

Trinitromethyl/trinitroethyl substituted CL-20 derivatives: structurally interesting and remarkably high energy

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Abstract A series of trinitromethyl/trinitroethyl substituted derivatives of 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo[5,5,0, 0^{3.11},0^{5.9}] dodecane (CL-20) were designed and investigated by theoretical methods. Intramolecular interactions between the trinitromethyl/trinitroethyl and the cage were investigated. The effects of trinitromethyl/trinitroethyl groups on stability of the parent compound are discussed. The results reveal a mutual influence of bond length and dihedral angle between the trinitromethyl and the cage. Compared to CL-20, the sensitivity of derivatives is barely affected. Properties such as density, heat of formation and detonation performance of these novel compounds were also predicted. The introduction of the trinitromethyl group can significantly enhance the oxygen balance, density and detonation properties of the parent compound. The remarkable energy properties make these novel cage compounds competitive high energy density materials.

Keywords Trinitromethyl · Trinitroethyl · CL-20 · Structure · Stability

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Introduction

In recent years, the chemistry of cage “hexaazaisowurtzitane” has gained considerable interest [1–3]. 2,4,6,8,10,12-Hexanitro-2,4,6,8,10,12-hexaazatetracyclo[5,5,0, 0^{3.11},0^{5.9}] dodecane (CL-20) is considered to be one of the most powerful explosives known [4–6].

New energetics must also meet increased performance requirements, where propellants must transport ever increasing payloads and explosives become ever more powerful. The design and synthesis of new energetic compounds superior to CL-20 represents one of the most attractive approaches in new energetic material research. Energetic materials chemistry pushes the limits of the unique molecules that can be created, while retaining some semblance of stability. The design of modern energetic materials is a modern scientific challenge [7].

Most research on “hexaazaisowurtzitane” has focused on the synthesis of hexa-functional-hexaazaisowurtzitane by condensation of primary amines with glyoxal as the starting material of CL-20 [8], or on optimization of the preparation of CL-20 [9]. The design and synthesis of new energetic compounds based on the CL-20 cage skeleton are not much reported. Ghule et al. [10] reported a theoretical study of triazole-substituted CL-20, but the predicted performance of all reported compounds was lower than that of CL-20.

The nitroform (trinitromethyl) group is an energetic group inherently rich in oxygen. An adequate oxygen content of the trinitromethyl group can significantly increase the oxygen balance (OB) value of a compound. CL-20 is a compound with negative OB. It would be reasonable to think that compounds of CL-20 series would perform better with improved OB. A number of nitroform derivatives including trinitromethyl and trinitroethyl groups are well synthesized [11, 12], but the thermal stability of trinitroethyl-substituted compounds is usually poor—reported to be generally limited to 150 °C when solid and 100 °C when molten

[13]. In a continuing effort to seek more powerful energetic materials, we synthesized 4-trinitroethyl-2,6,8,10,12-pentanitroheptazaaisowurtzitane [14], which proved to have surprisingly high thermal stability (the decomposition temperature is 236.16 °C). Furthermore, the impacted sensitivity of 7.8 J of **1** contrasted with the 3.0 J of CL-20, proving that **1** has a better stability. This stimulated us to investigate more hexaazaisowurtzitane cage compounds that are modified by trinitromethyl or trinitroethyl groups. So compounds **1–6** were designed as a series of energetic materials (Scheme 1). To shed some light on the origin of the stability of trinitromethyl/trinitroethyl-substituted CL-20 derivatives, a series of computations was carried out that addressed thermodynamic and structural questions, including the interaction between the cage and the trinitromethyl/trinitroethyl groups. Properties such as density (ρ), heat of formation (HOF), detonation velocity (D) and detonation pressure (P) are also discussed.

Computational methods

The Gaussian 03 program package [15] was employed in this study. All molecular structures were optimized using the B3LYP [16–18] method of density functional theory (DFT) and the 6–31 G(d) basis set [19, 20]. Results in this paper were all calculated at B3LYP 6–31 G(d) level unless otherwise stated. The results of vibrational analysis, without imaginary vibrational frequency, confirmed that the structures obtained correspond to the minima on their potential energy hypersurfaces.

The predictive density of energetic materials containing C, H, N and O elements can be gained conveniently by calculating the statistical average value of 100 molar volumes, which is estimated by the Monte-Carlo method based

on 0.001 electrons bohr⁻³ density. Xiao et al [21]. proved that there is little difference between the calculated density and the crystalline density according to this method.

