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Ab Initio Calculations of Ten Carbon/Nitrogen Cubanoids

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Abstract: The results of a uniform set of ab initio quantum-chemical calculations for 10 carbon/nitrogen cubanoids are presented. There are 22 possible C/N cubanoids with formulas $(CH)_{8-n}N_n$, where $0 \le n \le 8$. We give results for one cubanoid for each value of n; for $n = 4$ both the T_d and C_{4v} structures are discussed. The geometries were optimized on the RHF/6-31G*//RHF/6-31G* energy hypersurfaces, and the stationary points so obtained were characterized by vibrational analyses. The effect of electron correlation on the energies of these structures is examined via MP2/6-31G*//RHF/6-31G* theory. All 10 structures are predicted to be stable molecules, and the vibrational analyses indicate that their geometries are well-defined by the RHF/6-31G*// energy hypersurfaces. Heats of formation are predicted via appropriate isodesmic reactions. All the structures are found to have large positive ΔH_f's. Perhaps the most interesting result obtained is that the high-energy content of the nitrogen-rich cubanoids is *not* primarily due to bond strain, but rather to the high-energy content of the NN single bond. Comparisons of the ab initio ΔH_f values with semiempirical AM1, PM3, and MNDO predictions are made. If they can be synthesized and have reasonable kinetic stability, the C/N cubanoids containing four or more nitrogen atoms are likely to be important energetic materials. A brief discussion is given of the potential of these materials as propellants and explosives.

I. Introduction

In this article, we present a uniform set of ab initio calculations on 10 carbon/nitrogen cubanoids (see Figure 1 and its caption). There are 22 such cubanoids with molecular formula $(CH)_{8-n}N_n$, where $0 \le n \le 8$. The cubanoids containing nitrogen are also referred to as aza- and polyazacubanes.

The pure carbon form (**1**) was synthesized by Eaton and Cole in 1964.[2] For such a strained molecule,[3a] carbon cubane is thermally quite stable; it decomposes slowly when heated to ca. 200 °C.[3b] This high thermal stability is thought to originate from the symmetry forbiddenness of the unimolecular reactions that take it to smaller less-strained structures,[4] e.g., $(CH)_8 \rightarrow 4C_2H_2$. There are 21 isomers with the formula $(CH)_8$. The kinetic routes between the parent $(CH)_8$ annulene (i.e., cyclooctatetraene) and the other $(CH)_8$ structures have been discussed by others.[5a,b] Introducing nitrogen atoms in place of CH groups in the $(CH)_8$ isomers increases the number of possible isomers substantially. For example, rather than the unique carbon cubane, there are 22 C/N cubanoids. Insofar as the unimolecular disintegration of the C/N cubanoids is concerned, such processes are thermally forbidden and photochemically allowed. It is known that metal-ion catalysts can produce isomerizations of carbon cubane to less symmetric $(CH)_8$ structures, e.g., to the cyclobutadiene dimer. In this article, we do not give quantitative estimates of the kinetic barriers associated with any of the C/N cubanoid kinetic transformations. This topic is virtually unexplored and would be an interesting area for further work.

The limiting structures (i.e., $n = 0$ and $n = 8$) are true cubes with O_h point-group symmetry. Replacing (CH) groups in $(CH)_8$ with nitrogen atoms breaks the O_h symmetry and results in molecules of lower symmetry and similarly for N_8.

The CH group and a nitrogen atom are isoelectronic and, therefore, the C/N cubanoids are an isoelectronic set of structures. Because of this, unimolecular reaction paths that lead to the dissociation of the mixed C/N cubanoids are also symmetry forbidden. For example, the concerted reaction N_8 cubane $\rightarrow$ $4N_2$ is a highly symmetry-forbidden [4 + 4 + 4 + 4] cycloreversion reaction. These considerations point to the possibility that some of the C/N cubanoids may be quite robust structures. To the author's knowledge there has never been an experimental observation of any C/N cubanoid other than carbon cubane.

The high nitrogen C/N cubanoids are interesting molecules for at least two reasons. These are: (1) well-calibrated methods for estimating the mass densities of condensed-phase organic molecules indicate they would have very high mass densities for organic structures (>2 g/cm^3 in some cases) and (2) because of the large energy release that would result from their decomposition, they would be very efficient repositories for energy (e.g., significantly >2 kcal/g in some cases). These qualities make them prime candidates as new condensed-phase energetic materials.

Because of these considerations we have optimized the 10 structures of Figure 1 at the RHF/6-31G*//RHF/6-31G* level of theory and characterized the stationary points so found by vibrational analyses. All the structures are predicted to be stable, and the vibrational analyses produce lowest vibrational frequencies that suggest the equilibrium geometries are well-defined by the energy hypersurfaces. That is, there are probably not low-energy *unimolecular* paths for their disassembly.

Since electron correlation is known to substantially decrease the predicted metastability energy of nitrogen-ring structures, correlated energies have been determined at the MP2/6-31G*//RHF/6-31G* level of theory also. All the structures are predicted to have high-energy content at this level of theory.

Note that **1** to **5** do not have any nitrogen atoms bonded to nitrogen atoms. It is possible that N–N bonds may make a C/N cubanoid kinetically fragile. If so, **1** to **5** may be the kinetically more robust structures of the 10 studied. However, to be sure of this, multiconfiguration SCF studies should be carried out for some likely unimolecular disintegration routes for these structures.

Because of the possible importance of the C/N cubanoids as energetic materials, we briefly discuss the predicted mass densities and detonation and propellant performance characteristics of the 10 structures.

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[1] This work was supported by the U.S. Department of Energy.

[2] Eaton, P. E.; Cole, T. W. *J. Am. Chem. Soc.* **1964**, *86*, 3157.

[3] (a) Eaton, P. E.; Castaldi, G. *J. Am. Chem. Soc.* **1985**, *107*, 784. (b) Eaton, P. E.; Ravi Shankar, B. K.; Price, G. D.; Pluth, J. J.; Gilbert, E. E.; Alster, J.; Sandus, O. *J. Org. Chem.* **1984**, *49*, 185.

[4] Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Academic: New York, 1970.

[5] (a) Smith, L. R. *J. Chem. Educ.* **1978**, *55*, 569. (b) Balaban, A. T.; Banciu, M. *J. Chem. Educ.* **1984**, *61*, 766.

