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Theoretical studies on the crystal structure, thermodynamic properties, detonation performance and thermal stability of cage-tetranitrotetraazabicyclooctane as a novel high energy density compound

Guo-zheng Zhao · Ming Lu

Abstract The B3LYP/6-31G (d) method of density functional theory (DFT) was used to study molecular geometry, electronic structure, infrared spectrum (IR) and thermodynamic properties. The heat of formation (HOF) and calculated density were estimated to evaluate the detonation properties using Kamlet–Jacobs equations. Thermal stability of 3,5,7,10,12,14,15,16-octanitro- 3,5,7,10,12,14,15,16-octaaza-heptacyclo[7.5.1.1^{2,8}.0^{1,11}.0^{2,6}.0^{4,13}.0^{6,11}]hexadecane (cage-tetranitrotetraazabicyclooctane) was investigated by calculating the bond dissociation energy (BDE) at unrestricted B3LYP/6-31G (d) level. The calculated results show that the N–NO$_2$ bond is a trigger bond during thermolysis initiation process. The crystal structure obtained by molecular mechanics (MM) methods belongs to $Pna2_1$ space group, with cell parameters $a=12.840$ Å, $b=9.129$ Å, $c=14.346$ Å, $Z=6$ and $\rho=2.292$ g·cm^{-3}. Both the detonation velocity of 9.96 km·s^{-1} and the detonation pressure of 47.47 GPa are better than those of CL-20. According to the quantitative standard of energetics and stability, as a high energy density compound (HEDC), cage-tetranitrotetraazabicyclooctane essentially satisfies this requirement.

Keywords Bond dissociation energy ·
Cage-tetranitrotetraazabicyclooctane · Density functional theory · Detonation performance · Infrared spectra · Thermodynamic property

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Introduction

High energy density compounds (HEDCs) have been receiving considerable attention because of their superior explosive performance over the currently used explosive [1–4]. Searching for novel HEDCs to meet the demands of military and civilian applications has become one of the most active research areas and seems to be never-ending [5–8]. For HEDCs, besides high detonation performance, sensitivity is a prerequisite requirement. They should be safe, stable, and reliable enough to detonate under specific conditions. So good thermal stability and low impact and shock sensitivities are of equal importance to detonation performance, but these requirements are somewhat reciprocally exclusive, with improved insensitivity bringing inferior performance and vice versa. Therefore, the foremost objective is to find the molecule having better detonation performance and safety than those currently used in explosives.

Highly nitrated cage molecules constitute a new class of energetic materials that have gained great importance in recent years [9–11]. These strained rings of cage compounds possess a concomitant increase in the heat of formation and a high density, which makes them powerful explosives [12–14]. In this class, CL-20 [2,4,6,8,10,12-hexanitrohexaazaisowurtzitane (HNIW)] is a new nitramine explosive, which has six N–NO$_2$ groups in its polycyclic structure, resulting in an increased density and heat of formation [15–17]. CL-20 is reported as an attractive high thermally stable explosive with decomposition temperature 228 °C. Octanitrocubane (ONC) [18] is another highly energetic explosive [19]. The energy performance of ONC calculated at density 2.03 g/cm^3 give 20 % more energy output than HMX [20].

The energy of highly nitrated cage molecules is derived from their very high positive heats of formation (HOFs) rather than from the combustion of the carbon backbone or the ring/cage strain. The high HOF is directly attributable to the large number of inherently energetic C–N and N–N bonds. This shows that high-nitrogen compounds could ideally store a large amount of energy. On the other hand, compounds with compact structure usually have higher densities and can also release additional energy upon detonation as a consequence of the cage strain in these systems.

The optimization of molecules with high energy and density is the primary step for searching and synthesizing HEDCs. Owing to the difficulties in the synthesis of the molecules under consideration, computer tests become an effective way to design high energy density compounds theoretically. Theoretical studies not only make it possible to screen candidate compounds, but also provide understanding in terms of the relationships between molecular structure and property [21–24]. To date, there is limited information available to cover cage-tetranitrotetraazabicyclooctane. In the present work, density functional theory and molecular mechanics methods were employed to evaluate crystal structure and properties of cage-tetranitrotetraazabicyclooctane (Fig. 1), such as heat of formation, infrared spectrum, thermodynamic properties, detonation performance and thermal stability. These results show that cage-tetranitrotetraazabicyclooctane may be a very promising high energy density compound.