The value of HOF was estimated by the method of isodesmic reaction. The isodesmic reactions of CL-20, **1** and **5** are shown in Scheme 2. HOF values of compounds in the reaction were obtained from the literature. The values of total energies (E_0), zero point energies (ZPE), thermal corrections (ΔH_T) of compounds in the isodesmic reaction were listed in [Electronic supplementary material](#).

The solid-phase HOF was calculated by deducting the heat of sublimation (ΔH_s) from the gas-phase HOF. Politzer et al. [22] published a method to evaluate the ΔH_s using the parameters of SA, σ_{Tot}^2 and v . Later, Rice and coworkers [23, 24] took advantage of this method to speculate on the ΔH_s of many energetic materials, and proved that ΔH_s calculated by this method is in good agreement with experiment values. The following equations are indispensable:

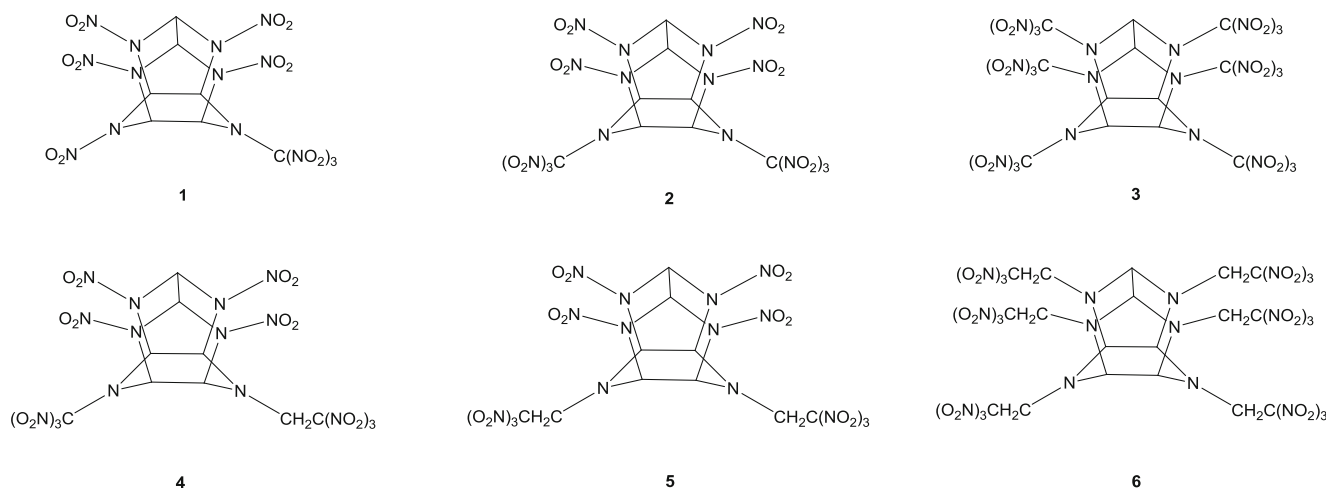
$$V(r) = \sum_A \frac{Z_A}{|R_A - r|} - \int \frac{\rho(r') dr'}{|r' - r|} \quad (1)$$

$$\Delta H(\text{Sublimation}) = a(\text{SA})^2 + b\sqrt{\sigma_{\text{Tot}}^2 v} + c \quad (2)$$

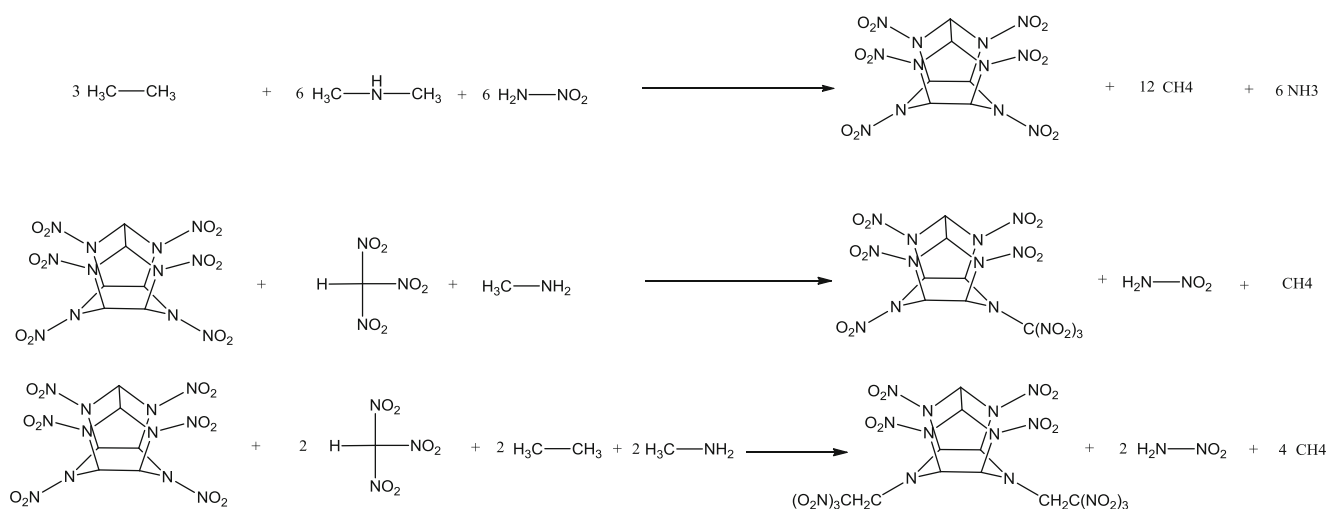
$$\sigma_{\text{Tot}}^2 = \sigma_+^2 + \sigma_-^2 = \frac{1}{m} \sum_{i=1}^m [V^+(r_i) - \bar{V}_S^+]^2 + \frac{1}{n} \sum_{j=1}^n [V^-(r_j) - \bar{V}_S^-]^2 \quad (3)$$