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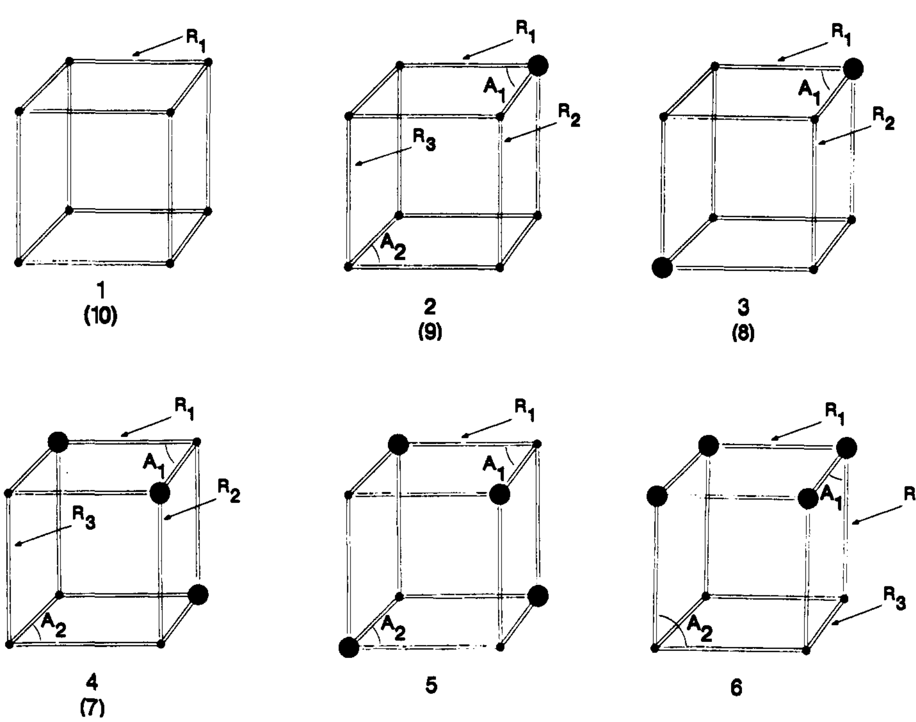

1 (10) 2 (9) 3 (8)

4 (7) 5 6

Figure 1. In this figure, the large and small black circles indicate nitrogen and CH groups, respectively. Structures **7** to **10** are obtained from structures **1** to **4** by replacement of nitrogen atoms by (CH) groups and vice versa. Note that none of the structures **1** to **5** have *any* nitrogen atoms bonded to nitrogen atoms. Numerical values for the bond lengths and angles shown in this figure are given in Table I.

II. Previous and Present Calculations

There have been numerous ab initio calculations of carbon cubane's geometry and vibrational spectrum (e.g., see refs 6 and 7 and references therein). Calculations of nitrogen cubane's properties are less common. The earliest reported such calculation is due to Trinquier et al.[8] This work is a valence-shell-only SCF calculation using a double-zeta basis set. O_h symmetry was assumed and the character of the stationary point found was not determined. Next, Engelke and Stine published energies and structures for N_8 cubane using levels of theory up to MP2/4-31G*//RHF/4-31G*.[9] The stationary points found were shown to be stable points by vibrational analyses and indicate that N_8 is a fairly rigid structure. The activation barrier to unimolecular decomposition was estimated to be ca. 40 kcal/mol via reaction-coordinate calculations. Recently, Lauderdale et al.[10] published an article that included optimizations of N_8's structure on the MP2 energy hypersurface with DZP and TZ2P basis sets; they showed that the stationary points so found are stable points. Coupled-cluster (CCSD) theory was also used at the MP2 geometries to find energies of N_8 relative to $4N_2$ molecules.

Some of the $N_8 \rightarrow 4N_2$ relative energies obtained by the various workers are shown in Figure 2. This figure shows that RHF relative energies, even with a basis set as good as 6-31G*, have significant errors; i.e., they are ca. 15% high (if one assumes the correct value is ca. 450 kcal/mol). Similarly, MP2/4-31G//RHF/4-31G theory overestimates the relative energy by ca. 25%. The MP2/*n*-31G*//RHF/*n*-31G* theories give quite good agreement with relative energies obtained from geometries optimized on a correlated (MP2) hypersurface, being in error by ca. 3% to 4%.

These facts indicate that in calculations on molecules of this type a basis set of, at least, DZ+P quality should be used. Furthermore, it appears that geometry *optimization* on a correlated hypersurface is not critical for determining reasonably accurate correlated relative energies—once the DZ+P level of basis set is reached. This same observation has been made before in connection with the energies (relative to $3N_2$) of the cyclic N_6 structures and for N_8 cubane.[10,11] Since geometry optimization on correlated hypersurfaces with DZ+P basis sets is computationally expensive, we will use this observation in the present work and include electron-correlation-energy effects via MP2/6-31G*//RHF/6-31G* theory.

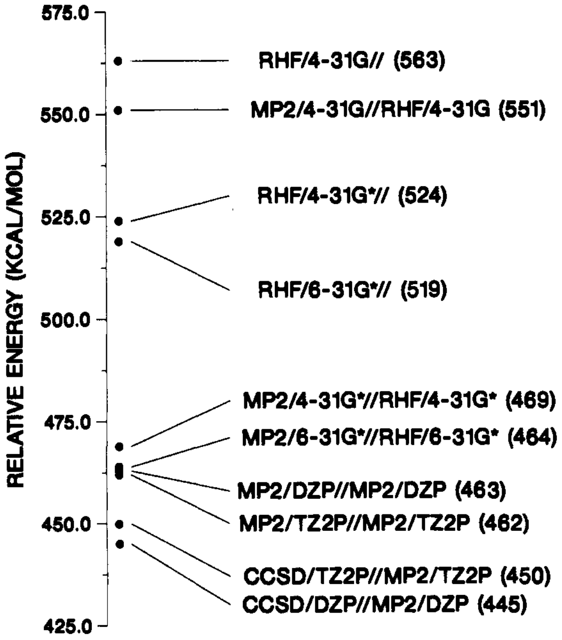

Figure 2. Calculated relative energy of N_8 cubane relative to $4N_2$ molecules obtained from various levels of theory. This figure shows that the basis set used should be, at least, of split valence + polarization function quality, and that geometry *optimization* on the correlated energy hypersurface is not of strong importance in estimating the correlated relative energy, once this level of basis set is reached. The relative energy for a model is given in parentheses after the model name.

