEX

Electronstatic potential PNTOPAHP   Electronstatic potential TEX
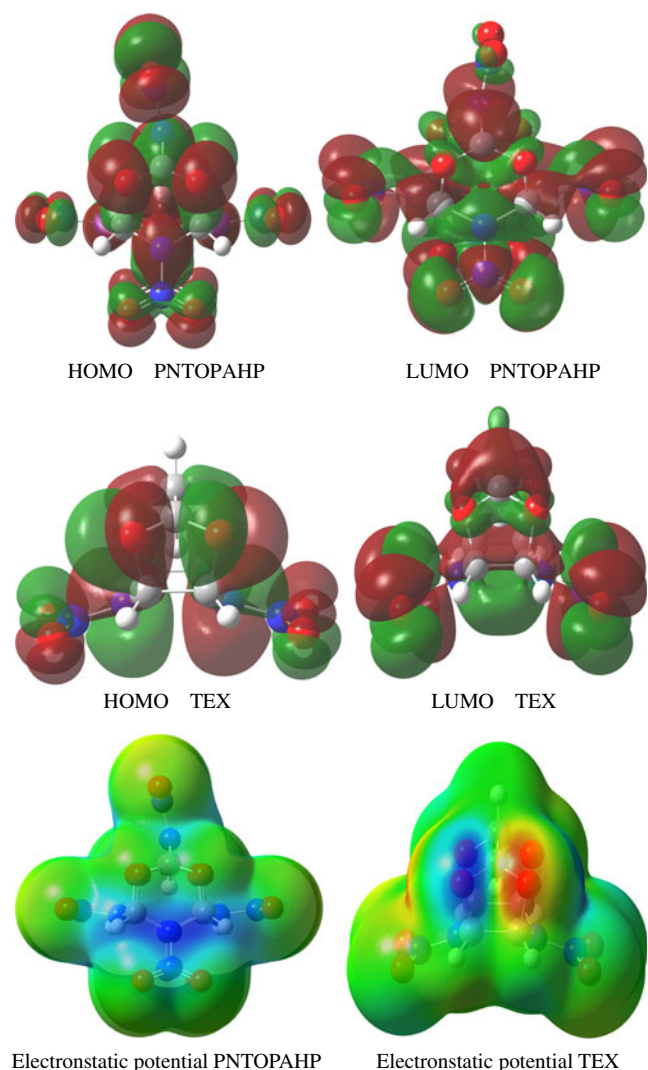
Fig. 2 HOMO, LUMO, and electrostatic potential mapped onto 0.001 electron/bohr^3 contour of the electronic density at the B3LYP/6-31G(d) level. Potential color range: from *red* (negative) to *blue* (positive)

Table 2 Energies of HOMO (E_H), LUMO (E_L) and their Gap $\triangle E(ev)$ of PNTOPAHP and TEX at B3LYP/6-31G(d) level

Compound	E_H	E_L	$\triangle E$
PNTOPAHP	−9.02	−3.10	5.92
TEX	−8.29	−2.41	5.88

Fig. 3 Calculated IR spectra for PNTOPAHP and TEX at the B3LYP/6-31G(d) level
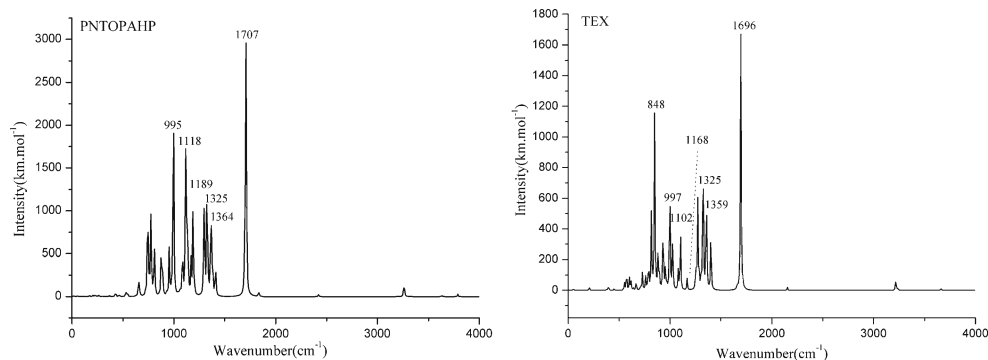
radicals in the unimolecular bond dissociation reaction, was fundamental to understand the chemical processes [26–28]. In the present study, the BDEs of all possible initiation bonds were evaluated using the following equation:

$$BDE(A - B) = [\Delta_f H(A) + \Delta_f H(B)] - \Delta_f H(A - B), \quad (8)$$

where $\Delta_f H$ (A-B), $\Delta_f H$ (A) and $\Delta_f H$ (B) represent the enthalpies of the parent compound and the corresponding radicals, respectively.

Results and discussion

Molecular geometry and electronic structure

The selected bond lengths and angles of this compound are listed in Table 1. For comparison, the geometry parameters of TEX are also exhibited. Obviously, the C-N bond lengths of both this compound and TEX are much longer than the normal C-N single bond length (1.47 Å), due to the cage strain in these systems. Whereas the N-N bond lengths of this compound and TEX range from 1.400 Å to 1.434 Å, which is shorter than the usual N-N single bond length (1.45 Å). This may be contributed from the hyperconjugation effects between nitro groups and nitrogen atoms. In

addition, the N-N bond lengths of this compound are similar to those of TEX (1.424 Å). Both experimental and theoretical studies have verified that the trigger bond of nitramine explosive usually refers to N-NO$_2$ [29–31]. The strength of chemical bond is closely related with the bond length. The longer the bond is, the less stable the bond is. The longer bond is much more easily broken by accidental external stimuli. Thus, we can deduce that this compound may have a comparable chemical stability to TEX.

Molecular orbital analysis can provide much useful information on the electronic structures, which is widely used in the chemical reaction [32–34]. Energy gap, the difference between LUMO and HOMO, indicates the capability of electron transition from occupied orbitals to unoccupied oribitals. Tables 2 lists the energies of HOMO, LUMO, and their gap △E of this compound and TEX. The energy gap △E of this compound is a little larger than that of TEX. The HOMO, LUMO and molecular electrostatic potentials (MEP) for this compound and TEX are shown in Fig. 2. Clearly, all the HOMO and LUMO levels are two-fold degenerate, which means that minor Jahn-Teller distortions are resulted by the small changes in charge state [35]. For this compound and TEX, the skeleton C-O, C-N or C-C orbitals all participate in both HOMO and LUMO levels, and addition of an electron to LUMO or removal of an electron from HOMO will break their skeleton structures. From the MEPs of this compound and TEX, it is easily figured out that oxygen atoms carry many

Table 3 HOFs of PNTOPAHP and TEX from isodesmic (1) and (2)

Compound	E_0/(a.u.)[a]	ZPE/(a.u.)	HOF/(kJ mol^{-1})
CH$_4$	−40.472096	0.043421	−74.40[b]
CH$_3$NO$_2$	−244.956720	0.048176	−80.80[b]
CH$_3$NH$_2$	−95.787915	0.061871	−22.05[b]
CH$_3$N(NO$_2$)CH$_3$	−339.557754	0.091974	−82.98[b]
CH$_2$CH(CH)$_2$CHCH$_2$	−234.467466	0.136814	84.20[b]
PNTOPAHP	−1831.696210	0.213666	251.04
TEX	−1052.400999	0.158058	71.63

[a] E_0 is after correction of the ZPE and H_T;
[b] ref 22

Table 4 Thermodynamic properties of PNTOPAHP at different temperatures [a]

Compound	T	200	298	300	400	500	600	700	800
PNTOPAHP	$C^0_{p,m}$	283.51	391.56	393.48	487.67	561.71	618.33	661.73	695.49
	S^0_m	592.69	726.33	728.75	855.33	972.46	1080.11	1178.83	1269.49
	H_T	33.58	66.79	67.51	111.74	164.37	223.50	287.59	355.52
TEX	$C^0_{p,m}$	149.28	223.66	225.03	292.63	345.92	386.55	417.71	442.08
	S^0_m	395.74	469.22	470.60	544.92	616.21	683.04	745.07	802.50
	H_T	17.27	35.58	35.99	61.99	94.03	130.75	171.03	214.06

[a] Units: T,K; $C^0_{p,m}$, J/mol$^/$K; S^0_m, J.mol$^/$K; H_T, kJ mol^{-1}

electrons and nitrogen atoms lost some electrons. Furthermore, oxygen atoms in TEX carry more electrons than those in this compound.