Computational methods

Computations were performed with Gaussian 03 package at B3LYP [25–27] method with 6-31G (d) basis set [28]. The geometric parameters were allowed to be optimized and no constraints were imposed on molecular structure during optimization process. Vibrational frequencies were
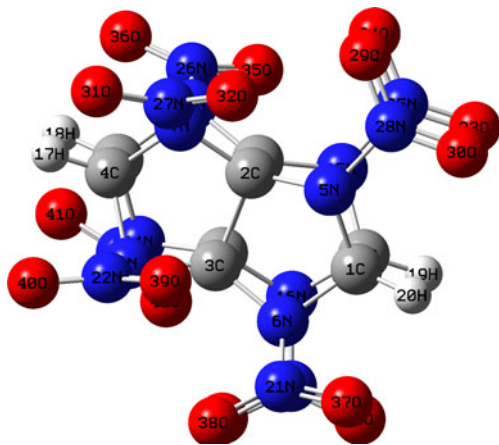

Fig. 1 Molecular structure of cage-tetranitrotetraazabicyclooctane

calculated for the optimized structure to enable us to characterize the nature of stationary point, zero–point energy (ZPE) and thermal correction (H_T). The optimized structure was characterized to be true local energy minima on potential energy surfaces without imaginary frequencies. On the basis of the principle of statistical thermodynamics [29], standard molar heat capacity $\left(C_{p,m}^{\theta}\right)$, standard molar entropy $\left(S_m^{\theta}\right)$ and standard molar enthalpy $\left(H_m^{\theta}\right)$ from 200 to 800 K were derived from the scaled frequencies using a self–compiled program.

Detonation velocity and pressure are the most important parameters to evaluate detonation characteristics of energetic materials. For the explosives with CHNO elements, the Kamlet and Jacob empirical equations were used to determine these parameters [30].

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

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

where P is detonation pressure in GPa, D is detonation velocity in km·s^{-1}, N is the number moles of gaseous detonation products per gram of explosive, M is the average molecular weight of the gaseous products, Q is the energy of explosion in J·g^{-1} of explosive and ρ is the crystal density in g·cm^{-3}. N, M and Q are determined according to the largest exothermic principle [31], i.e., for the explosives with CHNO elements, all the N atom converts into N_2, the O atom forms H_2O with H atom first and the remainder forms CO_2 with C atom. The remainder of C atom will exist in solid state if O atom does not satisfy full oxidation of C atom. The remainder of O atom will exist in O_2 if O atom is superfluous.

Since Q and ρ are unknown for the unsynthesized hypothetical compounds, to predict their detonation properties, the modified K–J equations based on the calculation results of quantum chemistry were recommended [12, 32, 33], in which the density of the explosives ρ was replaced by the crystal theoretical density (ρ_c) computed by the following equation:

$$\rho_c = -\frac{M}{V(0.001)}, \tag{3}$$

where M is the molecular mass (g/molecule) and $V(0.001)$ is the volume (cm^3/molecule) defined as the space inside a contour of electron density of 0.001 e Bohr^{-3}. However, the results obtained using this equation may have quite big errors for some systems, for example, molecules that can form strong hydrogen bonds. Politzer et al. [34] suggested that Eq. 3 should be corrected to better reflect the effects of intermolecular interactions in crystals. They have proposed

two modified equations and the better one is shown as follows [34]:

$$\rho_p = \alpha \left[\frac{M}{V(0.001)} \right] + \beta \left(\nu \sigma_{tot}^2 \right) + \gamma, \tag{4}$$

where α, β, and γ are regression coefficients and their values are taken from ref. [34]. ν is the degree of balance between the positive and negative charges on the isosurface. σ_{tot}^2 is a measure of the variability of electronic potential on the surface.

The chemical energy of the detonation reaction Q was calculated as the difference between HOFs of products and reactants. In this article, gas phase HOF was calculated using density functional method with the help of the following equations:

$$8C(s) + 2H_2(g) + 8O_2(g) + 8N_2(g)$$
$$= C_8H_4O_{16}N_{16}(g). \tag{5}$$
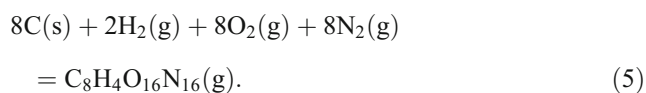
The HOF of $C_8H_4O_{16}N_{16}$ in gas phase ($\Delta_f H_{Gas}^\circ$) is readily obtained from (5) with the experimental HOFs of C(s), $H_2(g)$, $O_2(g)$, and $N_2(g)$, and the calculated enthalpies of all speries. The condensed-phase heat of formation ($\Delta_f H_{Cond}^\circ$) was then determined using $\Delta_f H_{Gas}^\circ$ and the heat of sublimation (ΔH_{Sub}) according to Hess'law [35]:

$$\Delta_f H_{Cond}^\circ = \Delta_f H_{Gas}^\circ - \Delta H_{Sub}. \tag{6}$$

The Politzer approach [36, 37] which links the ΔH_{Sub} to the MEP mapped onto the isodensity surface of an isolated molecule and has been successfully applied to many energetic compounds [38, 39] was employed to determine ΔH_{Sub}. The empirical expression of the approach is shown as:

$$\Delta H_{Sub} = \beta_1 A^2 + \beta_2 \left(\nu \sigma_{tot}^2 \right)^{0.5} + \beta_3. \tag{7}$$

