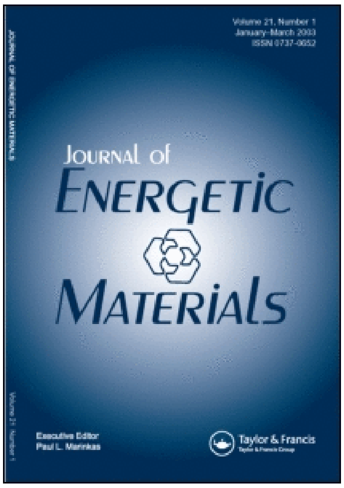

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Prediction of Caged Polyaza Polynitroamine (Tetracyclo-HMX) as Energetic Compound

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By fusing four HMX rings into a cage, a powerful nitroamine explosive was predicted. The heat of formation (HOF) of hetero pentacyclo-icosane nitro compound of dodecanitrododecaza-pentacyclo[9.5.1.1^{3,9}. 1^{5,15}. 1^{7,13}]icosane (DNDAPI or, alternatively, tetracyclo-HMX) was obtained by using density functional theory B3LYP method with 6-31G basis set. The isodesmic reactions designed for the evaluation of HOF keep most of the basic ring structures of the title compounds and thus ensure the credibility of the result. The value of HOF is 1394.59 kJ/mol. The predicted detonation velocity of the title compound is 10.6 km/s and detonation pressure is 56.8 GPa, even at 90% of its theoretical density. These values are much larger than those of the widely used 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), indicating that DNDAPI is a promising candidate of high energy material. The dissociation energy for the N-NO$_2$ bond in the cage skeleton of the title compound is 125.36 kJ/mol.*

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Keywords: bond dissociation energy, density functional theory detonation properties, dodecanitrododecaza-pentacyclo[9.5.1.$1^{3,9}$.$1^{5,15}$.$1^{7,13}$]icosane (DNDAPI, tetracyclo-HMX), group interactions, heat of formation

Nitroamine (H_2N-NO_2) and *N*-methyl-nitroamine [$NH(CH_3)NO_2$] are two of the simplest high energetic compounds. They are also the basic building units for heterocyclic nitro compounds, such as HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane), that are used extensively both for civil and military applications [1,,2]. In order to meet the updated requirements of future military and space applications, new materials with higher performance or enhanced insensitivity to thermal or shock insults are being developed worldwide. Some cage compounds containing the nitroamine unit were synthesized recently and exhibited high performance in terms of explosive pressure and velocity. CL-20 [2,4,6,8,10,12-hexanitrohexaazaisowurtzitane (HNIW)] is such a new cage *N*-nitro compound that is 20% more powerful that HMX [3]. CL-20 was a breakthrough in energetic materials with higher performance, minimum signature, and reduced-hazard characteristics. Many have called CL-20 the most significant energetic ingredient in the past 50 years [4–6]. Inspired by this fact, we designed another cage nitramine compound dodecanitrododecaza-pentacyclo [9.5.1.$1^{3,9}$.$1^{5,15}$.$1^{7,13}$]icosane (DNDAPI) in which two HMX rings are fused together by four N-NO_2 units to form a cage. Alternatively, the molecule can be regarded as four HMX rings being fused by sharing the CH-N(NO_2)-CH unit (here we call it tetracyclo-HMX). As to geometrical structure, the CH-N-NO_2 bonds are common to both HMX and DNDAPI. However, DNDAPI is more complex than HMX due to the presence of its CH-(N-NO_2) $_3$ unit instead of CH_2-(N-NO_2)$_2$, causing DNDAPI to be more symmetrical and less polar. This new molecule is characterized by four fused rings, as many as 12 N-NO_2 groups, positive oxygen balance value, and alternated C-N units in its skeletons (Fig. 1). These features enable the molecule high nitrogen contents, high density, and large energy release upon

