Theoretical Investigation on the Replacement of CH Groups by N Atoms in Caged Structure (CH)$_8$

Ge Zhou,[†] **Xu-Mei Pu,**[†] **Ning-Bew Wong,**[*,‡] **Anmin Tian,**[*,†] **and Hongwei Zhou**[†]

Faculty of Chemistry, Sichuan University, Chengdu 610064, People's Republic of China, and Department of Biology and Chemistry, City University of Hong Kong, Kowloon, Hong Kong

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A molecular design was performed for the caged molecule (CH)$_8$: the replacement of CH groups by N atoms to increase the content of N as well as reduce the content of H. A series of caged molecules were obtained: (CH)$_x$N$_{8-x}$ ($0 \leq n \leq 8$). The studied aspects are as follows: (i) molecular geometries and electronic structures, (ii) the analysis of the electronic structure using natural bond orbital (NBO) and atoms in molecules (AIM), and (iii) some physicochemical properties of studied molecules, such as the dipole moments, IR vibrational spectra, NMR chemical shifts, heats of formation, and relative specific impulses, were provided. Our studies show that these molecules should be a kind of potential and novel energetic material. Our work provides some useful information for the experimental study of these molecules. The effect of the substitution of N atoms for CH groups on the properties of this kind of caged molecule is presented.

Introduction

Extensive theoretical studies on N$_n$ clusters have indicated that they are high-energy density materials (HEDMs).[1−21] The decomposition of N$_n$ clusters results in the formation of N$_2$ and accompanies the release of a large quantity of energy. Nevertheless, N$_n$ clusters can be synthesized hardly. Early investigations on this kind of compound indicated that caged alkyl molecules possess high density, high strain, and some stability.[15,22−28] From the 1960s onward, marked progress has been made in synthesized chemistry.[29−31] Many caged alkyls, such as cubane,[32] homocubane,[33] dodecahedrane,[34] and pentaprosmane,[35] were synthesized successfully. Bliznyuk, Shen, and Schaefer et al have reported that N$_{20}$ possesses a meta-stable structure of dodecahedron similar to the pure carbon form (CH)$_{20}$ and it is also a kind of potential energetic material.[36] Therefore, caged alkyl (CH)$_8$ (Figure 1) was selected, and molecular design was performed to obtain some potential energetic material molecules. They possess not only energetic material properties similar to the N$_n$ clusters but also analogous stability caused by the CH groups. In the present work, the CH groups in caged alkyl (CH)$_8$ are replaced by N atoms to obtain a series of molecules (CH)$_x$N$_{8-x}$ ($0 \leq n \leq 8$). The replacement of CH groups by N atoms can increase N content and reduce H content so as to enhance the energy density of the molecules. When all CH groups are replaced by N atoms, N$_8$ is obtained. Many investigations on N$_8$ have been reported.[7,9,11,16,37−41] The strain energies and bond energies of N$_8$ and its isoelectronic (CH)$_8$ have been studied theoretically.[42] For this series of caged molecules (CH)$_x$N$_{8-x}$ ($0 \leq n \leq 8$), their geometries, electronic structures, heats of formation (HOFs), vibrational frequencies, NMR chemical shifts, and relative specific impulses (I_s) are studied in detail using the quantum chemistry method. Our study shows that these compounds may be a kind of potential and
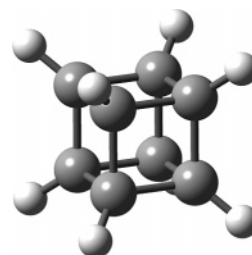

Figure 1. Caged alkyl (CH)$_8$.

novel energetic material, and our work provides some useful information for their experimental study.

Computational Methodologies

All calculations are performed using the Gaussian 98 program.[43] The geometries and harmonic vibrational frequencies of all the molecules are studied using density functional theory (DFT) methods at the B3LYP/aug-cc-pvdz level of theory, where B3LYP is a DFT method using Becke's three-parameter nonlocal functional[44] along with the Lee−Yang−Parr nonlocal correlation functional (LYP).[45] The aug-cc-pvdz is a Dunning's correlation-consistent double-ζ basis set[46] augmented with diffuse functions. The SCF convergence criterion is set to 10^{-8}. Force calculations are performed on studied molecules to characterize the stationary points obtained. All the Hessian matrixes are positive definite, which verifies that these optimizations have converged to local minima on the potential energy surface.

Natural Bond Orbital (NBO). The charge transfer (CT) in studied molecules is analyzed by means of the NBO[47] theory at the same theoretical level. The energetic stabilization due to CT interactions is estimated by second-order perturbation analysis and is denoted as $E^{(2)}$. Natural atomic charges are determined by natural population analysis. These calculations are performed using the Gaussian 98 implementation of the NBO 3.1 program.[48−55]

* To whom correspondence should be addressed. E-mail: suqcp@mail.sc.cninfo.net.
† Sichuan University.
‡ City University of Hong Kong.

Atoms in Molecules (AIM). A topological analysis of the electron density is performed using Bader's theory of AIM.[56] The AIM2000 program[57] is used for AIM analysis of the electron density ρ and its Laplacian $\nabla^2\rho$. The interatomic interactions can be assessed by the analysis of the bond critical points (BCPs) between two interacting atoms. The Laplacian of ρ, $\nabla^2\rho$, is defined as a sum of the eigenvalues (λ_1, λ_2, and λ_3) of the Hessian matrix of electron density. The topology of $\nabla^2\rho$ reveals regions of local charge concentration and depletion. We have also evaluated the ellipticity ϵ of ρ at any BCP. The value of ϵ provides a measure of the extent to which ρ is asymmetrically concentrated perpendicular to the bond path and thus can be used to determine the directionality of interatomic interactions.[58] All quantities derived from AIM analysis are given in atomic units.

Heat of Formation (HOF). The sums of electronic and thermal enthalpies obtained at the same computational level are used to calculate the HOFs of a studied series of molecules at 298 K. Calculating enthalpies of formation can be split into a few steps.

$$\Delta_f H°(M,0\text{K}) = \sum_{\text{atoms}} x\Delta_f H°(X,0\text{K}) - \left(\sum_{\text{atoms}} x\epsilon_0(M) - \epsilon_{\text{ZPE}}(M)\right)$$

The first step is to calculate the enthalpies of formation $\Delta_f H°(0\text{K})$ of the species involved in the reaction.

The second step is to calculate the enthalpies of formation of the species at 298 K.

$$\Delta_f H°(M,298\text{K}) = \Delta_f H°(M,0\text{K}) + (H_M°(298\text{K}) - H_M°(0\text{K})) - \sum_{\text{atoms}} x(H_X°(298\text{K}) - H_M°(0\text{K}))$$

In which, M stands for the molecule, X represents each element which makes up M, and x will be the number of atoms of X and M. $\epsilon_0(M)$ is the total energy of the molecule, $\epsilon_{\text{ZPE}}(M)$ is the zero-point energy of the molecule, $H_X°(298\text{K}) - H_X°(0\text{K})$ represents enthalpy corrections of the atomic elements, and $\epsilon_0(X)$ and $H_X°(298\text{K}) - H_X°(0\text{K})$ of elements H, C, O and N are taken from experimental data.[59] The other values involved in the calculation of the enthalpies of formation are calculated at the same level.