The number of reported ab initio calculations on the mixed C/N structures is sparse. The results of semiempirical AM1, PM3, and MNDO calculations for the full series of C/N cubanoids are given in refs 12 and 13a. In ref 13a, RHF/6-31G*// energies are given for **5** and **6**.

All the calculations reported here were done with the CADPAC set of codes on a CRAY X-MP computer.[14] In these calculations, integrals with magnitude $\leq 10^{-10}$ were neglected. The SCF convergence criteria for an acceptable change in density matrix elements from cycle to cycle

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(6) Almlof, J.; Jonvik, T. *Chem. Phys. Lett.* **1982**, *92*, 267.

(7) Dunn, K. M.; Pulay, P.; Van Alsenoy, C.; Boggs, J. E. *J. Mol. Spectrosc.* **1984**, *103*, 268.

(8) Trinquier, G.; Malrieu, J.; Daudey, J. *Chem. Phys. Lett.* **1981**, *80*, 552.

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

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

(11) Engelke, R. *J. Phys. Chem.* **1992**, *96*, 1992.

(12) Alkorta, J. E.; Rozas, I.; Balaban, A. T. *THEOCHEM* **1990**, *206*, 67.

Table I. RHF/6-31G*//Geometries and Electrical Properties

struct no.	stoichiometry	point group	bond lengths[a] ($R_1/R_2/R_3$), Å	angles (A_1/A_2), deg	dipole D	charge[b] (C/N/H)
1	$(CH)_8$	O_h	1.559/–/–	–/–	0	6.13/–/0.87
2	$(CH)_7N$	C_{3v}	1.503/1.549/1.563	92.4/90.1	2.13	6.06 ± 0.10/7.54/0.86
3	$(CH)_6N_2$	D_{3d}	1.507/1.539/–	90.0/–	0	5.96/7.55/0.86
4	$(CH)_5N_3$	C_{3v}	1.482/1.496/1.543	94.6/85.3	2.30	5.84 ± 0.19/7.52/0.85
5	$(CH)_4N_4$	T_d	1.486/–/–	94.5/85.4	0	5.65/7.52/0.83
6	$(CH)_4N_4$	C_{4v}	1.478/1.495/1.542	91.2/88.8	5.94	5.98/7.19/0.83
7	$(CH)_3N_5$	C_{3v}	1.489/1.488/1.477	84.9/91.7	2.73	5.64/7.33 ± 0.16/0.82
8	$(CH)_2N_6$	D_{3d}	1.472/1.489/–	92.9/–	0	5.61/7.20/0.80
9	$(CH)N_7$	C_{3v}	1.473/1.461/1.477	92.4/90.6	2.95	5.62/7.07 ± 0.09/0.79
10	N_8	O_h	1.466/–/–	–/–	0	–/7.00/–

[a] CH bond lengths in all cases fall within ±0.002 Å of 1.079 Å. [b] Electronic charges from Mulliken population analyses in units of –e. Values followed by ± signs indicate that nuclei of the same type carry different electronic charges. A feeling for the magnitude of these differences is given by listing the mean value of electronic charge for a particular nuclear type followed by one standard deviation about the mean value. Charges on hydrogen centers are the listed values within ±<0.01, even when the charges on the associated carbons are significantly different.

were 10^{-6} and 10^{-7} for gradient and second-derivative work, respectively. SCF calculations were started by use of the one-electron Hamiltonian. The criterion for having located a stationary point on the energy hypersurface was that the largest component of the (Cartesian coordinate) energy gradient be less than 10^{-5} hartree/bohr. Analytic second derivatives of the energy were used to determine the vibrational frequencies.

The geometry optimizations were very demanding of CPU time; therefore, it was necessary to do them as efficiently as possible. To aid in this, the full molecular point-group symmetry was used in the geometry files for optimization. However, CADPAC4 cannot perform energy second derivative, IR and Raman intensities, and MP2 calculations when the assumed point group has degenerate representations. Thus, to obtain the frequencies, intensities, and MP2 energies, a second set of geometry files was built that employed nondegenerate point groups.

III. Results

A. Geometries and Electrical Properties. The RHF/6-31G*// optimizations were done using starting geometries obtained from semiempirical (AM1) calculations.[13a] The RHF/6-31G*// optimized bond lengths and (some) angles are given in Figure 1 and Table I. The listed geometry parameters do not, in every case, fully define the structures; full geometries can be obtained from the author.

As can be seen from the Table I listing of structural angles, the cubanoid angles do not deviate strongly from that of a cube, the maximum deviation from 90° being ca. ±5°. Strain in the carbon-rich cubanoid structures increases bond distances from their normal values. For example, the RHF/6-31G*// optimized C–C and C–N bond lengths for the comparison structures $HC(Me)_3$ and $N(Me)_3$ are 1.553 and 1.445 Å, respectively. The RHF/6-31G*// predicted C–C bond length in $(CH)_8$ is larger than that from the $HC(Me)_3$ value by 0.006 Å. The predicted C/N bond lengths when a nitrogen is bonded to three carbons in a cubanoid are singificantly larger than that predicted for $N(Me)_3$; in some cases the deviations are larger than 0.05 Å. The RHF/6-31G*// value for the N–N bond length in hydrazine is 1.413 Å;[9] this is significantly shorter than the value of 1.466 Å predicted here for N_8. The CH bond lengths are not strongly altered by the presence of nitrogens in a cubanoid; in all cases, the are within ±0.002 Å of 1.079 Å.

The results of Mulliken population analyses of the RHF/6-31G*// wave functions are given in column 7 of Table I. One sees that there is a significant donation of electronic charge from the carbon to the nitrogen centers and a smaller donation by the hydrogens to the nitrogens. This effect will make the carbon/nitrogen centers subject to nucleophilic/electrophilic attack, respectively. N_8 cubane shows no net charges; however, it will no doubt also be susceptible to electrophilic attack due to the eight electron lone pairs on it.

Dipole moments, when not zero due to symmetry, are predicted to be ca. 2.5 D, except for **6**, which has a predicted large value of nearly 6 D due to the orderly placement of its nitrogen atoms and CH groups (see Table I).