$$v = \frac{\sigma_+^2 \sigma_-^2}{[\sigma_{\text{Tot}}^2]^2} \quad (4)$$

where Z_A is the charge on nucleus A , located at R_A , and $\rho(r)$ is the molecule's electronic density. $V(r)$ is a physical



Scheme 1 Structures of title compounds



Scheme 2 Isodesmic reaction of CL-20, compound **1** and compound **5**

observable, which can be determined experimentally by diffraction techniques as well as computationally [25, 26]; a , b , and c are fitting parameters; SA is molecular surface area; σ^2_{Tot} is total variance of calculated electrostatic potential on the molecular surface; ν is a balance parameter.

The detonation velocity and the detonation pressure of title compounds were predicted by the empirical Kamlet-Jacobs equations [27, 28] as they are used widely in evaluating the detonation properties of high energy density materials which contain C, H, O and N:

$$D = 1.01(NM^{1/2}Q^{1/2})^{1/2}(1 + 1.30\rho_0) \quad (5)$$

$$P = 1.55\rho_0^2NM^{1/2}Q^{1/2} \quad (6)$$

where D is detonation velocity (km s^{-1}), P represents detonation pressure (GPa); N moles of detonation gases per gram of explosive; M the average molecular weight of these gases; Q the chemical energy of detonation (J g^{-1}); and ρ_0 the density of explosive (g cm^{-3}). Table 1 shows how to calculate the parameters in the K-J equation. Heat of detonation (Q_V) is the negative of the enthalpy change of the detonation reaction and can be calculate from the differences in

HOF between the explosive and the products of detonation as follows [27]:

$$Q = \frac{-[\Delta H_f(\text{detonation products}) - \Delta H_f(\text{explosive})]}{\text{Formula weight of explosive}} \quad (7)$$

Q_V is decided according to the largest exothermic principle, i.e., for the explosives is composed of C, H, O and N, all N atoms are converted to N_2 , the O atom forms H_2O with the H atom first and then forms CO_2 with a C atom. The remaining C atom will exist in solid state. If O atoms are left, they will form O_2 .

Results and discussion

Structures

Studies on the activity of N atoms in tetraacetylhexaazaisowurtzitane (TAIW) [29] and TNIW [30] indicate that the N atoms of 4' and 10' are easier to substitute than the upper four N atoms, so 4-trinitromethyl-2,6,8,10,12-pentanitrohexaazaisowurtzitane (**1**), 4,10-ditritromethyl-2,6,8,12-tetranitrohexaazaisowurtzitane (**2**), 4-trinitroethyl-10-

Table 1 Methods for parameters calculation in K-J equations

	$c \geq 2a + b/2$	$2a + b/2 > c \geq b/2$	$b/2 > c$
N	$(b + 2c + 2d)/4 M'^a$	$(b + 2c + 2d)/4 M'$	$(b + d)/2 M'$
M	$4 M'/(b + 2c + 2d)$	$(56d + 88c - 8b)/(b + 2c + 2d)$	$(2b + 28d + 32c)/(b + d)$
$Q \times 10^{-3}$	$(28.9b + 4.05a + 0.239\Delta H_f^\circ)/M'^b$	$[28.9b + 4.05(c/2 - b/4) + 0.239\Delta H_f^\circ]/M'$	$(57.8c + 0.239\Delta H_f^\circ)/M'$

^a M' is molecular weight of explosive

^b ΔH_f° is heat of formation (HOF) of explosive

trinitromethyl-2,6,8,12-tetranitrohexaazaisowurtzitane (**3**), 2,4,6,8,10,12-hexatritromethylhexaazaisowurtzitane (**4**), 4,10-ditritroethyl-2,6,8,12-tetranitrohexaazaisowurtzitane (**5**), 2,4,6,8,10,12-hexatritroethylhexaazaisowurtzitane (**6**) could be designed.