Relative Specific Impulse (I_s). Some molecules discussed in the present paper may be novel candidates for HEDMs. To evaluate their HEDM performances, we have calculated their relative specific impulse introduced by Politzer et al.[60] The specific impulse (I_s), widely used as a means of characterizing and evaluating explosives, is often expressed in terms of the absolute temperature in the combustion chamber T_C and the number of moles of gaseous products produced per unit weight of explosive N by the simplified relationship given as eq 1.[61]

$$I_S \sim T_C^{1/2}N^{1/2} \qquad (1)$$

This proportionality can be rationalized by kinetic theory. To apply eq 1, it is necessary to establish the identities and amounts of the various products and to determine the combustion temperature. Depending upon the composition of the explosive, the major components of the gaseous products may include CO, CO_2, N_2, H_2O, or HF, with lesser quantities of other molecules and radicals such as H_2, NO, H, C, O, CHO, and N_2O.[60]

A simple approach to obtaining a rough approximation of the combustion temperature involves assuming that the heat of combustion of the explosive is used entirely to heat the product

gases to the combustion temperature, so that

$$-\Delta H_{\text{comb}} = C_{\text{p,gases}}(T_C - T_0) \qquad (2)$$

and

$$T_C = T_0 - \frac{\Delta H_{\text{comb}}}{C_{\text{p,gases}}} \qquad (3)$$

ΔH_{comb} is the enthalpy of combustion, $C_{\text{p,gases}}$ represents the total heat capacity of the gaseous products, and T_0 and T_C are the initial and the combustion temperatures. In eqs 2 and 3, it is assumed that ΔH_{comb} is constant over the temperature range between T_0 and T_C and that the pressure in the combustion chamber remains constant due to a steady-state situation; the rates of formation and discharge of product gases are taken to be equal. ΔH_{comb} can be calculated from knowledge of the molar heats of formation of the explosive and the gaseous products (eq 4).

$$\Delta H_{\text{comb}} = \sum_i^{\text{products}} N_i\Delta H_{f,i} - N_{\text{HEDM}}\Delta H_{f,\text{HEDM}} \qquad (4)$$

The latter are known, while the former can be determined in a number of ways; for example, a reasonable estimate can often be obtained from standard bond enthalpies plus any strain contributions. Politzer[60] has pointed out that the relative specific impulse is not highly sensitive to the method used for obtaining the heats of formation. In our work, we compute gas-phase heats of formation with the semiempirical AM1 method.

Results and Discussion

In the following parts, we discuss the series of novel molecules $(CH)_xN_{8-x}$ ($0 \leq n \leq 8$), with the CH groups replaced by N atoms in the caged molecule cubane $(CH)_8$. The basic structure, atom numbering, and molecular formula are presented in Figure 2. The basic structure of $(CH)_8$ is a symmetric cubic cage constructed by eight C atoms (Figure 2). Twelve C—C bonds are perpendicular to each other, which form a structure possessing both the strain and the stability.[62,63] As (1−8) N atoms replace CH groups, 22 cubic caged molecules $(CH)_{8-n}N_n$ ($0 < n \leq 8$) are obtained. As all CH groups are replaced by N atoms, the cubic N_8 is obtained. Many theoretical studies on N_8, the isoelectronic molecule of $(CH)_8$, have been reported.[7,11,25,41,64−67] Some studies reported that the reason that the N_8 molecule possesses high-density energy is not high strain of the structure but the weak N—N single bond. There has been a theoretical report on $(CH)_{8-n}N_n$ ($0 \leq n \leq 8$),[64] but in ref 64, the computational level is quite a bit lower and the semi-experiential methods AM1, PM3, and MNDO are used. In the following parts, these new molecules $(CH)_xN_{8-x}$ ($0 \leq n \leq 8$) are studied theoretically and systemically.

1. Geometries. According to the obtained data, it can be seen that all of the bond lengths and bond angles formed by the C atoms in $(CH)_8$ are equal, 1.574 Å and 90°, respectively. Obviously, the $(CH)_8$ is an O_h symmetry molecule. Each side is a four-membered ring, and the bond angle of C—C—C is 90°, which deviates from the normal angle of C—C—C formed by sp^3 hybridized C atoms. It implies that the O_h $(CH)_8$ have a large strain energy. The strain energy would be sent out when O_h $(CH)_8$ decomposes. Optimized geometries of $(CH)_{8-n}N_n$ ($0 \leq n \leq 8$) show that cube caged structures have some deformation after CH groups are replaced by N atoms. Selected bond lengths data are listed in Table 1. Theoretical studies on
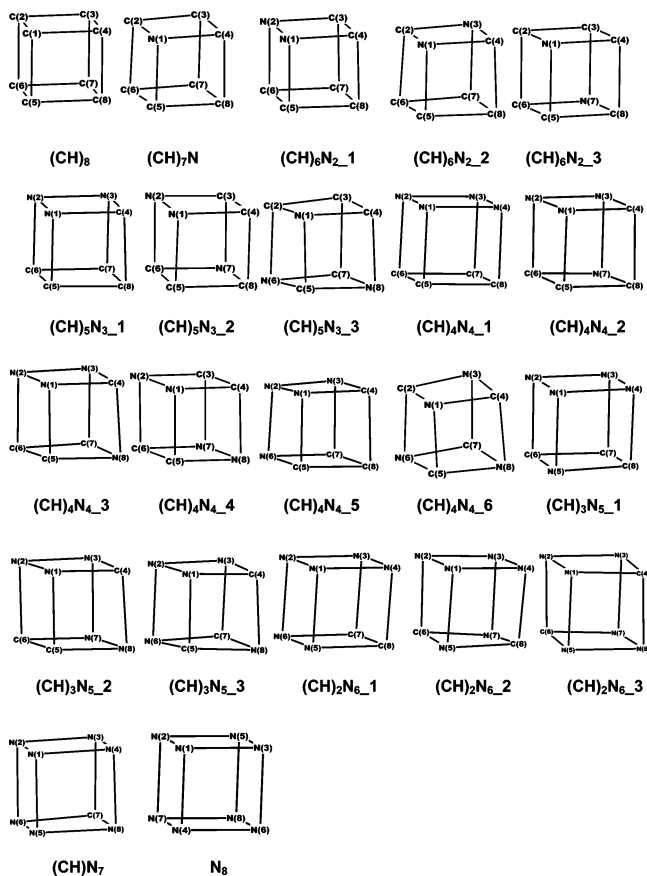
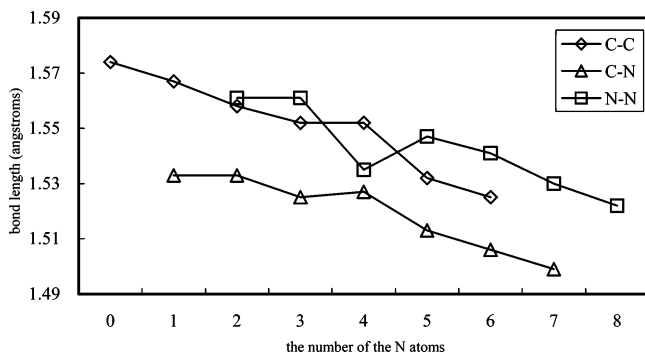**Figure 2.** Structures and atom numbering of (CH)$_{8-n}$N$_n$ ($0 \leq n \leq 8$).

Figure 3. Average bond lengths (in Å) as a function of the N content for (CH)$_{8-n}$N$_n$ ($0 \leq n \leq 8$).

N$_8$ show that the bond lengths of N−N at different theoretical levels are 1.529 (MP2/DZP),[68] 1.517 (B3LYP/DZP),[68] 1.517-(CCSD/DZP),[68] and 1.5218 Å (B3LYP/aug-cc-pvdz),[68] respectively. Compared with the reported values, our result (1.522 Å) is consistent with them at the same level and close to the values at higher levels.