B. Stability of the Structures and the Vibrations. All the RHF/6-31G*// normal vibrational frequencies of **1** to **10** are real; therefore, the structures are predicted to be stable within this model. The harmonic approximation frequencies indicate that the geometries are fairly rigidly defined by the RHF/6-31G*// energy hypersurface. The lowest normal mode frequencies (ν_0) vary quite uniformly (with respect to nitrogen content); ν_0 increases from 688 cm^{-1} for $(CH)_8$ to 727 cm^{-1} for N_8. Unless the hypersurface energy derivatives with respect to the space coordinates change very rapidly, these high ν_0's suggest quite robust structures.

The RHF/6-31G*// zero-point energies for structures **1** to **10** are given in Table II. They vary smoothly from 90.7 for $(CH)_8$ to 27.3 (kcal/mol) for N_8, when the RHF/6-31G*// model is used. The zero-point corrections (ZPC) between the cubanoids and their equilibrium reaction products are positive and quite small compared to the cubanoid energy content. For example, for the reaction $N_8 \rightarrow 4N_2$, the RHF/6-31G*// ZPC is the difference between 27.3 and 4 (3.95) (kcal/mol), i.e., +11.5; the same correction for the reaction $(CH)_8 \rightarrow 4C_2H_2$ is +16.5 kcal/mol. ZPCs of this size are probably of the same magnitude as the errors present due to deficiencies in the models.

In Figure 3, a and b, are the RHF/6-31G*// predictions of the frequencies and the intensities of the IR active modes of **1** to **10**. Raman intensities are also given for structures **1** and **10**. These modes cluster into two sets, one set being in the region $700 < \nu < 1500$ cm^{-1} and which arises primarily from the motions of the heavy nuclei. A second set with $3200 < \nu < 3300$ cm^{-1} is due to CH stretches. The frequencies and intensities shown in Figure 3 are only semiquantitative owing to the nature of their display; numerical values are available from the author.

For normal organic molecules, these predicted frequencies would be expected to be ca. 10–15% high.[15] Such a correction is probably safe for the CH stretches and, perhaps, for the high carbon content C/N cubanoids (i.e., $n \leq 3$). For the lower frequency modes, particularly those of the nitrogen-rich structures, the magnitude of the frequency correction is not so clear. For example, for N_6 prismane and N_6 Dewar benzene, raising the level of theory from RHF/4-31G*// to MP2/6-31G*// reduces the normal mode frequencies by as much as ca. 30%.[11] Similarly, for N_8 going from an RHF/DZP// to a MP2/DZP// calculation reduces some frequencies by as much as 57%; e.g., N_8's ν_0 changes from 741 cm^{-1} to 472 cm^{-1}.[10] Thus, it appears that, for at least some of the vibrations, a much larger correction than 10% will be required to bring the frequencies of Figure 3 into congruence with actual values. Note that though the cited corrections for

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(13) (a) Engelke, R. *J. Org. Chem.* **1992**, *57*, 4841. (b) Stine, J. R. *Prediction of Crystal Densities of Organic Explosives by Group Additivity*; Los Alamos Report LA-8920, Aug 1981.

(14) Amos, R. D.; Rice, J. E. *CADPAC, The Cambridge Analytic Derivative Package*, Issue 4.0, Cambridge, 1987.

(15) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986; pp 236–246, 298–308.

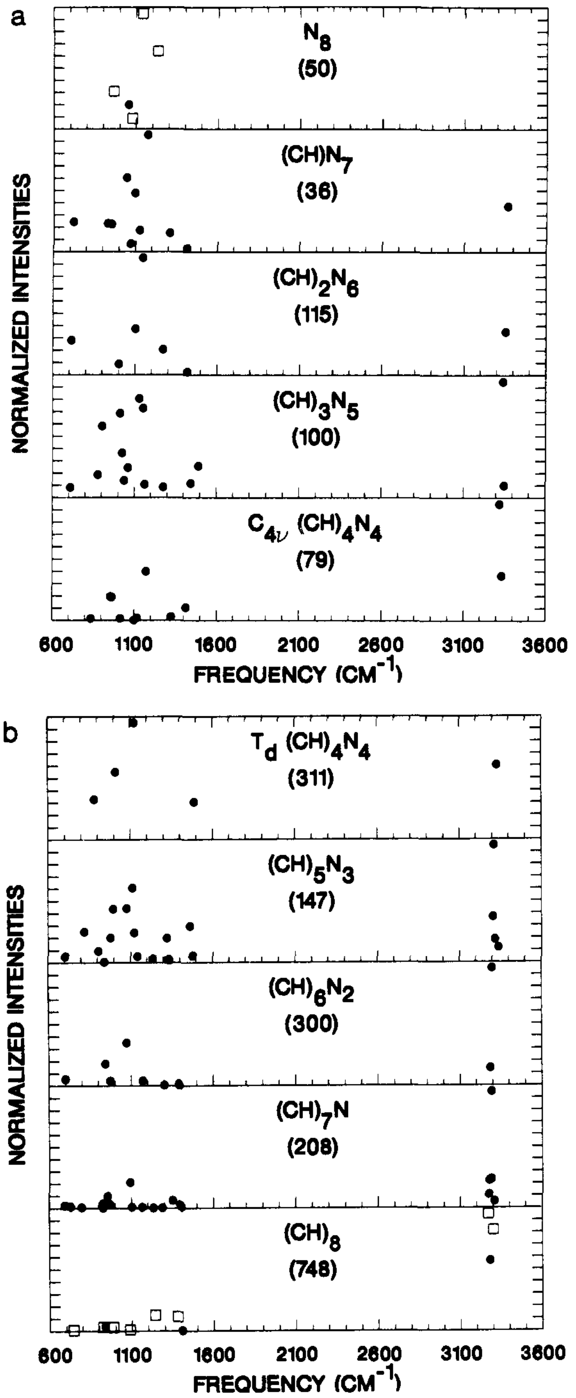

Figure 3. (a and b) Solid circles represent the infrared-active absorption frequencies and intensities of structures **1** to **10** as calculated with the RHF/6-31G*// model. The intensities for each molecule have been normalized so that the strongest line has an intensity of 0.95 on a scale of 0 to 1. To convert a normalized intensity to km/mol units, multiply the ordinate value by the number in parentheses given beneath the stoichiometric symbol for the molecule (e.g., 748 for $(CH)_8$). The intensities for degenerate lines are sums. The open squares on the N_8 and $(CH)_8$ figures are the intensities and frequencies of the Raman-active modes for these two cases, represented in the same way as the IR-active modes.

the N_6 and N_8 structures are large and reduce the predicted frequencies, they *do not* cause the predicted frequencies to become imaginary. That is, the stability prediction is robust against these improvements of model. Since N_8 cubane is the extreme case, it is essentially certain that this observation also applies to the intermediate C/N cubanoids.