ϵ -CL-20 was determined to be the parent compound since it performs better than other polymorphs in terms of density. The structure of ϵ -CL-20 comes from ref [31]. The optimized structures of compounds **1–6** are shown in Fig. 1 (the detailed data of structures are listed in [Electronic supplementary information](#)). Selected bond lengths and dihedral angles of optimized title compounds are shown in Tables 2 and 3. By investigating these molecular configurations, results as followed can be gained conveniently.

The first point to note is that the length of the C–NO₂ bond in the trinitromethyl group is longer than that of a standard C–N bond. Take **1** for instance, the longest length of C–NO₂ bond in the trinitromethyl is 1.584 Å, while the standard length is 1.47 Å [32]. From our point of view, there are several explanations for this: it is well known that nitro group is an electron-withdrawing group, the electron density of the C atom is bound to decline when the C atom is substituted by three nitro groups. Furthermore, the cage that connects to trinitromethyl is also an electron-deficient structure. The electron-deficiency of C31 is more obvious on this occasion. The relatively crowded molecular configuration of **1**, compared with CL-20, may be another reason explaining this result.

Moreover, the C–N bond between the cage and the trinitromethyl group is exceptionally short. As shown in Table 2, the lengths of N18–C31 are 1.389 Å and 1.394 Å in **1** and **2**, respectively. Compared with the C–NO₂ bond and standard C–N bond, these two bonds are exceptionally short. This result is not surprising; a similar phenomenon has been observed and discussed in chlorotritromethane [33]. In the light of Politzer's theory, this derives mainly from the Taft polar constant for the trinitromethyl group ($\sigma^*=4.54$), which is the largest determined for any electrically neutral group [34]. A classic interpretation of σ^* is that it represents the electron-donating or electron-withdrawing power of a substituent [35]. Owing to the strong electron-withdrawing power of the trinitromethyl group, electrons on the N18 atom are more likely to bond with C31. As a result, the N18–C31 bond of **1** and **2** are shorter than usual.

Thirdly, the length of the C–N bond adjacent to the trinitromethyl is stretched. The bond lengths of N18–C4 and N18–C9 are 1.467 Å and 1.469 Å in **1**, respectively. Nevertheless, the values are 1.440 Å and 1.444 Å in place of CL-20. That means not only that the cage structure has an influence on the trinitromethyl moiety, but also that the trinitromethyl influences the cage in return. This phenomenon results primarily from repulsion between the O atoms in the cage and O atoms in the trinitromethyl. Additionally, the

deviation of electrons on N18 also has a certain effect since C31–N18 is shorter and more stable than the usual C–N bond. So the effect of repulsion is reflected by the stretch of N18–C4 and N18–C9.

The above three phenomena occurred repeatedly in compound **2**, but **2** and **4** both displayed a new characteristic in molecular geometry. That is, the position of the nitro group connected with N7 or N10 will change slightly when the molecule is substituted with more nitro groups. Take **2** for example, more nitro groups coming from trinitromethyl groups would push the upper four nitro groups onto the cage. That is because the space beneath the cage is smaller than that of CL-20 when N17 and N18 are both substituted by trinitromethyl. This results in some intriguing changes in relative positions of three nitro groups. The distance between O33 and N10 is 3.086 Å in **2** instead of 3.957 Å in **1**. As a result, nitro groups that were connected with N7 and N10 moved backward and the configuration was no longer like that of ϵ -CL20. This is illustrated by the fact that the dihedral angle of C6–N10–C9–N25 is 139.21° in **2** instead of –151.30° in **1**.