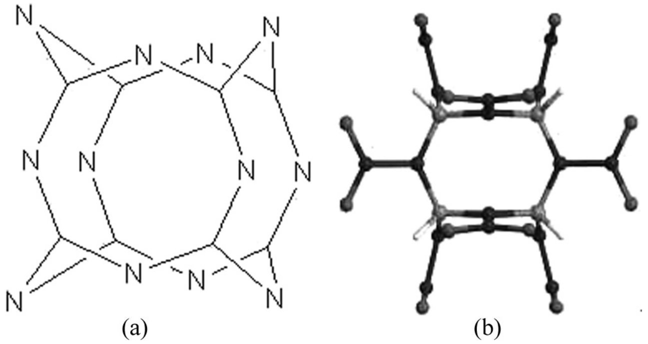


Figure 1. (a) Skeleton of dodecanitrododecaza-pentacyclo[9.5.1.1^{3,9}.1^{5,15}.1^{7,13}]icosane (all nitrogen atoms are attached by nitro groups; for clarity, nitro groups were omitted) and (b) stereo overlap of the molecule.

decomposition. In this article, we concentrated on DNDAPI with respect to heat of formation, performance, and stability. This high nitrogen content caged nitro compound was expected to be a novel candidate for future energetic materials that would offer higher strain energy, oxygen balance, and, most important, a good performance.

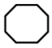
Computational Methods

The isodesmic reaction processes, in which the number of each kind of formal bond is conserved, are used with application of the bond separation reaction (BSR) rules. The molecule is broken down into a set of two heavy-atom molecules containing the same component bonds [7]. However, usual bond separation reaction rules generate large calculation errors of heat of formation (HOF) for compounds with cage skeletons. To minimize the systematic errors, we keep the basic ring structures in the equations of isodemic reactions and make the best use of the experimental HOFs for reference compounds.

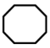
The isodesmic reactions used to derive the HOFs of heterocyclic nitro compounds at 298 K are as follows:

$$\mathrm{DNDAPI} + 8\mathrm{CH_4} \longrightarrow 4(\mathrm{CH_3})_2\mathrm{NNO_2} + 2\mathrm{HMX} \qquad (1)$$

We get the HOF of *N*,*N*-dimethyl-nitramide from the following isodesmic reaction:

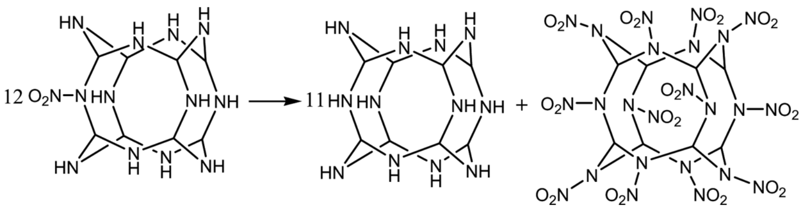
$\mathrm{HMX} + 4\mathrm{CH_3CH_2CH_3} \rightarrow 4(\mathrm{CH_3})_2\mathrm{NNO_2} +$  (2)

By subtracting (2) from (1), we obtained the following isodesmic reaction:

$\mathrm{DNDAPI} + 8\mathrm{CH_4} +$  $\rightarrow 3\mathrm{HMX} + 4\mathrm{CH_3CH_2CH_3}$ (3)

This isodesmic reaction keeps the basic ring structures of the title compound and thus ensures the credibility of the predicted HOF. Using the similar procedure of reaction (3), we calculated the HOF of *β*-HMX as a benchmark, with isodesmic reaction of 3HMX → 4RDX. The predicted value is 251.21 kJ/mol at the B3LYP/6-31G* level. This value is comparable with 272.8 kJ/mol that results from an indirect calculation of the experimentally determined enthalpy of formation of solid *β*-HMX of 87.9 ± 2.9 kJ/mol [8] and an estimated enthalpy of sublimation of 184.9 ± 1.7 kJ/mol [9]. They also somewhat intermediate among the previous theoretical estimations of 248.9 kJ/mol [10], 274.9 kJ/mol [11], and 283.8 kJ/mol [12]. Therefore, the isodesmic reaction is reliable for evaluation of HOF.

The energy needed for transferring groups from monosubstituted to polysubstituted derivatives is defined as disproportionation energy [13]. To determine the strength of the interactions among the substituent groups, we computed the disproportionation energy of mono-nitro derivatives to multinitro derivative and the parent compound, according to the energy change of the isodesmic reaction to dodecanitro isomer as an example:



To explore the origin of group interactions, we also performed calculations on the derivatives with less substituted groups in addition to the fully substituted.