Generally, in the unstrained systems, C−C, C−N, and N−N, single bond typical experimental data are 1.54 Å (C$_2$H$_6$), 1.47 Å (CH$_3$NH$_2$), and 1.45 Å (N$_2$H$_4$), respectively. That is, for the single bond, the bond length N−N < C−N < C−C. However, as shown in Table 1, in the same molecule, the N−N bond (if it exists) is the longest bond and the C−N bond (if it exists) is the shortest bond among three types bonds except four-substituent molecules ((CH)$_4$N$_4$). We conclude that, in the molecule which possesses the C and N atom, the N−N bond is the weakest and the C−N bond is the strongest; the N−N would readily break down when the molecule decomposes. The bond lengths of C−C, C−N, and N−N of studied molecules as a
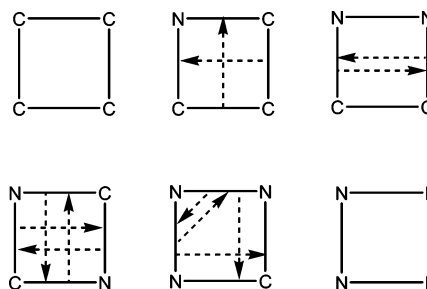

Figure 4. CT in six kinds of four-membered rings for a cubic caged structure. The dashed arrows show the CT from the bonding orbital to the antibonding orbital.
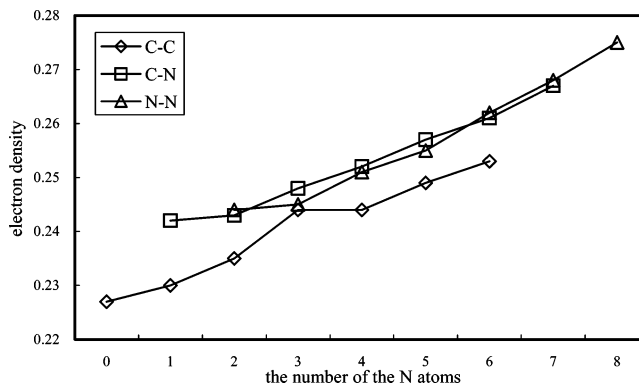

Figure 5. Electron density on BCPs as a function of N content for (CH)$_{8-n}$N$_n$ ($0 \leq n \leq 8$).

function of N content are plotted (Figure 3). As is seen from Table 1 and Figure 3, the bond lengths have obvious changes. There is a roughly monotonic decrease in C−C, C−N, and N−N bond lengths as the number of N atoms *n* increases from 0 to 8.

2. NBO Analysis. The charge transfer (CT) in studied molecules is analyzed by means of the NBO theory. It has been clearly observed that there exists the charge transfer (CT) from the bonding orbital of each bond to the antibonding orbitals of neighbor bonds.

The basic structures of (CH)$_{8-n}$N$_n$ ($0 \leq n \leq 8$) are cubic caged structures formed by the C or N atoms. Every side of the caged structure is a four-membered ring (Figure 4). The CT is shown as Figure 4. In Figure 4, the arrows point from the bonding orbitals to the antibonding orbitals. It is found that the CT only exists in the four-membered ring on the same side. When the four-membered rings are only formed by four C or N atoms, there is no interaction between the bonds in the computational threshold. When C and N atoms coexist in the same four-membered ring, there is CT from the bonding orbitals of all bonds to the antibonding orbitals of C−N bonds. The antibonding orbitals of C−N bonds accept abundant charges. Therefore, in the cubic caged structure, the electron delocalization exists (if it exists) in every four-membered ring on the same side. The more C−N bonds the four-membered ring possesses, the stronger the delocalization effect in the four-membered ring.

3. AIM Analysis. A topological analysis of electron density ρ and its Laplacian $\nabla^2 \rho$ is carried out by means of the AIM theory. The ellipticity ϵ at any BCP has been evaluated. The topological properties of the C−C, C−N, and N−N bonds of (CH)$_x$N$_{8-x}$ ($0 \leq n \leq 8$) are discussed. $\nabla^2 \rho$ identifies the regions of the space wherein the charge is locally depleted ($\nabla^2 \rho > 0$) or concentrated ($\nabla^2 \rho < 0$). The values of the Laplacian $\nabla^2 \rho$ at corresponding BCPs for all studied molecules are negative. This

TABLE 1: Selected Bond Lengths (in Å) of $(CH)_{8-n}N_n$ ($0 \leq n \leq 8$)[a]

ATOM i	j	$(CH)_8$	$(CH)_7N$	$(CH)_6N_2\_1$	$(CH)_6N_2\_2$	$(CH)_6N_2\_3$	$(CH)_5N_3\_1$
1	2	1.574	1.533(CN)	1.561(NN)	1.523(CN)	1.541(CN)	1.552(NN)
1	4	1.574	1.534(CN)	1.531(CN)	1.522(CN)	1.541(CN)	1.513(CN)
1	5	1.574	1.533(CN)	1.531(CN)	1.539(CN)	1.541(CN)	1.532(CN)
2	3	1.574	1.562	1.522(CN)	1.530(CN)	1.551	1.552(NN)
2	6	1.573	1.563	1.531(CN)	1.551	1.550	1.531(CN)
3	4	1.573	1.562	1.547	1.522(CN)	1.551	1.513(CN)
3	7	1.574	1.577	1.564	1.538(CN)	1.541(CN)	1.532(CN)
4	8	1.574	1.563	1.564	1.551	1.550	1.553
5	6	1.572	1.563	1.547	1.566	1.550	1.549
5	8	1.574	1.563	1.565	1.566	1.550	1.569
6	7	1.573	1.577	1.564	1.566	1.541(CN)	1.549
7	8	1.575	1.577	1.582	1.566	1.541(CN)	1.569

ATOM i	j	$(CH)_5N_3\_2$	$(CH)_5N_3\_3$	$(CH)_4N_4\_1$	$(CH)_4N_4\_2$	$(CH)_4N_4\_3$	$(CH)_4N_4\_4$
1	2	1.569(NN)	1.527(CN)	1.535(NN)	1.554(NN)	1.558(NN)	1.577(NN)
1	4	1.538(CN)	1.526(CN)	1.534(NN)	1.518(CN)	1.502(CN)	1.522(CN)
1	5	1.538(CN)	1.510(CN)	1.525(CN)	1.538(CN)	1.517(CN)	1.523(CN)
2	3	1.518(CN)	1.555	1.535(NN)	1.539(NN)	1.558(NN)	1.522(CN)
2	6	1.519(CN)	1.527(CN)	1.527(CN)	1.511(CN)	1.537(CN)	1.522(CN)
3	4	1.536	1.555	1.535(NN)	1.511(CN)	1.501(CN)	1.521
3	7	1.527(CN)	1.555	1.528(CN)	1.557(NN)	1.518(CN)	1.523(CN)
4	8	1.552	1.526(CN)	1.527	1.537	1.514(CN)	1.522(CN)
5	6	1.535	1.510(CN)	1.553	1.537	1.538	1.521
5	8	1.553	1.510(CN)	1.551	1.556	1.531(CN)	1.522(CN)
6	7	1.525(CN)	1.526(CN)	1.518(CN)	1.553	1.538(CN)	1.522(CN)
7	8	1.546(CN)	1.527(CN)	1.552	1.537(CN)	1.532(CN)	1.577(NN)