The molecular structure will change again if all nitro groups on the cage are substituted by trinitromethyls. As shown in Fig. 1, compound **3** is surrounded by many nitro groups. Due to the relatively small space around the cage and the repulsion between O atoms, the distribution of nitro groups on compound **3** is crowded and irregular. Since compound **3** is also a substitution product for trinitromethyls like **1** and **2**, they have similar molecular properties, such as a short N18–C31 bond and long N18–C4 bond. On the contrary, compound **5** and **6** present different results. Because of the buffering function of the middle C atom in the trinitroethyl, **5** does not demonstrate the same molecular character as that of **2**. Relatively longer carbon chains mean more room beneath the cage, which prevents interactions between nitro groups on the trinitroethyl and nitro groups on the cage in terms of molecular structures. Additionally, the methylene in the trinitroethyl plays an essential role in connecting the two electrophilic parts. Because of the existence of the methylene, the direct interaction between the cage structure and the trinitromethyl is eased. The situation in compound **6** is close to that of compound **5**, in that it has regular nitro group distribution and weak O atom repulsion; **6** is totally different from **3**.

The analysis above revealed some connections between the structure and stability of these compounds. To further study stability, electro-static potential (ESP) and bond dissociation energy (BDE) calculations were performed.

Stability

The ESP is an efficient way to relate the stability of a compound to other stimulations [36, 37]. Murray et al. [38]

Fig. 1 **a** Optimized structure and atom label of **1**. **b** Optimized structures of CL-20 and **2–6**

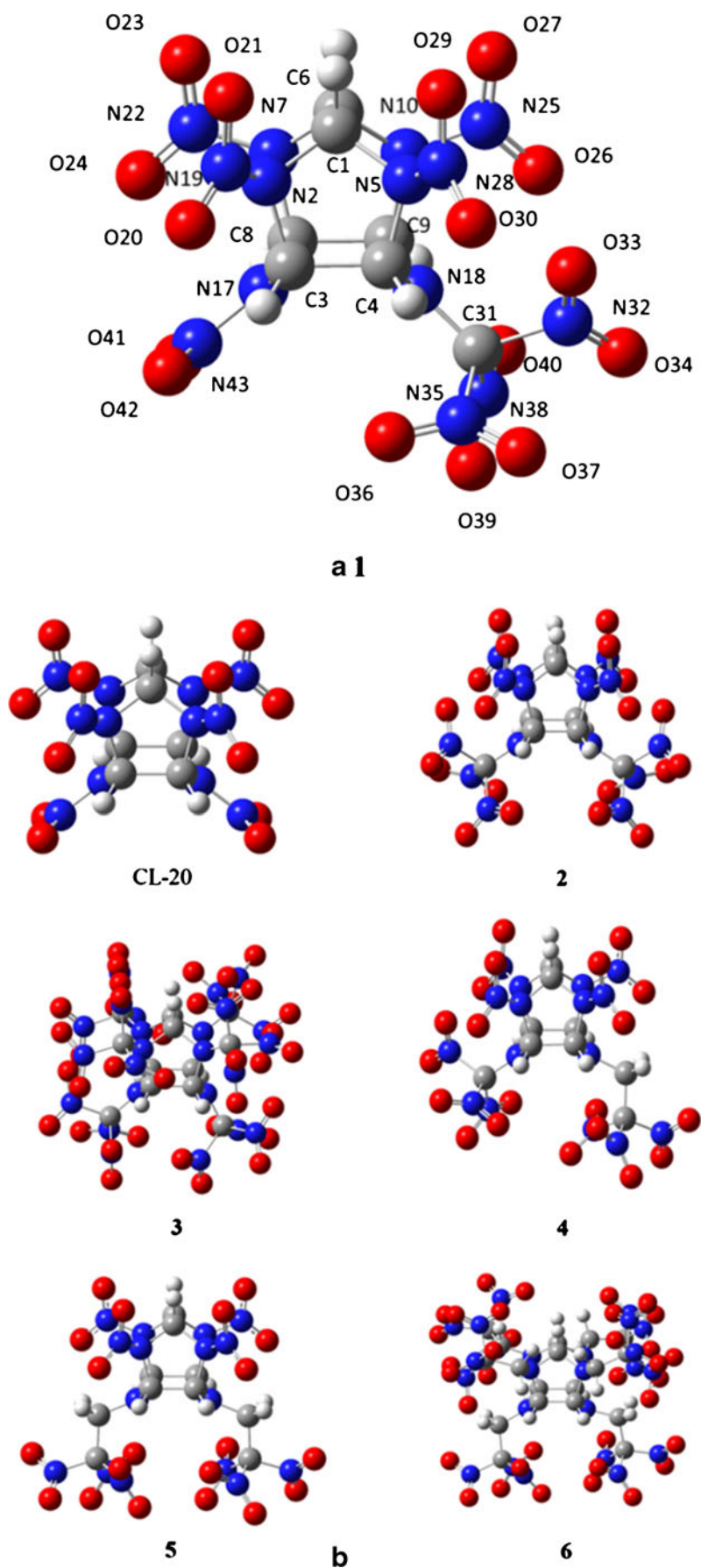


Table 2 Selected bond lengths of CL-20 and title compounds (Å)