IR and HOF

IR spectrum is an effective tool to investigate the basic properties of compounds and identify the substances. Moreover, it is quite related to the thermodynamics properties. Figure 3 provides the calculated IR spectrum of this compound based on the scaled harmonic vibrational frequencies, together with the IR spectrum of TEX for comparison. It is found that the calculated IR spectrum of TEX is in good agreement with the previous experimental result. Only some characteristic bands have been discussed, due to the complexity of vibrational modes. For this compound, two bands at 1325 and 1364 cm^{-1} correspond to the N-NO2 asymmetric stretch, while they are 1325 and 1359 cm^{-1} for TEX. The strongest characteristic peaks of this compound and TEX, belonging to the N-NO2 asymmetric stretch, appear at 1707, 1696 cm^{-1}, respectively. Furthermore, the weak peaks at 1118, 1189 cm^{-1} for this compound and 1102, 1168 cm^{-1} for TEX are associated with the C-O-C stretch modes. Finally, the peaks in the range of 600–1200 cm^{-1} are mainly dominated by the torsion of skeleton and the bend vibration of C-H, C-O bonds. The strongest peak in this region for this compound is at 995 cm^{-1}, while it turns to a rather weak peak and the strongest peak appears at 848 cm^{-1} for TEX.

HOF, one of the most practical parameters for experiments, is usually taken as the indicator as the "energy content" of a HEMD. It has been reported that the DFT method is a reliable method to evaluate the gas-phase HOF ($\triangle$fH0gas) of energetic materials by isodesmic reactions. Hence, the stand HOFs of this compound and TEX have been calculated by the isodesmic reaction (1) and isodesmic reaction (2). Table 3 shows the total energies (E0) and HOFs of the species involved in the reactions. As expected, the HOF of this compound (251.04 kJ mol^{-1}) is much larger than that of TEX (71.63 kJ mol^{-1}), due to the presence of more NO2 groups and a higher-strain cage skeleton.

Thermodynamic properties

On the basis of vibrational analysis and statistic thermodynamic method, standard thermodynamic functions, such as thermal correction to enthalpy (HT), standard molar heat capacity (C^0_p, m) and standard molar thermal entropy (S^0_m) from 200 to 800 K of this compound and TEX are evaluated and tabulated in Table 4. Obviously, the enthalpy, heat capacity and entropy increase sharply from 200 to 800 K, as the thermodynamic functions are contributed from the translation and rotation of molecules at low temperature and intensified

Fig. 4 Relationships between the thermodynamic functions (C^0p.m: J/mol/K; S^0m: J/mol/K, HT: kJ mol^{-1}) and temperature (T; K) for PNTOPAHP and TEX
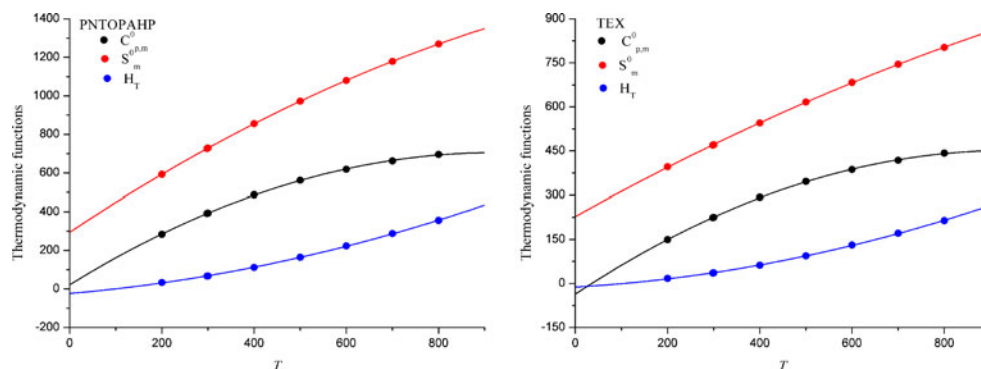
Table 5 Crystal structure of PNTOPAHP obtained with the Dreiding force field in senven of the most possible space groups