ATOM i	j	$(CH)_4N_4\_5$	$(CH)_4N_4\_6$	$(CH)_3N_5\_1$	$(CH)_3N_5\_2$	$(CH)_3N_5\_3$	$(CH)_2N_6\_1$
1	2	1.543(NN)	1.516(CN)	1.527(NN)	1.565(NN)	1.551(NN)	1.513(NN)
1	4	1.515(CN)	1.515(CN)	1.528(NN)	1.507(CN)	1.504(CN)	1.530(NN)
1	5	1.514(CN)	1.516(CN)	1.545(NN)	1.524(CN)	1.504(CN)	1.530(NN)
2	3	1.544(NN)	1.514(CN)	1.542(NN)	1.544(NN)	1.550(NN)	1.530(NN)
2	6	1.544(NN)	1.515(CN)	1.515(CN)	1.512(CN)	1.550(NN)	1.530(NN)
3	4	1.514(CN)	1.516(CN)	1.542(NN)	1.494(CN)	1.504(CN)	1.548(NN)
3	7	1.514(CN)	1.516(CN)	1.535(CN)	1.544(NN)	1.504(CN)	1.516(CN)
4	8	1.557	1.514(CN)	1.511(CN)	1.505(CN)	1.518(CN)	1.516(CN)
5	6	1.515(CN)	1.515(CN)	1.519(CN)	1.523	1.504(CN)	1.547(NN)
5	8	1.557	1.515(CN)	1.518(CN)	1.524(CN)	1.519(CN)	1.515(CN)
6	7	1.514(CN)	1.515(CN)	1.541	1.516(CN)	1.503(CN)	1.516(CN)
7	8	1.558	1.515(CN)	1.541	1.565(NN)	1.519(CN)	1.525

ATOM i	j	$(CH)_2N_6\_2$	$(CH)_2N_6\_3$	$(CH)N_7$	N_8
1	2	1.532(NN)	1.549	1.516(NN)	1.522(NN)
1	4	1.531(NN)	1.498(CN)	1.517(NN)	1.522(NN)
1	5	1.556(NN)	1.549(NN)	1.516(NN)	1.522(NN)
2	3	1.532(NN)	1.550(NN)	1.536(NN)	1.522(NN)
2	6	1.497(CN)	1.498(CN)	1.537(NN)	1.522(NN)
3	4	1.532(NN)	1.498(CN)	1.537(NN)	1.522(NN)
3	7	1.556(NN)	1.549(NN)	1.500(CN)	1.522(NN)
4	8	1.496(CN)	1.499(CN)	1.536(NN)	1.522(NN)
5	6	1.508(CN)	1.498(CN)	1.537(NN)	1.522(NN)
5	8	1.509(CN)	1.550(NN)	1.537(NN)	1.522(NN)
6	7	1.507(CN)	1.498(CN)	1.499(CN)	1.522(NN)
7	8	1.507(CN)	1.550(NN)	1.499(CN)	1.522(NN)

average bond length

	$(CH)_8$	$(CH)_7N$	$(CH)_6N_2$	$(CH)_5N_3$	$(CH)_4N_4$	$(CH)_3N_5$
C−C	1.574	1.567	1.558	1.552	1.552	1.532
C−N		1.533	1.533	1.525	1.527	1.513
N−N			1.561	1.561	1.535	1.547

	$(CH)_2N_6$	$(CH)N_7$	N_8
C−C	1.525		
C−N	1.506	1.499	
N−N	1.541	1.53	1.522

[a] The data without the mark correspond to the bond lengths of the C−C bonds.

TABLE 2: Natural Atomic Charges and Chemical Shift σ^{13}C (ppm) of C and N Atoms for (CH)$_{8-n}$N$_n$ ($0 \le n \le 8$)[a]

ATOM	charge	σ^{13}C	charge	σ^{13}C	charge	σ^{13}C	charge	σ^{13}C	charge	σ^{13}C
	(CH)$_8$		(CH)$_7$N		(CH)$_6$N$_2$_1		(CH)$_6$N$_2$_2		(CH)$_6$N$_2$_3	
1	−0.234	140.5(C)	−0.573	(N)	−0.372	(N)	−0.585	(N)	−0.563	(N)
2	−0.234	140.5(C)	−0.018	113.1(C)	−0.372	(N)	0.183	89.5(C)	−0.042	112.3(C)
3	−0.234	140.5(C)	−0.258	139.5(C)	−0.038	113.0(C)	−0.585	(N)	−0.042	112.3(C)
4	−0.234	140.5(C)	−0.018	113.1(C)	−0.038	113.0(C)	0.183	89.5(C)	−0.042	112.1(C)
5	−0.234	140.5(C)	−0.018	113.1(C)	−0.038	113.0(C)	−0.017	115.8(C)	−0.042	112.3(C)
6	−0.234	140.5(C)	−0.258	139.6(C)	−0.038	113.0(C)	−0.281	141.1(C)	−0.042	112.1(C)
7	−0.234	140.5(C)	−0.230	143.3(C)	−0.256	142.2(C)	−0.017	115.8(C)	−0.563	(N)
8	−0.234	140.5(C)	−0.258	139.9(C)	−0.256	142.2(C)	−0.281	141.1(C)	−0.042	112.3(C)
	(CH)$_5$N$_3$_1		(CH)$_5$N$_3$_2		(CH)$_5$N$_3$_3		(CH)$_4$N$_4$_1		(CH)$_4$N$_4$_2	
1	−0.383	(N)	−0.362	(N)	−0.595	(N)	−0.179	(N)	−0.376	(N)
2	−0.175	(N)	−0.385	(N)	0.184	92.1(C)	−0.179	(N)	−0.183	(N)
3	−0.383	(N)	−0.062	114.7(C)	−0.302	142.6(C)	−0.179	(N)	−0.183	(N)
4	0.171	90.0(C)	−0.062	114.7(C)	0.184	92.1(C)	−0.179	(N)	−0.064	115.8(C)
5	−0.037	114.9(C)	0.164	89.4(C)	0.374	71.1(C)	−0.061	114.3(C)	−0.064	115.8(C)
6	−0.058	113.8(C)	−0.042	114.5(C)	−0.595	(N)	−0.061	114.3(C)	0.150	91.3(C)
7	−0.037	114.9(C)	0.164	(N)	0.183	92.0(C)	−0.061	114.3(C)	−0.376	(N)
8	−0.282	141.9(C)	−0.578	159.6(C)	−0.595	(N)	−0.061	114.3(C)	−0.064	115.8(C)
	(CH)$_4$N$_4$_3		(CH)$_4$N$_4$_4		(CH)$_4$N$_4$_5		(CH)$_4$N$_4$_6		(CH)$_3$N$_5$_1	
1	−0.394	(N)	−0.378	(N)	−0.392	(N)	−0.601	(N)	0.011	(N)
2	−0.166	(N)	−0.378	(N)	0.017	(N)	0.371	73.0(C)	−0.190	(N)
3	−0.394	(N)	0.145	91.8(C)	−0.392	81.2(C)	−0.601	(N)	−0.171	(N)
4	0.362	71.1(C)	0.145	91.8(C)	0.171	(N)	0.371	72.8(C)	−0.190	(N)
5	0.163	91.0(C)	0.145	91.8(C)	−0.392	81.4(C)	0.371	72.9(C)	−0.389	(N)
6	−0.082	117.7(C)	0.145	91.8(C)	0.171	(N)	−0.601	(N))	0.148	91.8(C)
7	0.163	91.0(C)	−0.378	(N)	−0.307	142.5(C)	0.371	72.5(C)	−0.088	117.4(C)
8	−0.589	(N)	−0.378	(N)	0.171	91.7(C)	−0.601	(N)	0.148	91.8(C)
	(CH)$_3$N$_5$_2		(CH)$_3$N$_5$_3		(CH)$_2$N$_6$_1		(CH)$_2$N$_6$_2		(CH)$_2$N$_6$_3	
1	−0.391	(N)	0.027	(N)	0.003	(N)	0.018	(N)	−0.190	(N)
2	−0.176	(N)	−0.401	(N)	0.003	(N)	−0.199	(N)	−0.190	(N)
3	−0.193	(N)	0.359	(N)	−0.185	(N)	0.018	(N)	−0.190	(N)
4	0.348	73.3(C)	−0.401	89.5(C)	−0.185	(N)	−0.199	(N)	0.335	77.4(C)
5	0.141	92.4(C)	−0.402	89.4(C)	−0.185	(N)	−0.402	(N)	0.335	(N)
6	0.129	95.8(C)	0.359	(N)	−0.185	(N)	0.345	73.0(C)	−0.191	23.3(C)
7	−0.176	(N)	−0.600	151.9(C)	0.124	94.8(C)	−0.402	(N)	−0.190	(N)
8	−0.391	(N)	0.359	(N)	0.124	94.8(C)	0.345	73.0(C)	−0.190	(N)
	(CH)N$_7$		N$_8$							
1	−0.003	(N)	0.000	(N)						
2	0.009	(N)	0.000	(N)						
3	−0.198	(N)	0.000	(N)						
4	0.009	(N)	0.000	(N)						
5	0.009	(N)	0.000	(N)						
6	−0.198	(N)	0.000	(N)						
7	0.331	76.4(C)	0.000	(N)						
8	−0.198	(N)	0.000	(N)						