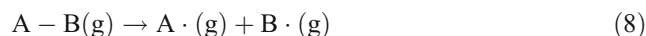
	CL-20	1	2	3	4	5	6
N17-C3	1.440	1.436	1.461	1.463	1.468	1.441	1.441
N17-C8	1.444	1.438	1.465	1.469	1.464	1.443	1.452
N18-C4	1.440	1.467	1.461	1.473	1.436	1.441	1.453
N18-C9	1.444	1.470	1.465	1.462	1.443	1.444	1.452
N2-NO ₂	1.440	1.439	1.410	–	1.403	1.419	–
N5-NO ₂	1.440	1.446	1.410	–	1.423	1.419	–
N7-NO ₂	1.395	1.395	1.417	–	1.423	1.376	–
N10-NO ₂	1.395	1.389	1.417	–	1.382	1.377	–
N18-C31	–	1.389	1.394	1.393	1.455	1.456	1.456

showed that there is a link between ESP, impact sensitivity and the C–NO₂/N–NO₂ BDE of an energetic compound. Other research has been done in order to maintain good detonation performance and simultaneously decrease the effect of stimulations [39–43]. The electrostatic potential at any point *r* is given in Eq. (1).

ESP calculations were computed based on the optimized structures of the title compounds. Figure 2 shows the electrostatic potentials for the 0.001 electron/bohr³ isosurfaces of electron density evaluated at the B3LYP level of theory. The colors range from –0.015 to +0.05 Hartrees with dark blue denoting extremely electron-deficient regions [$V(r) \geq 0.05$], red denoting electron-rich regions [$V(r) \leq -0.015$] and yellow denoting neutral regions. As shown in Fig. 2, compounds are characteristic of having a strongly positive central region and a negative periphery due to the strongly electron withdrawing property of nitro groups. The red color above the trinitromethyl of **1** is lighter than the color of the nitro group of CL-20 at the same place. This phenomenon reminds us that the electronic density over trinitromethyl is relatively low and nitro groups cannot attract as many electrons as the nitro group on CL-20. The ESP results of **1** and **2** suggest that their stability is similar to that of CL-20. Nevertheless, because the cage is attached with too many trinitromethyl groups, compound **3** has a yellow surface potential. The electron density of O atoms on compound **3** is lower than that on other compounds. This can be attributed mainly to the fact that the cage cannot supply sufficient electrons to so many trinitromethyl groups. The ESPs of **4** and **5** showed results that differ from those of **1**, **2** and **3**: since there is a methylene in the trinitroethyl group, the two

electron-deficient parts are separated and a blue region shows up over the methylene. In obvious contrast to compound **3**, the ESP of compound **6** is covered by a large blue region. It is acceptable to believe that the emergence of a blue region outside the central region means that the electron-deficiency of the center will be eased. In other words, the introduction of trinitroethyl plays a positive role in stabilizing the parent compound. As a consequence, compounds **4**, **5** and **6** are regarded to be more stable than compounds **1**, **2** and **3**.

For the purpose of testing the firmness of linkage between the cage and the polynitro group, the C–N bond dissociation energy was calculated according to the following equation:

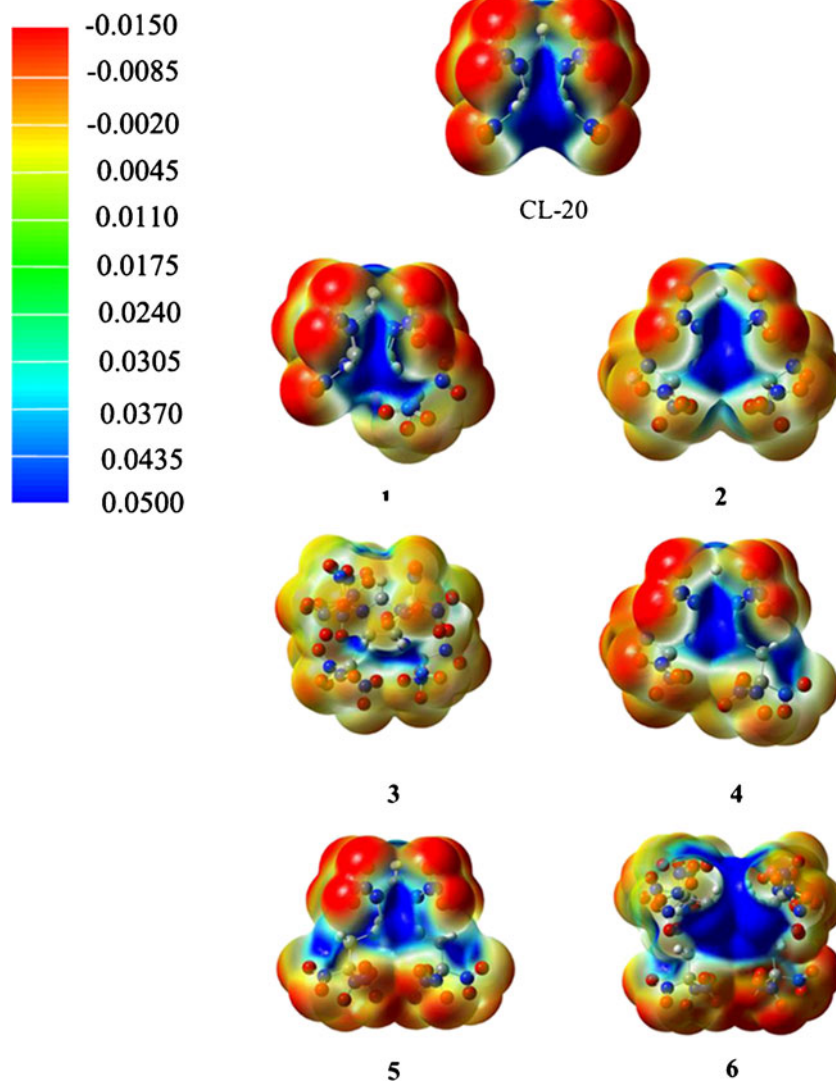


In most cases, the reaction enthalpy of reaction is almost numerically equivalent to the reaction energy. So the bond dissociation energy often appear alternatively in the literature with bond dissociation enthalpy [44]. Our previous work revealed that the M06/6-31+G(d,p) level can yield good accuracy when the BDE of the C–N bond is calculated [45]. The BDE results are shown in Table 4. “C–N” values denote the dissociation energy of the C–N bond that connected the cage and the trinitromethyl/ trinitroethyl. “C–NO₂” values denote the dissociation energy of the C–NO₂ bond in the trinitromethyl/ trinitroethyl. The C–NO₂ BDE is calculated based on the longest C–NO₂ bond in their groups. It can be seen from Table 4 that the BDE of C–N bonds between the cage and polynitro groups are large while the C–NO₂ BDE is relatively small. Another phenomenon is

Table 3 Selected dihedral angles of CL-20, **1**, **2**, **4** and **5** (°)

	CL-20	1	2	4	5
C1-N2-C3-N19	133.24	133.47	142.85	147.50	137.36
C1-N5-C4-N28	–133.23	–131.02	–142.71	–135.17	–137.02
C6-N7-C8-N22	144.67	143.98	–139.26	–135.91	151.04
C6-10-C9-N25	–144.60	–151.30	139.21	–147.21	–180.80

Fig. 2 Electrostatic potentials (ESPs) of CL-20 and title compounds. Color coding: *red* negative, *orange* slightly negative, *yellow* neutral, *green* slightly positive, *light blue* positive, *dark blue* very positive



that the C–NO₂ BDE in trinitroethyl is higher than that in trinitromethyl. This can be seen from the C–NO₂ BDE difference between compounds **2** and **5**. And all BDE results match well with the structure characteristics.

Through the analysis of the results of ESP and BDE above, we conclude that introducing trinitromethyl did not raise the sensitivity of the parent compound as is the case with other nitroform-substituted energetic compounds. On

the contrary, the trinitroethyl-substituted compounds are considered to be more stable than CL-20.

Heat of formation

The values of HOF, heat of sublimation and relevant parameters of the title compounds are listed in Table 5. The gas-phase HOF values of **1**, **2** and **3** are higher than that of CL-

Table 4 C–N bond dissociation energies (BDE) of title compounds

	1	2	3	4^a	4^b	5	6
C–N /kJ mol ⁻¹	354.69	360.79	312.44	363.41	368.31	355.96	325.06
C–NO ₂ /kJ mol ⁻¹	148.90	151.14	103.38	158.06	181.57	178.63	170.22