Here A is the area of the isosurface of 0.001 electrons/bohr^3 electronic density following Bader et al. [40]; ν is the degree of balance between positive and negative potential on the molecular surface; σ_{tot}^2 is a measure of variability of the electrostatic potential; and β_1, β_2, and β_3 are the correlation coefficients determined via fitting to the experimentally measured heats of sublimation of a selected set of known materials. The descriptors A, ν, and σ_{tot}^2 were calculated using the computational techniques as described by Byrd and Rice [38] and the values of β_1, β_2, and β_3 were taken as those published by them.

The strength of bonding, which can be evaluated by the bond dissociation energy, is fundamental to understanding chemical processes [41]. BDE is the required energy in homolysis of a bond and is commonly denoted by difference between total energies of product and reactant after zero–point energy correction. The expressions for the homolysis of A—B bond (8) and for calculating its BDE (9) are shown as follows [42]:

$$A—B(g) \rightarrow A \bullet (g) + B \bullet (g) \tag{8}$$
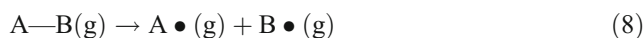
$$BDE(A—B)_{ZPE} = E(A\bullet)_{ZPE} + E(B\bullet)_{ZPE}$$
$$- E(A—B)_{ZPE}, \tag{9}$$

where A—B stands for neutral molecules and A•and B•for the corresponding product radicals after bond dissociation; BDE(A—B) is the BDE of bond A—B; $E(A—B)_{ZPE}$, $E(A\bullet)_{ZPE}$ and $E(B\bullet)_{ZPE}$ are zero-point energy corrected total energies of parent compound and corresponding radicals, respectively.

Because high energy density compounds are usually in condensed phases, especially solid forms, we predicted the possible polymorphs and crystal structure of cage-tetranitrotetraazabicyclooctane by rigorous molecular packing calculations using polymorph module of Materials Studio [43]. The Compass force field capable of predicting the condensed phase properties by searching the possible molecular packing among the most probable seven space groups ($P2_1/c$, $P-1$, $P2_12_12_1$, $Pbca$, $C2/c$, $P2_1$ and $Pna2_1$) [44–47].

Results and discussion

Molecular geometry and heat of formation

Optimized bond lengths of cage-tetranitrotetraazabicyclooctane are listed in Table 1. Because of steric hindrance effect, the N–NO$_2$ groups all depart from attached ring plane. It is proposed that the longest C–C bond in cage-tetranitrotetraazabicyclooctane corresponds to C1–C12 bond, which is 1.648 Å, while the shortest one is 1.593 Å. Thus, all the C–C bonds in cage-tetranitrotetraazabicyclooctane are much longer than the normal C–C single bond that is referred to 1.54 Å, which are elongated due to the cage strain in the system. The C–N bond of cage-tetranitrotetraazabicyclooctane is found to be shorter than the normal C–N single bond that is referred to 1.49 Å [48], while the difference is not significant. Bond lengths of N–NO$_2$ bonds in cage-tetranitrotetraazabicyclooctane lie in the range of 1.416–1.492 Å, which are longer than the usual N–N bond lengths (1.35–1.40 Å) in nitramines [49] because of the electron withdrawing inductive effect of nitro group. From data in Table 1, the longest N–O bond in cage-tetranitrotetraazabicyclooctane corresponds to the N25–O33 and N28–O30 (1.221 Å), while the shortest one turns out of N22–O40 (1.206 Å). Thus all the N–O bonds in nitro groups are around the normal N–O double bond in nitro group (about 1.2 Å) [48].

Table 1 Selected bond lengths[a] of cage-tetranitrotetraazabicyclooctane computed at B3LYP/6-31G (d) level