C. The Energies. RHF/6-31G*// and MP2/6-31G*//RHF/6-31G* absolute energies for **1** to **10** are given in Table II. The energies of primary interest here are the heats of formation (ΔH_f). We can use the absolute energies in Table II to calculate these values. We shall use the isodesmic reactions

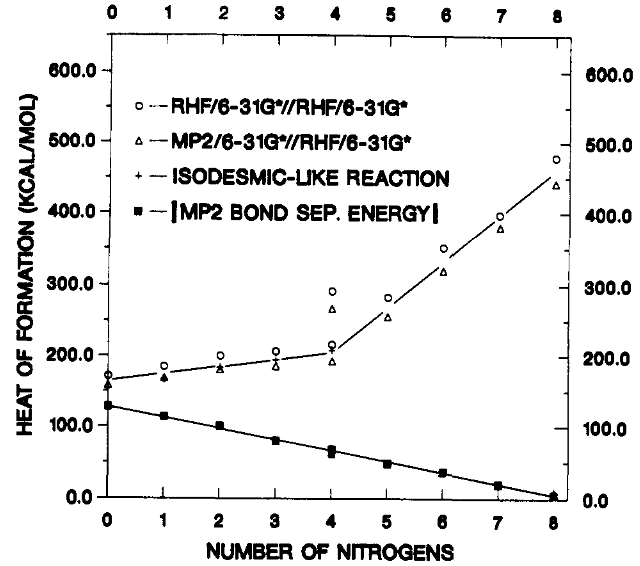

Figure 4. The calculated RHF/6-31G*// and MP2/6-31G*//RHF/6-31G* heats of formation for structures **1** to **10**. The absolute values of the MP2/6-31G*//RHF/6-31G* bond separation energies are also shown. The bond separation energy line indicates that strain becomes less important in the energetics of the C/N cubanoids as *n* increases.

$$(CH)_{8-n}N_n + \alpha NH_3 + (16-\alpha)CH_4 \rightarrow \beta N_2H_4 + (n+\alpha-2\beta)CNH_5 + (12-n-\alpha+\beta)C_2H_6 \quad (1)$$

to do this. In eq 1, the parameter *n* is the number of nitrogens in the cubanoid, and the vector $[\alpha,\beta]$ defines the stoichiometry of a particular reaction. For structures **1** to **10**, respectively, the $[\alpha,\beta]$ vectors are [0,0], [2,0], [4,0], [6,0], [8,0], [8,4], [10,3], [12,6], [14,9], and [16,12].

Isodesmic reactions, such as shown in eq 1, are constructed so that the number of bonds of each type (e.g., C–N or N–H) are balanced on the two sides of the reaction equation.[15] The purpose of this balancing is to decrease the error in a calculated ΔH_f when there is a bond-type change in going from the molecule being treated to the elements in their reference state; for example, $N_8 \rightarrow 4N{\equiv}N$. Such changes in bond type introduce significant energy errors because of a model's nonuniform treatment of electron correlation for molecules containing different bond types. An isodesmic reaction deals with this nonuniformity by using experimental ΔH_f's for the smaller structures in eq 1.

Before calculating the ΔH_f's for the C/N cubanoids using eq 1, it is necessary to introduce the concept of bond separation energy (≡BSE(1)). For eq 1 the bond separation energy is defined to be

$$\mathrm{BSE}(1) = \beta E[N_2H_4] + (n+\alpha-2\beta)E[CNH_5] + (12-n-\alpha+\beta)E[C_2H_6] - E[(CH)_{8-n}N_n] - \alpha E[NH_3] - (16-\alpha)E[CH_4] \quad (2)$$

where *E*[ ] indicates the calculated absolute energy of the molecule. BSE(1) is a measure of the greater or lesser stability of the cubanoid structure relative to the smaller molecular structures, arising from, e.g., ring strain. A negative BSE(1) indicates that the cubanoid is less stable than the smaller structures.

We now add two other corrections to BSE(1) that account for zero-point energy changes (ZPC) and for thermal corrections due to the mole change in the reactions described by eq 1.

The thermal correction is simple since in the case of eq 1 the mole change is always −5. If we assume that reaction products

Table II. Ab Initio Absolute Energies, Bond Separation Energies, and ΔH_f's

structure no.	stoichiometry	ZPE[a] (kcal/mol)	RHF/6-31G*//[b] RHF/6-31G* energy (hartrees)	MP2/6-31G*//[b,c] RHF/6-31G* energy (hartrees)	RHF bond[a] separation (kcal/mol)	MP2 bond[c] separation (kcal/mol)	RHF/6-31G*[d] ΔH_f (kcal/mol)	MP2/6-31G*[d] ΔH_f (kcal/mol)
1	$(CH)_8$	90.7	−307.407 754 6	−308.523 040 1	−140.4	−127.7	171.1	158.1
2	$(CH)_7N$	83.4	−323.389 253 6	−324.527 876 0	−128.9	−113.1	184.4	168.6
3	$(CH)_6N_2$	76.0	−339.367 330 0	−340.529 627 6	−119.6	−100.4	200.2	181.0
4	$(CH)_5N_3$	68.7	−355.360 504 3	−356.543 937 8	−100.8	−79.9	206.5	185.7
5	$(CH)_4N_4$	61.2	−371.348 948 9	−372.554 140 6	−85.0	−61.9	215.9	192.8
6	$(CH)_4N_4$	59.9	−371.230 243 4	−372.447 358 8	−92.0	−67.7	291.8	267.5
7	$(CH)_3N_5$	52.7	−387.246 684 9	−388.484 179 8	−75.5	−48.4	283.0	255.9
8	$(CH)_2N_6$	44.1	−403.142 222 0	−404.411 454 4	−67.4	−36.5	351.6	320.7
9	$(CH)N_7$	35.8	−419.047 235 5	−420.346 324 3	−53.4	−19.9	397.6	380.9
10	N_8	27.3	−434.949 162 9	−436.278 766 4	−41.3	−4.8	479.1	442.6

[a] ZPE ≡ zero-point energy; values obtained from the RHF/6-31G*// model. [b] Absolute energies for N_2 are −108.943 949 5 and −109.254 668 2 hartrees for the RHF/6-31G*// and MP2/6-31G*//RHF/6-31G* models, respectively. [c] Values obtained from the MP2/6-31G*//RHF/6-31G* model. [d] Values obtained from bond separation energies and isodesmic reactions corrected to 298 K; see text.