[a] The element symbols are marked in parentheses.

is typical for a closed-shell interaction accompanied by concentration of electron density between interacting nuclei. It indicates that studied molecules still keep the cubic caged structure after CH groups are replaced by N atoms. According to the values of electron density ρ at the BCPs, for (CH)$_8$ and N$_8$, the electron density ρ at the BCP(C−C) and BCP(N−N) are equal, 0.227 and 0.275, respectively, which implies that the bond strength of all the C−C bonds in (CH)$_8$ are equal and the N−N bonds in N$_8$ are as well. In the same molecule, the electron density ρ at the BCPs of the C−C bonds, which are farther from the N atoms, is smaller, that is, the C−C bonds are weaker. For example, for (CH)$_6$N$_2$_1, the electron density ρ of the C7−C8 bond is the smallest (0.223 au), and it locates on the furthest diagonal edge from N1−N2. The average values of ρ at the BCPs of the C−C, C−N, and N−N bonds as a function of N content are presented (Figure 5). As shown in Figure 5, the introduction of N atoms has some influence on the electron density at the BCPs of the C−C, C−N, and N−N bonds. The

values of ρ at the BCPs increase as N content increases. The above geometric analyses found that the three kinds of bonds shorten as N content increases. Bond shortening results in an electron density increase. The analyses of the electron density at BCPs are consistent with the geometric analyses. We have also evaluated the ellipticity ϵ of ρ at any BCP. For this series of molecules, the ϵ values at corresponding BCPs are quite small (<0.02 au), far smaller than the ones of the C−N and N−N bonds (the largest value is close to 0.1 au), which indicates that the C−C bonds are σ-bonds. The above NBO analyses also show that a few charges transfer to the C−C bonds and most charges transfer to the C−N bonds. This proves that the C−N bonds possess much more π-bonding character than the C−C bonds and the C−N bonds take part in electron delocalization. The distances from the nucleus to the BCPs are studied. For the C−C and N−N bonds, the distances between bonding atoms (C/N) and the BCPs are influenced by adjoining atoms. When linking atoms are the same, the distances between bonding atoms

TABLE 3: Dipole Moments, Total Energies, and Relative Energies for $(CH)_{8-n}N_n$ ($0 \leq n \leq 8$)

|	dipole moment (Debye)	total energy (au)	relative energy (kcal/mol)
$(CH)_8$	0.00	−309.490327	
$(CH)_7N$	2.01	−325.523892	
$(CH)_6N_2\_1$	3.48	−341.535190	14.79
$(CH)_6N_2\_2$	2.41	−341.558752	0.00
$(CH)_6N_2\_3$	0.00	−341.554984	2.36
$(CH)_5N_3\_1$	4.22	−357.548458	28.88
$(CH)_5N_3\_2$	2.21	−357.567953	16.65
$(CH)_5N_3\_3$	2.18	−357.594481	0.00
$(CH)_4N_4\_1$	5.37	−373.538772	57.71
$(CH)_4N_4\_2$	3.69	−373.559671	44.59
$(CH)_4N_4\_3$	2.68	−373.582475	30.28
$(CH)_4N_4\_4$	0.00	−373.578842	32.56
$(CH)_4N_4\_5$	4.47	−373.563383	42.26
$(CH)_4N_4\_6$	0.00	−373.630732	0.00
$(CH)_3N_5\_1$	4.53	−389.551725	29.25
$(CH)_3N_5\_2$	2.36	−389.572134	16.44
$(CH)_3N_5\_3$	2.30	−389.598330	0.00
$(CH)_2N_6\_1$	4.03	−405.541809	15.22
$(CH)_2N_6\_2$	2.73	−405.566059	0.00
$(CH)_2N_6\_3$	0.00	−405.563482	1.62
$(CH)N_7$	2.51	−421.533813	
N_8	0.00	−437.501888	

(C/N) and the BCPs are equal; contrarily, there are small differences. For example, for $(CH)_7N$, BCP(C5−C6) is closer to C6 and BCP(C3−C4) is closer to C3. This relates to the N atom linking C4 or C5. The electronegative N atom enhances the electronegativity of adjoining C atoms, so C5 and C4 possess larger atomic radii than C3 and C6 in the C5−C6 and C3−C4 bonds. For the C−N bonds, the distances between the BCP-(C−N) and N atoms (∼1.6 au) are much larger than the ones between the BCP(C−N) and C atoms (∼1.2 au), that is, N atoms possess a larger atomic radius than C atoms for the C−N bonds. So, the C−N bonds are more highly polarized bonds than the C−C and N−N bonds. Moreover, it is found that the increase in N content has little influence on the distances between the BCPs and bonding atoms.

4. Atomic Charge and NMR Chemical Shift. To study further the electronic structures of designed molecules, molecular ^{13}C NMR chemical shifts $\sigma(^{13}C_i)$ in the gas phase are calculated using the GIAO method[69−71] at the same theoretical level. The above optimized molecular structures are used. Generally, the chemical shift reflects the electron density on the atom. The change of atom chemical surroundings is reflected by its chemical shift.

The NMR chemical shifts $\sigma(^{13}C_i)$ of $(CH)_{8-n}N_n$ ($0 \leq n \leq 8$) are listed in Table 2. From Table 2, it is found that the N atoms linking C atoms possess a negative charge and the C atoms linking N atoms possess a positive charge. It verifies that the above AIM analyses show the charge transfer from the C atom to N atom in the C−N bond. The N atoms reduce the electron density on the C atoms and result in an increase in the positive charge on the C atoms. This effect is more obvious as the N atoms increase. Due to the deshielding effect of the N atom, it can be predicted that the chemical shifts $\sigma^{13}C$ will be lower for the C atoms which possess more positive charges. This conclusion can be verified by the chemical shift data in Table 2. The C atoms linking more N atoms show smaller values for the chemical shifts.