Bond		Bond		Bond		Bond	
C1-C12	1.648	C9-N14	1.441	N13-NO$_2$	1.457	N24-O43	1.214
C2-C3	1.603	C9-N16	1.435	N14-NO$_2$	1.444	N24-O44	1.220
C2-C11	1.600	C10-N14	1.482	N15-NO$_2$	1.416	N25-O33	1.221
C3-C9	1.593	C11-N13	1.444	N16-NO$_2$	1.434	N25-O34	1.215
C4-C10	1.604	C11-N15	1.430	N21-O37	1.216	N26-O35	1.213
C9-C11	1.599	C12-N16	1.491	N21-O38	1.215	N26-O36	1.215
C1-N6	1.456	N5-NO$_2$	1.427	N22-O39	1.217	N27-O31	1.220
C2-N7	1.444	N6-NO$_2$	1.424	N22-O40	1.206	N27-O32	1.210
C3-N6	1.445	N7-NO$_2$	1.445	N23-O41	1.218	N28-O29	1.215
C3-N8	1.446	N8-NO$_2$	1.492	N23-O42	1.212	N28-O30	1.221

a) Bond lengths in Angstroms

With the calculated enthalpies of all species and experimental sublimation enthalpy of graphite, it is easy to obtain the HOF of cage-tetranitrotetraazabicyclooctane in gas phase. The related data are collected in Table 2. The $\Delta_f H_{Cond}^o$ value has been predicted using the Politzer approach. The related results of molecular surface area A (351.16), the degree of balance between negative and positive potential ν (0.05), the square of the variability of the electrostatic potential σ_{tot}^2 (228.45 kcal·mol^{-1}), and the heat of sublimation ΔH_{Sub} (39.27 kcal·mol^{-1}) are obtained. The condensed-phase heat of formation ($\Delta_f H_{Cond}^o$) of 1206.69 kJ·mol^{-1} is larger than that of CL-20 (691.30 kJ·mol^{-1}) [9] and benefits the heat release during the detonation. This may be due to the large strain energy together with the energy content of the C–N bonds in the rigid skeleton [50]. Therefore, the high energy content of the title compound satisfies the necessary characteristic of energetic materials.

Crystal structure

Compass force field [51], capable of producing the gas-phase and condensed-phase properties reliably for a broad range of systems including nitramines such as CL-20 [52, 53], has been employed to predict the crystal structure of cage-tetranitrotetraazabicyclooctane in this paper. The approach is based on the generation of possible packing arrangements in all reasonable space groups to search for the low-lying minima in the lattice energy surface. The B3LYP/6-31G (d) level-optimized ground-state geometry is considered as the input structure for the polymorph search. The high-density polymorph is sorted out from the large number of potential crystal structures, and lattice parameters of the same are presented in Table 3. We see that the energies are in the range from −344.67 to −339.20 kJ·mol^{-1}·cell^{-1} and the structure with $Pna2_1$ symmetry has the lowest energy. Therefore, cage-tetranitrotetraazabicyclooctane tends to exist in the $Pna2_1$ space group (Fig. 2) since the stable polymorph usually possesses lower Gibbs free energy (or total energy at 0 K). The corresponding cell parameters are Z=6, a= 12.840 Å, b=9.129 Å, c=14.346 Å and ρ=2.292 g·cm^{-3}. In addition, we carefully compared the density of CL-20 predicted from the Compass force field (2.173 g·cm^{-3}) and from the volume inside an electron density contour of 0.001 e·Bohr^{-3} using Monte Carlo method (2.040 g·cm^{-3}) with the experimental value (2.035 g·cm^{-3}). For CL-20, the value predicted from the molecular structure is closer to the experimental one. Therefore, we believe 2.050 g·cm^{-3} obtained using Eq. 4 from the volume inside an electron density contour of 0.001 e·Bohr^{-3} for cage-tetranitrotetraazabicyclooctane is more reliable. The title compound may exhibit good detonation performance because density is the key factor affecting the detonation properties of high energetic density compounds.

Infrared spectra and thermodynamic properties

Figure 3 presents the simulated IR spectrum of cage-tetranitrotetraazabicyclooctane. A scaled factor of 0.96 is adopted on these frequencies because DFT-calculated harmonic vibrational frequencies are usually larger than those observed experimentally [54]. For cage-tetranitrotetraazabicyclooctane, it can be obviously seen from Fig. 3 that there are four main characteristic regions. The

Table 2 Calculated total energies of species

	C(g)	H$_2$	O$_2$	N$_2$	C$_8$H$_4$N$_{16}$O$_{16}$
E_0[a] (a.u.)	−37.84629	−1.16534	−150.31630	−109.51853	−2385.422404
$\Delta_f H$ (kJ·mol^{-1})	710.52 [b]	0	0	0	1371.08

[a] E_0 is the total energy after correction of the zero-point energy.
[b] from ref. [42]

Table 3 Unit cell parameters of the possible molecular packings of cage-tetranitrotetraazabicyclooctane