Table III. Absolute Energies and ΔH_f for Small Molecules

molecule	RHF/6-31G*// energy (hartrees)	MP2/6-31G*[a] energy (hartrees)	ΔH_f(exptl)[b] (kcal/mol)	ZPE[c] (kcal/mol)
CH_4	−40.201 704 8	−40.369 854 8	−17.8	29.8
NH_3	−56.195 544 6	−56.386 600 9	−9.3	22.6
N_2H_4	−111.178 635 9	−111.539 340 2	+26.2	35.9
H_2NCH_3	−95.221 860 3	−95.558 707 7	−5.5	43.0
H_3CCH_3	−79.238 235 0	−79.553 683 2	−20.0	49.7
NMe_3	−173.282 985 8	−173.920 297 9	−5.7	80.6
$HCMe_3$	−157.314 556 3	−157.930 681 0	−32.1	87.7

[a] Values for the MP2/6-31G*//RHF/6-31G* model. [b] Values are for $T = 298$ K. [c] Zero-point energy ≡ (ZPE) from the RHF/6-31G*// model.

are a mixture of perfect gases and that vibrational and electronic excitations due to temperature are negligible, the heat content change due to the change in the number of rotational and translation degrees of freedom is

$$\Delta H(T) = -5[3/2 + 3/2 + 1]RT = -20RT \qquad (3)$$

which is −11.9 kcal/mol at 298 K.

The ZPC can be found by evaluating an equation analogous to eq 2 with BSE(1) replaced by (−)ZPC on the left side and E replaced everywhere by the zero-point energy (ZPE) on the right side. The ZPCs obtained in this way are then scaled down by the standard 0.9 factor normally used with RHF frequencies.[15]

A graph of the ZPEs given in Table II shows them to be closely proportional to the number of CH groups, N atoms, or vibrational degrees of freedom. This observation allows one to make ZPE predictions for the isomers not calculated here.

Thus, we define our complete bond separation energy (BSE) as

$$\mathrm{BSE} = \mathrm{BSE}(1) + \Delta H(T) + 0.9\mathrm{ZPC} \qquad (4)$$

In the cubanoid case, BSE(1) and $\Delta H(T)$ are negative, while the ZPC is positive. Use of the absolute energies and ZPEs for the cubanoids and the smaller molecules given in Tables II and III yields the BSEs for the cubanoids given in Table II. Note that the absolute energies for the small molecules in Table II all correspond to stable points on their RHF/6-31G*// hypersurfaces; this was checked via RHF/6-31G*// vibrational frequency calculations.

The cubanoid BSEs are all negative. This indicates an energy expenditure is required to form them from the smaller molecules in eq 1. Furthermore, the absolute values of the BSEs decrease in a uniform manner as nitrogens replace CH groups in the cubanoid. The MP2/6-31G*//RHF/6-31G* BSEs change from −127.7 to −4.8 kcal/mol as n increases from 0 to 8 (see Figure 4). The large negative values of the BSE for $(CH)_8$ is a measure of the large strain energy associated with that structure. In striking contrast, the BSE value is −4.8 kcal/mol for N_8 cubane. Thus, the altered electronic structures resulting from substitution of N's for CH groups in the cubanoids reduces the strain energy significantly. We conclude that the high-energy content of the nitrogen-rich cubanoids is *not* due to strain energy, but has its origin elsewhere. This will be discussed further below.

To estimate the ΔH_f values for the C/N cubanoids, we use

$$\Delta H_f[(CH)_{8-n}N_n] = \beta\Delta H_f[N_2H_4] + (n + \alpha - 2\beta)\Delta H_f[CNH_5] + (12 - n - \alpha + \beta)\Delta H_f[C_2H_6] - \alpha\Delta H_f[NH_3] - (16 - \alpha)\Delta H_f[CH_4] - \mathrm{BSE} \qquad (5)$$

where the BSEs and the experimental ΔH_f's for the molecule on the right side of eq 5 are given in Tables II and III.

The estimates of ΔH_f's obtained from eq 5 are given in Table II and Figure 4 for both the RHF/6-31G*// and MP2/6-31G*//RHF/6-31G* models. The values from the MP2 approach are undoubtedly the better estimates. It is pleasing that the MP2/6-31G*//RHF/6-31G* estimate for the ΔH_f of $(CH)_8$ is within 10 kcal/mol of the experimental value.[16] Also, the ΔH_f for N_8 cubane, obtained from the isodesmic reaction, is consistent with the best values of earlier works (see Figure 2 and refs 9 and 10). Even with the isodesmic approach there are still significant differences between the RHF and MP2 ΔH_f's. These differences are on the order of 10%, with the RHF model being consistently high.

The question of the source of the high-energy content of the nitrogen-rich cubanoids can now be addressed. This quality can be traced to the high-energy content of the N–N single bond. For example, if thermal, ZPC, and BSE(1) energies are neglected, eq 5 gives for the ΔH_f of N_8 cubane

$$\Delta H_f[N_8] = 12\Delta H_f[N_2H_4] - 16\Delta H_f[NH_3] \qquad (6)$$

Since Table III gives $\Delta H_f[N_2H_4] = +26.2$ and $\Delta H_f[NH_3] = -9.3$ kcal/mol, we find $\Delta H_f[N_8] = +463$ kcal/mol. This compares favorably with the results from the more detailed calculations using eq 5 (see Table II). Therefore, the essential contribution to the high ΔH_f of the nitrogen-rich cubanoids is due to the energetics of the N–N single bond. This is in strong contrast to the case of $(CH)_8$ where the MP2/6-31G*//RHF/6-31G* BSE and ΔH_f are −127.7 and +158.1 kcal/mol, respectively. That is, the energy release in the reaction of carbon cubane to acetylene is in most part due to strain energy.