5. Dipole Moment and Molecular Total Energy. The dipole moments and molecular total energies of $(CH)_{8-n}N_n$ ($0 \leq n \leq 8$) are listed in Table 3. The relative energies in Table 3 are the energy differences between the conformers. The data in Table 3 show that the molecule possesses higher total energy as its
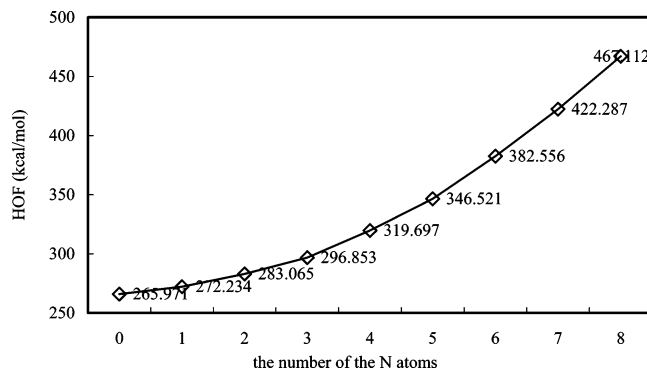
Figure 6. HOFs of $(CH)_{8-n}N_n$ ($0 \leq n \leq 8$) as a function of N content.

dipole moment becomes larger. The dipole moment is not the only factor deciding the molecular stability, and it influences the molecular total energy to some extent. The dispersive location of the N atoms makes the dipole moments created by the C−N bonds counteract partly, which increases the molecular stability. Therefore, we believe that the molecule with higher dipole moment is more unstable among the conformers.

6. Heat of Formation (HOF). It is well-known that evaluation of the explosive performance of energetic materials requires the knowledge of the HOF. Moreover, HOFs are of great importance for researchers involved in thermochemistry. The experimental data of HOFs for many stable compounds have been obtained. However, it is impractical or dangerous for energetic materials to measure their HOFs experimentally. In these cases, many computational methods are employed to obtain HOFs. To our knowledge, no experimental HOFs for designed molecules are available. The HOFs for $(CH)_{8-n}N_n$ ($0 \leq n \leq 8$) have been reports using semiempirical methods AM1, PM3, and MNDO.[18] In the following part, the HOFs have been obtained via the calculation method mentioned above.

The HOFs of studied molecules as a function of N content are presented in Figure 6. As shown in Figure 6, it is found that their HOFs are all quite large and positive values, which is one of the necessary characteristics of energetic material. They can be regarded as a kind of endothermal material. The values of HOFs in Figure 6 are averaged over the conformers for $(CH)_{8-n}N_n$ ($0 \leq n \leq 8$). As shown in Figure 6, the HOFs become larger as the N content increases. The larger the molecular HOF is, the more the molecule stores energy. Our calculation can prove that the molecule with higher N content stores more energy, which is agreement with the general experimental conclusion. For $(CH)_{8-n}N_n$ ($0 \leq n \leq 8$), compared with the values in ref 18, calculated HOFs using the B3LYP method are far larger than the ones using semiempirical methods but the whole tendency is similar. In ref 18, the HOFs are plotted and the tendency is similar to the one in Figure 6: the HOFs increase as the N content increases. The molecular total energies and zero-point correction ($\epsilon_0 + \epsilon_{ZPE}$), thermal correction to enthalpies (H_{corr}), and calculated HOFs of studied molecules are listed in Table 4. According to the data in Table 4, it is found that the HOF of the molecule, which is more stable, is lower for the conformers. The total energies of conformers show the same tendency as their HOFs.

7. Relative Specific Impulse (I_s). According to the above HOFs, we found that the studied molecules should be a kind of novel energetic material molecule. To evaluate their performance as a kind of energetic material, we calculate the relative specific impulse (I_s) introduced by Politzer et al.[60] The relative specific impulse (I_s), widely used as a means of characterizing and evaluating explosives, is also calculated to evaluate the perfor-

Replacement of CH Groups by N atoms in (CH)$_8$

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TABLE 4: Calculated Thermochemistry Values of (CH)$_{8-n}$N$_n$ (0 ≤ n ≤ 8)

	$\epsilon_0 + \epsilon_{ZPE}$ (au)	H_{corr} (au)	HOF (kcal/mol)	AM1[21] (kcal/mol)	PM3[21] (kcal/mol)	MNDO[21] (kcal/mol)	average (kcal/mol)
(CH)$_8$	−309.3578	0.138367	265.971	151.1	113.8	99.1	265.971
(CH)$_7$N	−325.4024	0.126874	272.234	187.6	126.0	115.7	272.234
(CH)$_6$N$_2$_1	−341.4255	0.114986	291.752	235.4	154.5	142.7	
(CH)$_6$N$_2$_2	−341.4485	0.115508	277.655	224.1	138.1	131.0	283.065
(CH)$_6$N$_2$_3	−341.4449	0.115327	279.789	229.9	139.6	133.7	
(CH)$_5$N$_3$_1	−357.4507	0.103014	309.926	286.0	182.0	168.3	
(CH)$_5$N$_3$_2	−357.4698	0.103419	298.228	274.5	167.1	159.3	296.853
(CH)$_5$N$_3$_3	−357.4956	0.104044	282.404	263.3	147.3	145.2	
(CH)$_4$N$_4$_1	−373.4535	0.090528	341.839	349.1	226.3	204.0	
(CH)$_4$N$_4$_2	−373.4739	0.090968	329.298	327.2	193.5	183.9	
(CH)$_4$N$_4$_3	−373.4962	0.091408	315.565	338.6	211.1	195.3	319.697
(CH)$_4$N$_4$_4	−373.4926	0.091367	317.787	339.0	208.5	192.8	
(CH)$_4$N$_4$_5	−373.4775	0.091055	327.083	327.1	196.0	186.7	
(CH)$_4$N$_4$_6	−373.5434	0.092415	286.61	304.5	156.0	158.4	
(CH)$_3$N$_5$_1	−389.4785	0.078358	359.954	382.2	218.9	207.8	
(CH)$_3$N$_5$_2	−389.4985	0.078767	347.675	393.7	239.2	221.6	346.521
(CH)$_3$N$_5$_3	−389.5241	0.079295	331.933	404.3	254.4	230.2	
(CH)$_2$N$_6$_1	−405.4813	0.065703	391.785	471.2	284.1	258.5	
(CH)$_2$N$_6$_2	−405.505	0.066138	377.132	462.2	281.7	255.9	382.556
(CH)$_2$N$_6$_3	−405.5025	0.066142	378.75	473.0	299.6	266.9	
(CH)N$_7$	−421.486	0.052957	422.287	547.0	344.0	303.4	422.287
N$_8$	−437.4674	0.039681	467.112	630.7	406.2	350.7	467.112

TABLE 5. Idealized Stoichiometric Decomposition Reactions and Relative Specific Impulse (I_s) for HMX and (CH)$_{8-n}$N$_n$ (0 ≤ n ≤ 8)