Space groups	P-1	$P2_1$	$P2_12_12_1$	$P2_1/C$	$Pna2_1$	$Pbca$	$C2/c$
Z	2	2	4	4	6	8	8
E(kJ·mol^{-1}·cell^{-1})	−339.20	−339.93	−340.41	−341.19	−344.67	−341.69	−342.13
ρ (g·cm^{-3})	2.343	2.327	2.216	2.346	2.292	2.326	2.188
a (Å)	17.858	7.065	9.239	19.595	12.840	14.161	30.697
b (Å)	7.730	13.541	12.810	20.531	9.129	26.078	8.734
c (Å)	8.509	8.669	14.692	12.069	14.346	8.975	34.801
α (°)	76.94	90.00	90.00	90.00	90.00	90.00	90.00
β (°)	128.82	93.12	90.00	160.22	90.00	90.00	157.82
γ (°)	115.76	90.00	90.00	90.00	90.00	90.00	90.00

modes in 3000–3210 cm^{-1} are associated with the C–H stretch. In this region the strongest characteristic peak is at 3110 cm^{-1}. The remarkable signal centering in 1660 cm^{-1} is associated with the N=O asymmetric stretch of nitro groups and the strong characteristic peak at 1310 cm^{-1} is characterized to the C–H wagging in plane. Band at 970 cm^{-1} is composed of the N–N asymmetric stretch of heterocycle skeleton together with C–H twisting out of plane. The peak at 850 cm^{-1} is composed of the C–H scissoring in plane. The weak peaks less than 900 cm^{-1} are mainly caused by the deformation of heterocycle skeleton and the bending vibration of C–H and C–C bonds.

Based on the scaled vibrational results, the principle of statistic thermodynamics and self–compiled program, thermodynamic properties ranging from 200 to 800 K were obtained and listed in Table 4. The correlation equations between the thermodynamic functions and temperature in the range of 200–800 K are shown as follows and can be expressed as in Fig. 4. The dependences of thermodynamic functions on temperature were analyzed and would be

helpful for further studies on other physical, chemical and energetic properties of cage-tetranitrotetraazabicyclooctane. The correlation equations are as follows:

$$C_{p,m}^{\theta} = 24.32 + 1.91T - 1.05 \times 10^{-3}T^2$$

$$S_m^{\theta} = 276.19 + 2.03T - 5.91 \times 10^{-4}T^2$$

$$H_m^{\theta} = -30.59 + 0.27T + 4.26 \times 10^{-4}T^2.$$

The corresponding correlation coefficients are 0.9996, 1.0000, and 0.9997, respectively. From these data, it is found that all the thermodynamic functions increase with temperature evidently. This is because the main contributions to thermodynamic functions are from the translations and rotations of molecules when temperature is low. However, at the higher temperature, the vibrational movement is intensified and therefore makes greater contributions to thermodynamic properties, which leads to the increase in thermodynamic functions. It is obvious that, as the temperature increases, the gradients of $C_{p,m}^{\theta}$ and S_m^{θ} decrease, while that of H_m^{θ} increases constantly. The relationship between the
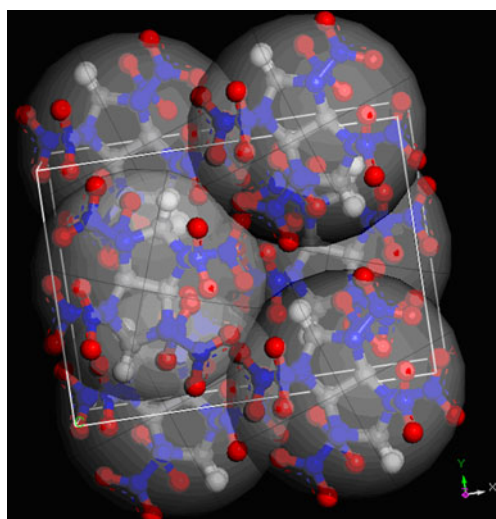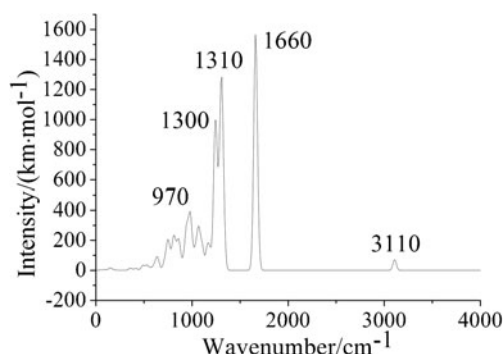

Fig. 2 Molecular packing of cage-tetranitrotetraazabicyclooctane in $Pna2_1$ space group

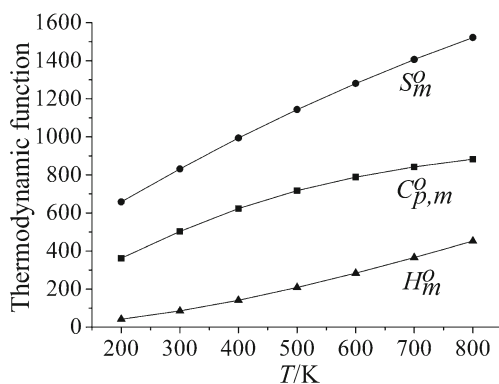**Fig. 3** Calculated IR spectra of cage-tetranitrotetraazabicyclooctane at B3LYP/6-31G (d) level