The large coefficients in eq 2 (e.g., α and β) and in the analogous ZPC equation make it possible that significant errors have been introduced into the ΔH_f estimates in Table II via errors in, e.g., the ZPC estimates. In order to examine this question we have used a second "pseudo" isodesmic reaction that minimizes this worry. This reaction is

$$(CH)_{8-n}N_n + n\mathrm{HC(Me)_3} \rightarrow (CH)_8 + n\mathrm{N(Me)_3} \qquad (7)$$

where Me indicates the methyl group. This is *not* an isodesmic

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(16) Pedley, J. B.; Naylor, R. D.; Kirby, S. P. *Thermochemical Data of Organic Compounds*; Chapman and Hall: New York, 1986.

reaction because in eq 7 the cubanoid structure is not reduced to the simplest possible smaller structures. It is useful here, however, because there are available experimental ΔH_f's for $(CH)_8$, $HC(Me)_3$, and $N(Me)_3$.[16,17] For the C/N cubanoids where no N–N bonds are formed upon replacement of a CH group by N, eq 7 is a useful reaction. This is so for cubanoids **2** to **5**. There is *no* mole change for the eq 7 reactions, and the ZPC corrections are small (ca. −1 kcal/mol) because of the similarity of the structures on the two sides of the equation. We have evaluated the MP2/6-31G*//RHF/6-31G* BSEs and ΔH_f's for **2** to **5** using eq 7, the ΔH_f and ZPC values in Table III, and the experimental value of ΔH_f for $(CH)_8$ which is 148.7 kcal/mol.[16] One finds for structures **2**, **3**, **4**, and **5** values of ΔH_f of 165.3, 183.9, 194.6, and 207.8 kcal/mol, respectively. These values are in satisfactory agreement with the MP2/6-31G*//RHF/6-31G* results obtained from eq 5 and listed in Table II. One concludes that the errors produced by use of eq 5 are moderate.

Given the ΔH_f's listed in Table II, one can predict ΔH_f's for the remaining 12 C/N cubanoids via bond-additivity arguments. In fact, use of only the MP2/6-31G* ΔH_f's for **1**, **5**, and **10** gives C–C, C–N, and N–N bond energies of 13.2, 16.1, and 36.9 kcal/mol, respectively. These bond-energy values allow one to predict, for example, the ΔH_f of **6** as 264.8 kcal/mol. This value is in good agreement with the MP2/6-31G* value of 267.5 kcal/mol given in Table II. Note that the large value for the energy of the N–N bond "explains" the break in the ΔH_f curve of Figure 4, since structure **6** is where N–N bonds begin to appear in the calculated structures. We plan to discuss this point more thoroughly elsewhere.

One interesting aspect of the BSEs corresponding to eq 7 is that the thermodynamics favors the nitrogen-loaded cubanoids. That is, the reverse of the eq 7 reaction is thermodynamically favored as is shown by the positive BSEs of +9.6, +17.2, +32.7, and +45.6 kcal/mol for **2** to **5**, respectively. This may suggest possible synthesis routes to the mixed cubanoids starting from carbon cubane.

It is worth examining the probable errors in the MP2/6-31G*//RHF/6-31G* ΔH_f's. We have a few pieces of information to guide us. These are (1) the calculated $(CH)_8$ ΔH_f is 10 kcal/mol higher than experiment; (2) the MP2 ΔH_f's for **2**, **3**, **4**, and **5** obtained from eq 7 (and which are probably quite accurate) differ from those obtained from eq 5 by −3.3, +2.9, +8.9, and +15.0 kcal/mol, respectively; and (3) the high level CCSD/TZ2P//MP2/TZ2P calculation of Lauderdale et al.[10] for the reaction $N_8 \rightarrow 4N_2$ gives a relative energy of 450 kcal/mol, which is 7.4 kcal/mol higher than our MP2/6-31G*//RHF/6-31G* ΔH_f estimate for N_8. From these considerations, we suggest that an educated guess for the error in the MP2/6-31G*//RHF/6-31G* ΔH_f's of Table II is ca. ±10 kcal/mol.

Since the ab initio calculations discussed here are computationally expensive, it is of interest to examine how they compare with results from semiempirical methods. There are MNDO, AM1, and PM3 ΔH_f's available in the literature for all 22 C/N cubanoids.[12,13a] These values have been plotted in Figure 5, along with the 10 ΔH_f's obtained from eq 5 with the MP2/6-31G*//RHF/6-31G* model. One sees that there is very good agreement between the MP2 model and AM1 for $(CH)_8$ cubane and poor agreement with the MNDO and PM3 models. However, as the nitrogen content in the cubanoid increases, the MP2 model values deviate strongly from the AM1 results until, for the $(CH)_4N_4$ structures, the MP2 and PM3 values are in good agreement and disagree with AM1 values. As the amount of nitrogen increases further, the MP2 and PM3 ΔH_f's are in reasonable agreement and differ from the AM1 value by more than 100 kcal/mol. These observations suggest that for small ring structures, rich in nitrogen, the preferred semiempirical method of the MNDO class is PM3 and that the AM1 model is deficient when applied to such structures.

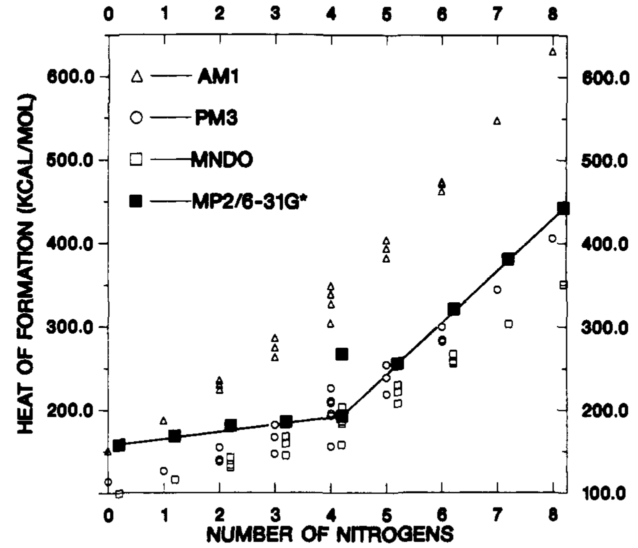

Figure 5. Comparison of the ΔH_f's obtained from the MP2/6-31G*//RHF/6-31G* model and isodesmic reactions with values obtained with the AM1, PM3, and MNDO semiempirical models. The origins of the MNDO, AM1, and PM3 models are discussed by M. J. S. Dewar and W. Thiel (*J. Am. Chem. Soc.* **1977**, *99*, 4899), M. J. S. Dewar et al. (*J. Am. Chem. Soc.* **1985**, *107*, 3902), and J. J. P. Stewart (*J. Comput. Chem.* **1989**, *10*, 209), respectively.