molecule	reaction	Relative I_s
HMX	C$_4$N$_8$O$_8$H$_8$ → 4CO + 4N$_2$ + 4H$_2$O	1
(CH)$_8$	C$_8$H$_8$ → 4H$_2$ + 8C	1.02
(CH)$_7$N	C$_7$NH$_7$ → 1/2N$_2$ + 7/2H$_2$ + 7/2C	1.13
(CH)$_6$N$_2$_1	C$_6$N$_2$H$_6$ → N$_2$ + 3H$_2$ + 6C	1.30
(CH)$_6$N$_2$_2	C$_6$N$_2$H$_6$ → N$_2$ + 3H$_2$ + 6C	1.22
(CH)$_6$N$_2$_3	C$_6$N$_2$H$_6$ → N$_2$ + 3H$_2$ + 6C	1.22
(CH)$_5$N$_3$_1	C$_5$N$_3$H$_5$ → 3/2N$_2$ + 5/2H$_2$ + 5C	1.37
(CH)$_5$N$_3$_2	C$_5$N$_3$H$_5$ → 3/2N$_2$ + 5/2H$_2$ + 5C	1.34
(CH)$_5$N$_3$_3	C$_5$N$_3$H$_5$ → 3/2N$_2$ + 5/2H$_2$ + 5C	1.32
(CH)$_4$N$_4$_1	C$_4$N$_4$H$_4$ → 2N$_2$ + 4H$_2$ + 4C	1.60
(CH)$_4$N$_4$_2	C$_4$N$_4$H$_4$ → 2N$_2$ + 4H$_2$ + 4C	1.48
(CH)$_4$N$_4$_3	C$_4$N$_4$H$_4$ → 2N$_2$ + 4H$_2$ + 4C	1.46
(CH)$_4$N$_4$_4	C$_4$N$_4$H$_4$ → 2N$_2$ + 4H$_2$ + 4C	1.46
(CH)$_4$N$_4$_5	C$_4$N$_4$H$_4$ → 2N$_2$ + 4H$_2$ + 4C	1.48
(CH)$_4$N$_4$_6	C$_4$N$_4$H$_4$ → 2N$_2$ + 4H$_2$ + 4C	1.41
(CH)$_3$N$_5$_1	C$_3$N$_5$H$_3$ → 5/2N$_2$ + 3/2H$_2$ + 3C	1.61
(CH)$_3$N$_5$_2	C$_3$N$_5$H$_3$ → 5/2N$_2$ + 3/2H$_2$ + 3C	1.59
(CH)$_3$N$_5$_3	C$_3$N$_5$H$_3$ → 5/2N$_2$ + 3/2H$_2$ + 3C	1.56
(CH)$_2$N$_6$_1	C$_2$N$_6$H$_2$ → 3N$_2$ + H$_2$ + 2C	1.73
(CH)$_2$N$_6$_2	C$_2$N$_6$H$_2$ → 3N$_2$ + H$_2$ + 2C	1.71
(CH)$_2$N$_6$_3	C$_2$N$_6$H$_2$ → 3N$_2$ + H$_2$ + 2C	1.71
(CH)N$_7$	CN$_7$H → 7/2N$_2$ + 1/2H$_2$ + C	1.85
N$_8$	N$_8$ → 4N$_2$	1.98

mance of all these compounds as energetic materials. To facilitate comparisons, our values are given relative to HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane), a widely used HEDM. The idealized stoichiometric decomposition reactions are given for HMX and (CH)$_{8-n}$N$_n$ (0 ≤ n ≤ 8) in Table 5. All N atoms are assumed to go to N$_2$, C to C, and H to H$_2$. The results show obviously that this series of molecules can be regarded as a kind of novel potential energetic material. Compared with HMX, their relative specific impulses are all larger, which implies that their explosive performances might excel HMX. The relative specific impulses of this series of molecules as a function of N content are presented in Figure 7. For (CH)$_{8-n}$N$_n$ (0 ≤ n ≤ 8), the I_s values are averaged over the conformers. As shown in the figure, the introduction of the N atoms increases the relative specific impulse. Moreover, the more N content enhances this tendency for the relative specific impulses. It makes a main contribution for the relative specific impulses that the N atoms turn into N$_2$.

Summary

In our work, the molecular design is carried out for cubic caged molecules (CH)$_8$. When the CH groups are replaced by N atoms, a series of novel molecules were obtained: (CH)$_{8-n}$N$_n$ (0 ≤ n ≤ 8). By the use of the quantum chemistry method, their geometries, electronic structures, heats of formation, vibrational frequencies, NMR chemical shifts, and relative specific impulses are studied in detail. The results are obtained as follows:

(1) Caged skeletons of the series of molecules have quite large strain energies. The caged structures are not destroyed and have somewhat deformation after CH groups are replaced by N atoms. Such a tendency exists for C−C, C−N, and N−N: the bonds shorten as the N atoms increase. It implies that the molecular structure becomes tighter, that is, the molecular density increases. In the same molecule, the N−N bond is always the longest and the weakest bond. Therefore, the N−N bond should break down first when the molecules decompose.

(2) NBO analyses are carried out for the series of molecules. For (CH)$_{8-n}$N$_n$ (0 ≤ n ≤ 8), the CT exists only in the same four-membered ring on the same side. The more C−N bonds present in a four-membered ring, the stronger the delocalization.

(3) Through AIM analyses, it is verified that polyhedral caged structures still remain after the CH groups are replaced by N atoms. For (CH)$_8$ and N$_8$, the bonds are σ-bonds. For the others,
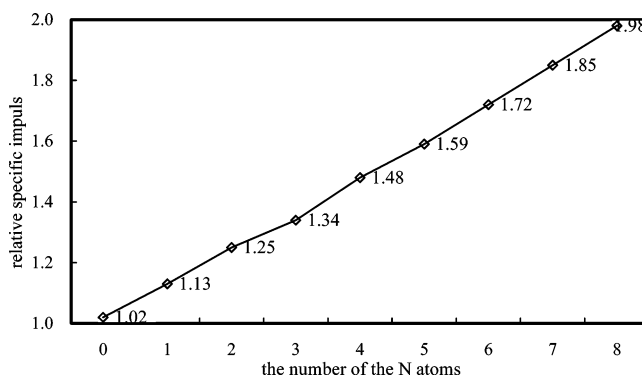
Figure 7. The relative I_s as a function of N content for (CH)$_{8-n}$N$_n$ (0 ≤ n ≤ 8).

the N−N and C−N bonds possess some π-bond component. The π-bond component in the C−N bonds is greater. For $(CH)_{8-n}N_n$ ($0 \leq n \leq 8$), the distances from the BCP(C−C) and BCP(N−N) to bonding atoms are influenced by adjoining atoms. The electron density at the BCPs increases as the N atoms increase.

(4) The NMR chemical shifts and natural atomic charges are analyzed. It is found that the introduction of N atoms lowers the electron density on the C atoms. This effect is enhanced by introduction of more N atoms.

(5) The relations of the dipole moments and the total energies are discussed. It is found that the total energy of the molecule with a larger dipole moment is higher and the structure is more unstable. Calculated HOFs of the series of caged molecules are all large and positive values. This means that they belong to endothermal materials and are candidates of HEDMs. The HOF of the molecules with higher N content is larger for the conformers. For the molecules with the same numbers of C, H and N atoms, the dipole moment becomes larger as molecular total energy and HOFs increase.

(6) The specific impulses of the series of molecules are calculated and compared with HMX. The results show that the I_s values of studied molecules are larger than HMX. The introduction of N atoms increases the I_s. Moreover, as N content increases, the increase tendency of I_s is enhanced.

Our studies show that $(CH)_{8-n}N_n$ ($0 \leq n \leq 8$) should be a kind of potential and novel energetic material, and our work provides some useful information for the experimental study of these molecules.

References and Notes

(1) Caswit, C.; Wenninger, J.; Roberts, J. D. *J. Am. Chem. Soc.* **1981**, *103*, 6248.

(2) Workentin, M. S.; Wagner, B. D.; Negri, F.; Zgierski, M. Z.; Lusztyk, J.; Siberand, W.; Wayner, D. D. M. *J. Phys. Chem.* **1995**, *99*, 94.

(3) Workentin, M. S.; Wagner, B. D.; Lusztyk, J.; Wayner, D. D. M. *J. Am. Chem. Soc.* **1995**, *117*, 119.

(4) Vogel, A.; Wright, R. E.; Kenkley, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 717.

(5) Wright, J. S. *J. Am. Chem. Soc.* **1974**, *96*, 4573.

(6) Guest, M. F.; Hillier, I. H.; Saunders, V. R. *J. Chem. Soc., Faraday. Trans. 2* **1972**, *68*, 2070.

(7) Trinquer, G.; Malrieu, J. P.; Daudey, J. P. *Chem. Phys. Lett.* **1981**, *80*, 552.