Table 4 Thermodynamic properties of cage-tetranitrotetraazabicyclooctane at different temperatures

T/K	$C_{p,m}^{\theta}/\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$S_m^{\theta}/\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$	$H_m^{\theta}/\text{kJ} \cdot \text{mol}^{-1}$
200.0	362.24	658.11	41.85
298.1	499.84	828.68	84.23
300.0	502.31	831.78	85.16
400.0	623.18	993.46	141.65
500.0	717.52	1143.13	208.90
600.0	788.63	1280.54	284.37
700.0	842.13	1406.32	366.04
800.0	882.87	1521.54	452.38

Table 5 Detonation properties of cage-tetranitrotetraazabicyclooctane, 1,3,5,7-tetranitro-2,4,6,8-tetraazacubane and CL-20

Molecule	ρ(g/cm³)	D(km/s)	P(Gpa)
$C_8H_4O_{16}N_{16}$	2.05	9.96	47.47
CL-20	1.97[a] (2.04)[b]	9.73[a] (9.38)[b]	44.64[a]
1,3,5,7-tetranitro-2,4,6,8-tetraazacubane	1.94[c]	9.80[c]	44.40[c]

[a] Calculated value from ref. [9] [b] Experimental value from ref. [55]
[c] Calculated value from ref. [56]

thermodynamic functions and the temperature makes the evaluation of the thermodynamic functions at different temperatures very easy and is necessary for predicting reactive properties at various temperatures. Because there are no experimental values for cage-tetranitrotetraazabicyclooctane, our results may be used as references for experimental work and further studies on the physical and chemical properties of cage-tetranitrotetraazabicyclooctane.

Detonation performance

Table 5 summarizes the detonation properties of cage-tetranitrotetraazabicyclooctane, 1,3,5,7-tetranitro-2,4,6,8-tetraazacubane as well as CL-20. Together with the density of 2.05 g/cm³ obtained using Eq. 4 from the volume inside an electron density contour of 0.001 e·Bohr⁻³, the detonation velocity (D) and detonation pressure (P) of cage-tetranitrotetraazabicyclooctane are computed by Kamlet–Jacobs empirical equations on the basis of theoretical density (ρ_p) and condensed-phase heat of formation ($\Delta_f H_{\text{Cond}}^o$), which are the important parameters to evaluate performances of explosion of energetic materials.

Fig. 4 Relationships between the thermodynamic functions ($C_{p,m}^{\theta}$, S_m^{θ} and H_m^{θ}) and temperature (T) for cage-tetranitrotetraazabicyclooctane

In comparison with famous caged explosives 1,3,5,7-tetranitro-2,4,6,8-tetraazacubane and CL-20, cage-tetranitrotetraazabicyclooctane exhibits much better detonation performance (ρ=2.05 g/cm³, D=9.96 km/s, P=47.47 GPa). Therefore, the above prediction indicates that cage-tetranitrotetraazabicyclooctane appears to be a promising candidate comparable to explosives 1,3,5,7-tetranitro-2,4,6,8-tetraazacubane and CL-20. According to energy criterion for HEDC, i.e., ρ≈1.90 g/cm³, D≈9.0 km/s, and P≈40.0 GPa, it is found from Table 5, that cage-tetranitrotetraazabicyclooctane satisfies the requirements as a novel high energy density compound.

Thermal stability

Thermal stability is a fundamental and very important property of energetic materials. It can be deduced on the basis of bond dissociation energies (BDE). At present, people have reached a consensus that nitro groups often represent the primary cause of initiation reactivity of organic polynitro compounds [57–61]. Therefore, we select the weakest bonds (N–N bonds) as the breaking bond to calculate BDE at B3LYP/6-31G(d) level. The calculated BDE_{ZPE} value indicates relative sensitivity of cage-tetranitrotetraazabicyclooctane. Considering the practical requirements and based on the results of these studies, a quantitative criteria associated stability (BDE of the trigger bond) requirement, i.e., BDE ≈ 80–120 kJ mol⁻¹ [62], is proposed and employed to filtrate and recommend potential HEDCs [63]. The BDE_{ZPE} value of cage-tetranitrotetraazabicyclooctane (81.81 kJ mol⁻¹) essentially satisfies this requirement. By analyzing the structure of title compound, it is easy to find that cage-tetranitrotetraazabicyclooctane has a symmetric structure. The symmetry delocalizes π electron cloud density of system, which makes BDE_{ZPE} of cage-tetranitrotetraazabicyclooctane increase. This shows that the structure of cage-tetranitrotetraazabicyclooctane has a great influence on the thermal stability. The above investigations provide important theoretic information for molecular design of high energetic density compounds.