In this article, the HOF was calculated for DNDAPI using density functional theory (DFT-B3LYP) method with 6-31G* basis set. Detonation properties were evaluated by using the empirical Kamlet formula [14]. The density of a compound needs the datum of the molecular volume. The molecular volume was defined as inside a contour of 0.001 electrons/bohr^3 density, which was evaluated using a Monte Carlo integration. However, the molecular volumes thus obtained are random digits with normal distribution. We therefore performed 100 single-point calculations at the PM3 [15] level from the B3LYP/6-31G* optimized structure to get an average volume. In addition, to predict the stability of the title molecules upon stimuli such as heat and mechanic impact, we calculated bond dissociation energies of different types of bonds. Semiempirical PM3 calculation for molecular volume was performed with Gaussian 03 [16]. All DFT calculations have been performed with the Q-Chem package [17].

Results and Discussion

Geometrical Structure

As to geometrical structure, DNDAPI is more symmetrical and less polar than HMX. It possesses T_h symmetry and its dipole moment is almost zero (0.0048) due to its symmetry. The structure of each individual eight-numbered ring inside the cage is similar to HMX, with alternative axial (*a*-) and equatorial (*e*-) nitro groups. However, due to the molecular symmetry, *a*-nitro in one ring is actually *e*-nitro in its neighbor ring. Consequently, each pair of HMX moieties on the opposite sides of the cage is fully overlapped (Fig. 1b) and all the N-NO_2 bonds are identical. The C-N bond length is 0.145–0.146 nm, and N-NO_2 bond is 0.143–0.144 nm. The former is close to the experimental value of HMX (0.144–0.147), but the latter is slightly lengthier than the corresponding

N-NO_2 length of 0.135–0.137 nm of HMX. Because N-NO_2 is for most nitroamines an initiator of decomposition, DNDAPI is slightly less stable than HMX.

Heat of Formation and Detonation Properties

Table 1 shows the experimental heats of formation of the reference compounds, total energy (E_0), zero-point energy (ZPE), value of thermal correction (H_T-H_0), and heat of formation (ΔH) of DNDAPI. The predicted HOF of DNDAPI is 1394.59 kJ/mol. Although DNDAPI consists of four HMX rings fused together, its HOF is larger than four times of HMX's HOF by 303.39 kJ/mol. There are 24 pairs of 1,3-nitro group interactions. Apparently, these group interactions account mainly for the large HOF compared to that of four times HMX. As can be seen from Table 2, the density of DNDAPI is as high as 2.518 g/cm^3, which is much higher than that of HMX. The main reason for its unusual high density is that the molecule itself is highly compacted in a cage. The predicted detonation velocities and pressure are 11.5 km/s and 70.1 GPa, respectively. Of course, these values are the upper limits because the detonation performance is sensitive to the actual

Table 1

Total energy (E_0), zero-point energy (ZPE), values of thermal correction (H_T), and heats of formation (ΔH_f)[a]

Compd.	E_0	ZPE	H_T-H_0	ΔH_f
Methane	−40.518209	113.99	9.14	−74.6[b]
Cyclooctane	−314.488626	577.87	21.39	−124.4[b]
HMX	−1196.544853	486.88	48.94	272.8[c]
Propane	−119.143805	262.50	14.58	−103.8[b]
DNDAPI	−3427.440206	934.74	104.34	1394.59

[a] E_0 is in a.u., ZPE, HOF, and H_T-H_0 are in kJ/mol. The scaling factors for the ZPE are 0.96 [18].

[b] From Lide [19].

[c] From Krien et al. [8] and Lyman et al. [9].

Table 2
Density, chemical energy (Q), detonation velocity (D), and pressure (P) of DNDAPI

ρ (g/cm^3)	Q (J/g)	D (km/s)	P (GPa)
2.518	6686.7	11.5	70.1
2.266[a]	6686.7	(10.6)	(56.8)

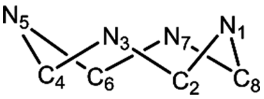
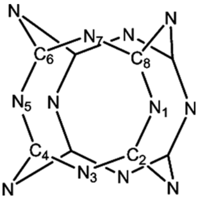
[a] Ninety percent of the theoretical density. Data in parentheses are from 90% of the theoretical density.

density, whereas the loading density is usually smaller than the predicted value [20]. If the actual loading density for the title compound approaches 90% of its theoretical value as HMX at the same computational level, the detonation velocity of the title compounds is still larger than and pressure is much larger than those (D = 9.1 km/s and P = 39.5 GPa) of HMX [21]. By fusing into a caged structure from HMX moieties, the DNDAPI gains much more energetic density compared to HMX.