Space group	Z	ρ (g/cm³)	E (kcal/mol/asym.cell)	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
P-1	2	1.95	160.92	6.44	15.80	9.35	86.00	110.53	61.94
Pbca	8	1.91	73.68	15.57	10.49	18.84	90.00	90.00	90.00
Pna2₁	4	1.86	74.98	8.05	30.68	6.80	90.00	90.00	90.00
P2₁/C	4	1.90	73.77	25.62	35.37	19.11	90.00	174.89	90.00
C2/c	8	1.94	72.76	29.78	6.42	32.69	90.00	151.05	90.00
P2₁	2	1.90	162.87	8.63	7.93	11.70	90.00	75.18	90.00
P2₁2₁2₁	4	1.95	72.98	17.89	6.42	13.13	90.00	90.00	90.00

vibrations at high temperature. In addition, the enthalpy, heat capacity and entropy of this compound are larger than those of TEX, which is resulted due to more vibrational motions of nitro groups in this compound. The temperature dependent relations of thermodynamic functions in the range of 200–800 K are concluded as follows and shown in Fig. 4.

PNTOPAHP :
$$C^0_{p,m} = 21.811 + 1.477T - 7.974 \times 10^{-4}T^2 \left(R^2 = 0.9997, \ SD = 2.6147\right)$$
$$S^0_m = 294.338 + 1.585T - 4.586 \times 10^{-4}T^2 \left(R^2 = 1; \ SD = 0.4078\right)$$
$$H_T = -23.443 + 0.207T + 3.360 \times 10^{-4}T^2 \left(R^2 = 0.9997. \ SD = 1.9272\right)$$

TEX :
$$C^0_{p,m} = -36.086 + 1.038T - 5.529 \times 10^{-4}T^2 \left(R^2 = 0.9998; \ SD = 1.6316\right)$$
$$S^0_m = 227.782 + 0.870T - 1.876 \times 10^{-4}T^2 \left(R^2 = 0.9999; \ SD = 1.2421\right)$$
$$H_T = -12.238 + 0.092T + 2.408 \times 10^{-4}T^2 \left(R^2 = 0.9996; \ SD = 1.3615\right)$$

Where R^2 and SD represent the correlation coefficient and standard deviation, respectively.

Crystal structure

Monte Carlo simulation, which are widely used to calculate the crystal structure of energetic materials [36–38], is performed to predict the crystal structure of this compound in this paper. Table 5 collects the unit cell parameters of the packing with the lowest energy in seven of the most possible space groups [39–43]. It has been found that the energies range from 72.98 to 162.87 kJ mol⁻¹ cell⁻¹ and the structure with the C2/c symmetry has the lowest energy. Thus, this compound is most likely to crystallize in C2/c space group (Fig. 5). The corresponding lattice parameters are Z=8, a=29.78 Å, b=6.42 Å, c=32.69 Å, α=90.00°, β=151.05°, γ=90.00° and ρ=1.94 g/cm³. Obviously, this compound is a HDEM, and it may exhibit a good detonation performance.