Conclusions

In this study, density functional theory and molecular mechanics methods were employed to study the molecular geometry, electronic structure, IR spectrum, thermodynamic functions, heat of formation, detonation performance and thermal stability of a novel high energy density compound, cage-tetranitrotetraazabicyclooctane. The most possible packing structure belongs to $Pna2_1$ space group. Calculation results of detonation velocity and detonation pressure indicate that cage-tetranitrotetraazabicyclooctane ($\rho=2.05$ g/cm^3, $D=9.96$ km/s, $P=47.47$ GPa) outperforms CL-20, which essentially satisfies the quantitative criteria for the energy as HEDC. An analysis of bond dissociation energies for several relatively weak bonds suggests that N–NO$_2$ bond is the weakest one and is possible to happen in thermal decomposition. These results provide theoretical support for molecular design and experimental synthesis of HEDCs.

References

1. Bushuyev OS, Brown P, Maiti A, Gee RH, Peterson GR, Weeks BL, Hope-Weeks LJ (2012) J Am Chem Soc 134:1422–1425
2. Ravi P, Gore GM, Tewari SP, Sikder AK (2012) Propelllants Explos Pyrotech 18:52–58
3. Zhang JY, Du HC, Wang F, Gong XD, Huang YS (2011) J Phys Chem A 115:6617–6621
4. Zhang JG, Niu XQ, Zhang SW, Zhang TL, Huang HS, Zhou ZN (2011) Comput Theor Chem 964:291–297
5. Tan BS, Peng RF, Long XP, Li HB, Jin B, Chu SJ (2012) J Mol Model 18:583–589
6. Wang F, Du HC, Zhang JY, Gong XD (2011) J Phys Chem A 115:11788–11795
7. Fischer N, Izsak D, Klapotke TM, Rappengluck S, Stierstorfer J (2012) Chem Eur J 18:4051–4062
8. Li XH, Zhang RZ, Zhang XZ (2010) J Hazard Mater 183:622–631
9. Ghule VD, Jadhav PM, Patil RS, Radhakrishnan S, Soman T (2010) J Phys Chem A 114:498–503
10. Bayat Y, Mokhtari J (2011) Def Sci J 61:171–173
11. Odbadrakh K, Lewis JP, Nicholson DM (2010) J Phys Chem C 114:7535–7540
12. Qiu L, Xiao HM, Gong XD, Ju XH, Zhu WH (2006) J Phys Chem A 110:3797–3807
13. Xu XJ, Xiao HM, Ju XH, Gong XD, Zhu WH (2006) J Phys Chem A 110:5929–5933
14. Richard RM, Ball DW (2008) J Mol Struct 858:85–87
15. Maksimowski P, Fabijanska A, Adamiak J (2010) Propelllants Explos Pyrotech 35:353–358
16. Bayat Y, Hajimirsadeghi SS, Pourmortazavi SM (2011) Org Process Res Dev 15:810–816
17. Lin CP, Chang CP, Chou YC, Chu YC, Shu CM (2010) J Hazard Mater 176:549–558
18. Zhang MX, Eaton PE, Gilardi R (2000) Angew Chem Int 39:401–404
19. Ravi P, Gore GM, Sikder AK, Tewari SP (2012) Int J Quantum Chem 112:1667–1677
20. Sharia O, Kuklja MM (2011) J Phys Chem B 115:12677–12686
21. Zhang XW, Zhu WH, Xiao HM (2010) J Phys Chem A 114:603–612
22. Wei T, Zhu WH, Zhang XW, Li YF, Xiao HM (2009) J Phys Chem A 113:9404–9412
23. Turker L, Atalar T, Gumus S, Camur Y (2009) J Hazard Mater 167:440–448
24. Zhang GH, Zhao YF, Hao FY, Zhang PX, Song XD (2009) Int J Quantum Chem 109:226–235
25. Becke AD (1992) J Chem Phys 97:9173–9177
26. Lee C, Yang W, Parr RG (1988) Phys Rev B 37:785–789
27. Becke AD (1993) J Chem Phys 98:5648–5652
28. Frisch MJ, Trucks GW, Schlegel HB, Scuseria GE, Robb MA, Cheeseman JR, Montgomery JA, Vreven T Jr, Kudin KN, Burant JC, Millam JM, Iyengar SS, Tomasi J, Barone V, Mennucci B, Cossi M, Scalmani G, Rega N, Petersson GA, Nakatsuji H, Hada M, Ehara M, Toyota K, Fukuda R, Hasegawa J, Ishida M, Nakajima T, Honda Y, Kitao O, Nakai H, Klene M, Li X, Knox JE, Hratchian HP, Cross JB, Adamo C, Jaramillo J, Gomperts R, Stratmann RE, Yazyev O, Austin AJ, Cammi R, Pomelli C, Ochterski JW, Ayala PY, Morokuma K, Voth GA, Salvador P, Dannenberg JJ, Zakrzewski VG, Dapprich S, Daniels AD, Strain MC, Farkas O, Malick DK, Rabuck AD, Raghavachari K, Foresman JB, Ortiz JV, Cui Q, Baboul AG, Clifford S, Cioslowski J, Stefanov BB, Liu G, Liashenko A, Piskorz P, Komaromi I, Martin RL, Fox DJ, Keith T, Al-Laham MA, Peng CY, Nanayakkara A, Challacombe M, Gill PM, Johnson B, Chen W, Wong MW, Gonzalez C, Pople JA (2003) Gaussian 03. Gaussian Inc, Pittsburgh, PA
29. Hill TL (1960) Introduction to statistic thermodynamics. Addison-Wesley, New York
30. Kamlet MJ, Jacobs ST (1968) J Chem Phys 48:23–30
31. Zhang XH, Yun ZH (1989) Explosive chemistry. National Defence Industry Press, Beijing
32. Xu XJ, Xiao HM, Gong XD, Ju XH, Chen ZX (2005) J Phys Chem A 109:11268–11274
33. Bulat FA, Toro-Labbé A, Brinck T, Murray JS, Politzer P (2010) J Mol Model 16:1679–1691
34. Politzer P, Martinez J, Murray JS, Concha MC, Toro-Labbé A (2009) Mol Phys 107:2095–2101
35. Atkins PW (1982) Physical Chemistry, 2nd edn. Oxford University Press, Oxford
36. Politzer P, Ma Y, Lane P, Concha MC (2005) Int J Quantum Chem 105:341–347
37. Politzer P, Murray JS, Grice ME, Desalvo M, Miller E (1997) Mol Phys 91:923–928
38. Byrd EFC, Rice BM (2006) J Phys Chem A 110:1005–1013
39. Jaidann M, Roy S, Abou-Rachid H, Lussier LS (2010) J Hazard Mater 176:165–173
40. Bader RFW, Carroll MT, Cheeseman JR, Chang C (1987) J Am Chem Soc 109:7968–7979
41. Politzer P, Murray JS (1996) J Mol Struct 376:419–424
42. Lide DR (ed) (2002) CRC Handbook of Chemistry and Physics. CRC, Boca Raton
43. Materials Studio 4.4. (2008) Accelrys
44. Chernikova NY, Belsky VK, Zorkii PM (1990) J Struct Chem 31:661–666
45. Mighell AD, Himes VL, Rodgers JR (1983) Acta Crystallogr A 39:737–740
46. Srinivasan R (1992) Acta Crystallogr A 48:917–918
47. Baur WH, Kassner D (1992) Acta Crystallogr B 48:356–369
48. Cao XZ, Song TY, Wang XQ (1987) Inorganic chemistry. Higher Education Press, Beijing
49. Archibald TG, Gilardi R, Baum K, George C (1990) J Org Chem 55:2920–2924