^a Values refer to the BDE of the trinitromethyl on compound **4**

^b Values refer to the BDE of the trinitroethyl on compound **4**

Table 5 Predicted HOF and heat of sublimation of title compounds and CL-20

	SA/Å ²	σ ² _{tot} / (kcal mol) ²	v	ΔH _(sub) / kJ mol ⁻¹	ΔH _{f(gas)} / kJ mol ⁻¹	ΔH _{f(solid)} / kJ mol ⁻¹
20	311.57	229.63	0.066635	147.93	715.93	568.00
1	362.47	251.24	0.060079	186.09	721.95	535.86
2	418.85	246.54	0.040479	230.31	719.51	489.20
3	544.08	105.22	0.044831	358.26	773.87	415.61
4	430.83	212.62	0.058054	244.13	657.79	413.66
5	439.75	193.16	0.065556	253.12	609.76	356.64
6	694.40	223.33	0.057636	576.11	531.00	-45.11

20. That is to say, a higher gas-phase HOF can be gained when the nitro group is replaced with trinitromethyl. But due to the large molecular surface area, ΔH_s of compounds in this study are all large. Compare with CL-20, these new molecules have lower solid-phase HOF.

Oxygen balance and density

OB values near or greater than zero are highly desirable in order to reduce toxic fume gases like carbon monoxide. In the wake of introducing trinitromethyl, the OB value and density of **1**, **2** and **3** exceeded that of CL-20. Data of OB and the density of relative compounds are listed in Table 6. The OB value of **1** is -2.95 %, which is close to zero OB. Compounds **2** and **3** even became positive oxygen-balanced compounds (OB=2.48 %, 13.55 %). Considering the OB value of CL-20 (OB=-10.96 %), the OB of the title compounds has increased remarkably with the help of trinitromethyl.

Density is quite crucial to an energetic compound since the detonation pressure, according to the K-J equation, is proportional to the square of the density. As shown in Table 6, calculated densities of all new compounds in this study have surpassed 2.0 g cm⁻³, while the density of HMX

is 1.90 g cm⁻³. The densities of **1**, **2** and **3** reached 2.07 g cm⁻³, 2.09 g cm⁻³ and 2.16 g cm⁻³, respectively. Obviously, compounds with a crowded molecular configuration tend to have high densities and the substitution of trinitromethyl contributes a lot to the improvement of density.

Detonation performance

Heat of detonation, detonation velocity and detonation pressure are key parameters used to assess the performance of an explosive. All three aspects can be calculated from the densities and the solid-phase HOF we predicted. Full details of Q, D and P are shown in Table 6. The values exceed those of the highest energy density materials, e.g., the Q value of 7,290.09 J g⁻¹ of **1** is next to the 7,297.56 J g⁻¹ of CL-20, and Q values of most compounds are higher than that of HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane) (Q=6,145 J g⁻¹) [46]. The detonation velocity and detonation pressure of these compounds are also large and positive. The values of D and P of **1** and **2** have all surpassed 9.9 km s⁻¹ and 48 Gpa. The eminent performances of **1** and **2** originate mainly from their high density and high HOF.

Table 6 Predicted properties of title compounds, CL-20 and HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane)

	OB/%	ρ/g•cm ⁻³	Qv/ J•g ⁻¹	D/km•s ⁻¹	P/Gpa
1	-2.95	2.07	7290.09	9.95	48.45
2	2.48	2.09	6957.97	9.92	48.42
3	13.55	2.16	5645.33	9.62	46.35
4	-4.85	2.03	7129.00	9.71	45.71
5	-11.87	2.02	7028.47	9.57	44.21
6	-12.56	2.00	6841.08	9.39	42.39
CL-20	-10.96	2.04 ^a	7297.56	9.78	46.46
β-HMX	-21.62	1.90 ^b	6145 ^c	9.11 ^c	37.97 ^c

^a The experimental value is 2.04 g cm⁻³

^b Experimental value from ref [39]

^c Calculated values based on K-J equations from ref [46]

Conclusions

In this study, systematic calculations on six trinitromethyl/trinitroethyl modified derivatives of CL-20 were performed. With the addition of trinitromethyl and trinitroethyl, the compounds in this study showed remarkable energetic properties. The results of optimized structures reveal a mutual influence of bond length and dihedral angle between trinitromethyl and the cage. Studies on the stability of the title compounds prove that introduction of the trinitromethyl into CL-20 has little effect on its stability and the joint between the two electron-deficient parts is steady. The introduction of trinitroethyl also plays a positive role in stabilizing the parent compound. The trinitromethyl group dramatically increases the density detonation velocity and detonation pressure of new cage compounds. These results prove

trinitromethyl/trinitroethyl substituted derivatives of CL-20 to be good potential candidates for high energy density materials. Further study on this series of compounds is underway.

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