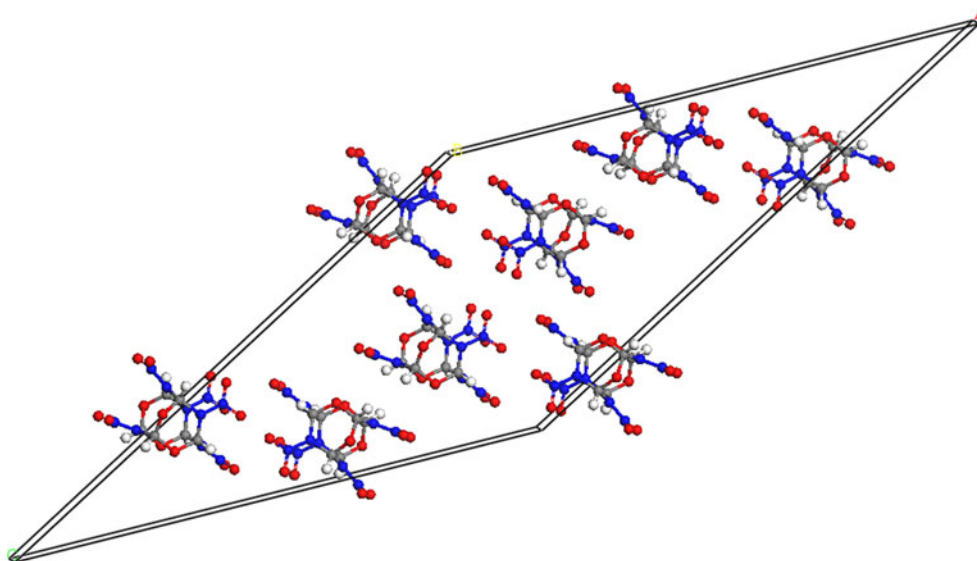**Fig. 5** Most possible crystal structure of PNTOPAHP

Table 6 Detonation performance of PNTOPAHP and TEX

Compound	ρ (g/cm³)	V_{det} (km/s)	P_{CJ} (GPa)	Q (kJ/g)
PNTOPAHP	1.94	9.82	44.67	7.21
TEX	2.01	9.28	40.72	5.65

Pyrolysis mechanism and thermal stability

Thermal stability is a fundamental property of energy materials. Previous research has shown that the nitro group is the primary trigger bond in the polynitro energetic compounds. Due to the symmetry of the structure of this compound, BDEs of three different N-NO2 bonds have been calculated, including the N(13)-NO2, N(15)-NO2 and N(3)-NO2 bonds. The results are 157.64, 153.09, 186.04 kJ mol^{-1}, respectively. The BDEs of these trigger bonds are slightly smaller than that of TEX (190.16 kJ mol^{-1}). Therefore, this compound is chemically stabile, which is quite consistent with the conclusion derived from the bond length of N-NO2 analysis. Additionally, the BDE of the trigger bond for this compound is large enough and suffices the stability requirement of HEDM [44], which is that BDE should be larger than 80 kJ mol^{-1} and for an exploitable HEDM, 120 kJ mol^{-1}.

Detonation performance

The detonation velocity (Vdet), detonation pressure (P_{CJ}) and detonation energy (Q) have been evaluated by the empirical Kamlet-Jacobs equations with the above predicted crystal density and HOF. The detonation parameters are listed in Table 6. Though the density of this compound is smaller than that of TEX, the detonation velocity, detonation pressure and detonation energy of this compound are larger than those of TEX, due to the higher HOF and better oxygen balance. The detonation performance of this compound equals to that of CL-20 (ρ=2.04 g/cm³, Vdet=9.4 km/s, P_{CJ}=42 GPa) [5], and detonation performance of this compound meets the requirements of HEDMs (i.e., ρ≈1.90 g/cm³, Vdet≈9.00 km/s, P_{CJ}≈40.0 GPa) [44].

Conclusions

A novel high energy compound 4,8,11,14,15-pentanitro-2,6,9,13-tetraoxa−4,8,11,14,15–pentaazaheptacyclo [5.5.1.1^{3,11}.1^{5,9}]pentadecane(PNTOPAHP) has been proposed and investigated by the DFT and molecular mechanics methods. Electronic structure, IR spectrum, thermodynamic properties, HOF, crystal structure, thermal stability and detonation performance have been predicted. The most possible packing structure has the C2/c symmetry.

The results also show that HOF, detonation velocity and detonation pressure of this compound are larger than those of TEX. In addition, this compound has a comparable chemical stability to TEX by N-NO2 trigger bond length analysis and BDE calculation. BDE calculation also reveals that this compound also has a high thermal stability. All calculations suggest that this compound has a comparable performance with CL-20 and is a potential candidate of HEDMs.

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