50. Fan XW, Qiu L, Ju XH (2009) Struct Chem 20:1039–1042
51. Sun H (1998) J Phys Chem B 102:7338–7364
52. Xu XJ, Zhu WH, Xiao HM (2007) J Phys Chem B 111:2090–2097
53. Xu XJ, Zhu WH, Xiao HM (2008) Chin J Chem 26:602–606
54. Scott AP, Radom L (1996) J Phys Chem 100:16502–16513
55. Sikder AK, Sikder N (2004) J Hazard Mater 112:1–15
56. Politzer P, Lane P, Murray JS (2011) Central Eur J Energetic Mater 8:39–52
57. Owens FJ, Jayasuriya K, Abrahmsen L, Politzer P (1985) Chem Phys Lett 116:434–438
58. Xiao HM, Fan JF, Gu ZM, Dong HS (1996) Chem Phys 226:15–24
59. Murray JS, Politzer P (1990) Chemistry and physics of energetic materials. Kluwer, Dordrecht
60. Michels HH, Montgomery JA (1993) J Phys Chem 97:6602–6606
61. Murray JS, Concha MC, Politzer P (2009) Mol Phys 107:89–97
62. Chung G, Schmidt MW, Gordon MS (2000) J Phys Chem A 104:5647–5650
63. Xiao HM, Xu XJ, Qiu L (2008) Theoretical design of high energy density materials. Science Press, Beijing