Interactions among Substituted Groups

The disproportionation energies $E_{\text{disproportion}}$ shown in Table 3 indicate that the nitro group introduces positive disproportionation energy with larger 1,3- group interaction compared to 1,5- group interaction. Unexpectedly, both 1,3- and 1,5- group interaction of HMX analogy are larger than those of DNDAPI analogy. For HMX, there are four 1,3- group interactions and two 1,5- interactions. Obviously, the total disproportional energy of HMX is 76.57 kJ/mol less than the sum of 1,3- and 1,5- disproportional values $(46.34*4+32.55*2=250.46)$. As can be seen from Table 3, the average negative charges on the nitro groups (in terms of absolute values) decrease when groups become closer. Furthermore, the charges decrease dramatically with the number of nitro groups increasing. These led to the total disproportional energy being less than expected. Similarly, the disproportional energy of 1,3,5,7-isomer is 21.21 kJ/mol less than the sum of its corresponding 1,3- and

Table 3
Disproportional energies and average charges on nitro group of dodecazacycloicosane and tetraazacyclooctane derivatives[a]

Atomic numbering	Compd.	E_{total}	$E_{\text{disproportion}}$	$Q_{\text{Ave,nitro}}$
	1,3-[b]	−787.5856553	46.34	−0.1843
	1,5-	−787.5909081	32.55	−0.2065
	HMX	−1196.544853	173.89	−0.1375
	1,3-	−1382.694729	31.23	−0.2210
	1,5-	−1382.697871	22.98	−0.2124
	1,3,5,7-	−1791.652996	149.67	−0.1498
	DNDAPI	−3427.440206	743.84	−0.0334

[a] Total energies are in a.u. and disproportional energies are in kJ/mol, Q is in a.u.

[b] 1,3- denotes 1,3-dinitro-1,3,5,7-tetraazacyclooctane; i.e., only the 1,3-positions are attached by nitro groups. Others are similar.

1,5- disproportional values $(31.23*4+22.98*2=170.88)$. There are 24 meta- group interactions and twelve 1,5- interactions in DNDAPI. The disproportional energy of DNDAPI is much less than the sum of these 1,3- and 1,5- interactions, since

Table 4
Bond dissociation energy (kJ/mol)

DNDAPI			HMX		
Bond	BDE_0	BDE^a	Bond	BDE_0	BDE^a
C-N	300.04	282.07	C-N	293.28	268.03
N-Nitro	143.03	125.36	N-Nitro	186.41	166.38
			N-Nitro	173.68	152.07

[a] Zero-point energy corrected BDE.

the average charges of nitro groups are much less than those of the 1,3- or 1,5- isomers.

Bond Dissociation

Table 4 lists the bond dissociation energy of DNDAPI and HMX at the B3LYP/6-31G* level. There are two types of N-NO_2 bonds in HMX—i.e., axial and equatorial—related to the HMX ring. The difference of bond dissociation energies between these two types of N-NO_2 bonds is small. The N-NO_2 bonds are much weaker than those of the alternating C-N bonds on the rings for both the molecules. The C-N bond on the rings of DNDAPI is slightly stronger than those of HMX. However, the N-NO_2 bonds of the former are weaker than those of the latter. Judged by the N-NO_2 BDE value of DNDAPI, the molecule is sensitive to stimuli like heat and impact.

Conclusions

Based on density functional calculation and isodesmic reaction, the HOF of DNDAPI was predicted to be as high as 1394.59 kJ/mol, which is overwhelmingly larger than the HOF of the present explosives. Due to the compacted cage structure, the density is especially large. These enable the compound to have an extraordinarily good detonation performance. Group interactions in DNDAPI are surprisingly small, since the average charges of nitro groups decrease dramatically with the number of nitro groups increasing, which enables the ease of synthesizing the molecule. However, the N-NO_2 bonds are weak and therefore the molecule is in general easy to decompose upon stimuli such as impact and thermal.

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