(8) Lauderdale, W. J.; Stanton, J. F.; Bartlett, R. J. *J. Phys. Chem.* **1992**, *96*, 1173.

(9) Lee, T. J.; Rice, J. E. *J. Chem. Phys*. **1991**, *94*, 1215.

(10) Glukhovtsev, M. N.; Schleyer, P. V. R. *Chem. Phys. Lett.* **1993**, *204*, 394.

(11) Leininger, M. L.; Scherrill, C. D.; Schaefer, H. F., III. *J. Phys. Chem.* **1995**, *99*, 2324.

(12) Li, Q. S.; Qu, H.; Zhu, H. S. *Chin. Sci. Bull.* **1996**, *41*, 515.

(13) Chen, C.; Sun, K. C.; Shyu, S. F. *J. Mol. Struct. (THEOCHEM)* **1999**, *459*, 113.

(14) Ren, Y.; Wang, X.; Wong, N. B.; et al. *Int. J. Quantum. Chem.* **2001**, *82*, 34.

(15) Patil, D. G.; Brill, T. B. *Combus. Flame* **1991**, *87P*, 145.

(16) Engelke, R. *J. Phys. Chem.* **1989**, *93*, 5722.

(17) Engelke, R. *J. Am. Chem. Soc.* **1993**, *115*, 2961.

(18) Engelke, R. *J. Org. Chem.* **1992**, *57*, 4841.

(19) Engelke, R.; Stine, J. R. *J. Phys. Chem.* **1990**, *94*, 5689.

(20) Nguyent, M. T. *J. Phys. Chem.* **1990**, *94,* 6923.

(21) Engelke, R. *J. Phys. Chem.* **1990**, *94*, 6924.

(22) Beckhaus, H.-D.; Ruchardt, C.; Lagerwall, D. R.; Paquette, L. A.; Wahl, F.; Prinzbach, H. *J. Am. Chem. Soc.* **1994**, *116*, 11775.

(23) Beckhaus, H.-D.; Ruchardt, C.; Lagerwall, D. R.; Paquette, L. A.; Wahl, F.; Prinzbach, H. *J. Am. Chem. Soc.* **1995**, *117*, 8885.

(24) Wiberg, K. B. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 312.

(25) Schulman, J. M.; Disch, R. L. *J. Am. Chem. Soc.* **1984**, *106*, 1202.

(26) Kybett, B. D.; Carroll, S.; Natalis, P.; Bonnell, D. W.; Margrave, L.; Franklin, J. L. *J. Am. Chem. Soc.* **1966**, *88*, 626.

(27) Disch, R. L.; Schulman, J. M. *J. Phys. Chem.* **1996**, *100*, 3504.

(28) Nagase, S. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 329.

(29) Griffin, G. W.; Marchard, A. P. *Chem. Rev.* **1989**, *89*, 997.

(30) Marchand, A. P. *Chem. Rev.* **1989**, *89*, 1011.

(31) Klurder, A. J. H.; Zwanerbing, B. *Chem. Rev.* **1989**, *89*, 1035.

(32) Eaton, P. E.; Cole, T. *J. Am. Chem. Soc.* **1964**, *86*, 962.

(33) Scherer, K. V. *Tetrahedron Lett.* **1965**, *30*, 1199.

(34) Paquette, L. *J. Am. Chem. Soc*. **1982**, *104*, 4503.

(35) Eaton, P. E. *Tetrahedron* **1986**, *42*, 1621.

(36) Bliznyuk, A. A.; Shen, M.; Schaefer, H. F. *Chem. Phys. Lett.* **1992**, *198*, 249.

(37) Lauderdale, W. J.; Stanton, J. F.; Bartlett, R. J. *J. Phys. Chem.* **1992**, *96*, 1173.

(38) Francl, M. M.; Chesick, J. P. *J. Phys. Chem.* **1990**, *94*, 526.

(39) Venanzi, T. J.; Schulman, J. M. *Mol. Phys.* **1975**, *30*, 281.

(40) Trinquier, G.; Malrieu, J. P.; Daudeym, J. P. *Chem. Phys. Lett.* **1981**, *80*, 552.

(41) Engelke, R.; Stine, J. R. *J. Phys. Chem.* **1990**, *94*, 5689.

(42) Gimarc, B. M.; Zhao, M. *Inorg. Chem.* **1996**, *35*, 3289.

(43) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. m. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.11; Gaussian, Inc.: Pittsburgh, PA, 2001.

(44) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(45) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(46) Woon, D. E.; Dunning, T. H., Jr. *J. Chem. Phys.* **1993**, *98*, 1358.

(47) Weinhold, F. Natural Bond Orbital Methods. In *Encyclopedia of Computational Chemistry*; Schleyer, P. V. R., Allinger, N. L., Clark, T., Gasteiger, J., Kollman, P. A., Schaefer, H. F., III, Schreiner, P. R., Eds.; John Wiley & Sons: Chichester, U.K., 1998; Vol. 3, p 1792.

(48) Carpenter, J. E.; Weinhold, F. *J. Mol. Struct. (THEOCHEM)* **1988**, *169*, 41.

(49) Carpenter, J. E. Ph.D. Thesis, University of Wisconsin, Madison, WI, 1987.

(50) Foster, J. P.; Weinhold, F. *J. Am. Chem. Soc.* **1980**, *102*, 7211.

(51) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, *78*, 4066.

(52) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, 1736.

(53) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.* **1985**, *83*, 735.

(54) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899.

(55) Weinhold, F.; Carpenter, J. E. *Plenum* **1988**, 227.

(56) Bader, R. W. F. *Atoms In Molecules. A Quantum Theory*; University Press: Oxford, U.K., 1990.

(57) Biegler-König, F.; Schönbohm, J.; Derdau, R.; Bayles, D.; Bader, R. W. F. *AIM 2000*, version 2.0; McMaster University, Ontario, Canada, 2002.

(58) Poperlier, P. L. A. *Atoms In Molecules: An Introduction*; Prentice Hall: New York, 2000.

(59) Curtiss, L. A.; Raghavachari, K.; Redferm, P. C.; Pople, J. A. *J. Chem. Phys.* **1997**, *106*, 1063.

(60) Politzer, P.; Murray, J. S.; Grice, M. E.; Sjoberg, P. In *Chemistry of Energetic Materials*; Olah, G. A., Squire, D. R., Eds.; Academic Press: San Diego, CA, 1991; pp 77−93.

(61) Mayer, R. *Explosives*; VCH: Weinheim, Germany, 1987.

(62) Lukin, K. A.; Li, J. C.; Eaton, P. E. *J. Am. Chem. Soc.* **1997**, *119*, 9591.

(63) Hassenück, K.; Martin, H.; Walsh, R. *Chem. Rev.* **1989**, *89*, 1125.

(64) Alkorta, I.; Elguero, J.; Rozas, I.; Balaban, A. T. *J. Mol. Struct. (THEOCHEM)* **1990**, *206*, 67.

(65) Purvis, G. D.; Bartlett, R. J. *J. Chem. Phys.* **1982**, *76*, 1910.

(66) Raghavachari, K.; Trucks, G. W.; Pople, J. A.; Head-Gordon, M. *Chem. Phys. Lett.* **1989**, *157*, 479.

(67) Tian, A.; Ding, F.; Zhang, L.; Xie, Y.; Schaefer, H. F. *J. Phys. Chem. A* **1997**, *101*, 1946.

(68) Bartlett, R. J. Structure and Stability of Polynitrogen Molecules and Their Spectroscopic Characteristics. To be submitted for publication.

(69) London, F. *J. Phys. Radium* **1937**, *8*, 3974.

(70) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789.

(71) Wolinski, K.; Himton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251.