D. Predicted Mass Densities and Energetic Material Properties. Because of the high ΔH_f's of some of the CN cubanoids, it is of interest to examine their potential as energetic materials.

An important characteristic of an energetic material is its mass density. Stine[13b] has generated a semiempirical procedure for estimating the mass density of organic materials. This method is based on the premise that the molar volume of an organic crystal is a linear combination of the volumes of the molecule's constituent parts. These volumes are a function of the types of atom present and their bonding configuration. For the C/N cubanoids, Stine's method gives the mass density (in g/cm³) as

$$\rho_0(n) = 1.660\left[n\frac{M_N}{V_N} + (8-n)\frac{(M_C + M_H)}{(V_C + V_H)}\right] \qquad (8)$$

where n is the number of nitrogens present, the M_i's are the atomic masses, and V_N, V_C, and V_H have the values 8.76 ± 0.71, 9.76 ± 0.35, and 5.98 ± 0.30 Å³ for the N, C, and H atoms, respectively, in the cubanoid bonding configuration. Use of eq 8 give the mass densities listed in Table IV. One notes from these values that the C/N cubanoids with $n \geq 4$ are quite dense materials (for organic structures) and that **8**, **9**, and **10** are very dense. If one places N_8 cubane in the class of organic molecules, it appears to be near the high density limit for such structures. Arguments given elsewhere indicate that the density estimates in Table IV are ca. 10% high.[13a] These predicted high densities play an important role in suggesting the possible usefulness of the C/N cubanoids as energetic materials.

Next we turn to the question of predicting the performance of the C/N cubanoids as energetic materials. Three properties will be estimated. Using the ΔH_f's and ρ_0's found above, we will predict the explosive properties detonation pressure (P_{CJ}) and detonation velocity (D_{CJ}) and the propellant property specific impulse (I_{sp}).

The quantity D_{CJ} is the velocity at which the chemical reaction zone traverses an explosive when the phenomena are one-dimensional and steady. P_{CJ} is the pressure produced by the detonation chemistry at the point where the exothermic chemistry is complete, again for the case where the phenomena are one-

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[17] Wagman, D. D., et al. The NBS Tables of Chemical Thermodynamic Properties. *J. Phys. Chem. Ref. Data* **1982**, *11*, 2-64, 65.

Table IV. Predicted Energetic Material Properties[a]

structure no.	stoichiometry	mass[b] density	CJ[c] pressure	CJ[c] det. vel.	Q[c] (kcal/mol)	I_{sp}[c] (s)
1	$(CH)_8$	1.374	17.9	7.78	1.52	327
2	$(CH)_7N$	1.468	20.1	7.63	1.60	335
3	$(CH)_6N_2$	1.574	24.8	7.73	1.71	347
4	$(CH)_5N_3$	1.694	29.4	8.22	1.73	349
5	$(CH)_4N_4$	1.832	37.6	8.94	1.78	354
6	$(CH)_4N_4$	1.832	44.1	9.44	2.47	416
7	$(CH)_3N_5$	1.990	53.8	10.18	2.35	406
8	$(CH)_2N_6$	2.175	73.5	11.62	2.91	452
9	CHN_7	2.392	99.8	13.39	3.43	491
10	N_8	2.655	150.1	15.26	3.95	527

[a] Units are: density (g/cm^3), detonation velocity (mm/μs), and pressure (GPa). [b] See ref 13 for details concerning the density calculations. [c] CJ det. vel and CJ pressure are the Chapman–Jouguet detonation velocity and pressure, respectively. $Q \equiv$ specific energy = $(\Delta H_f/M)$, where M is the molecular weight and the specific inpulse is $I_{sp} = 265\sqrt{Q}$. The MP2/6-31G*//RHF/6-31G* ΔH_f's were used to compute these quantities.

dimensional and steady. Knowledge of D_{CJ} and P_{CJ} allow one to compare the performance of explosives. See ref 18 for a more complete discussion of D_{CJ} and P_{CJ}.

D_{CJ} and P_{CJ} were calculated with the chemical equilibrium computer code TIGER.[19] This code calculates the equilibrium chemical composition at the detonation state by use of the Euler equations of compressible fluid mechanics and the Becker–Kistiakowsky–Wilson equation of state for the explosive material. Given the initial mass density, ΔH_f, and the molecular formula of the explosive, one obtains the detonation state and the chemical composition of the reaction products; see ref 20 for more detail.

The results of such calculations are given in Table IV. In order to place these values in perspective, it is useful to give analogous values for the most powerful chemical explosive in common use. This material (a cyclic nitramine) is octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (commonly known as HMX), having the following properties: $\Delta H_f = +18$ kcal/mol, crystal density = 1.90 g/cm^3, and molecular formula $C_4H_8N_8O_8$.[21] The TIGER code results for HMX are $D_{CJ} = 9.14$ mm/μs and $P_{CJ} = 40.5$ GPa at $\rho_0 = 1.90$ g/cm^3. Experimental values are 9.11 mm/μs and 39.3 GPa at density 1.89 g/cm^3.

Comparing the HMX values with those calculated for the C/N cubanoids (see Table IV) shows the C/N cubanoids that contain four or more nitrogens are competitive with HMX. The cubanoids containing more than four nitrogens are predicted to be superior to HMX. N_8 is predicted to be an extremely powerful explosive, in a class by itself.

Another important property of an energetic material is its characteristics as a propellant. The theoretical performance of a propellant is measured in terms of its "specific impulse" (I_{sp}). Rosen[22] has generated an expression for I_{sp} using specified nozzle conditions and assumptions about the fluid flow (e.g., one-dimensional); his relationship is

$$I_{sp} = 265\sqrt{\Delta H_f/M} \tag{9}$$

where the numerator in the square-root of eq 9 is the total energy release of the propellant (which we have taken as ΔH_f) and M is its molecular weight. As a comparison propellant we take an O_2 to H_2 mixture ratio of 4.7 by weight. This propellant gives a specific impulse of 456 s, when used in eq 9.[22] Comparison of this value with those listed in Table IV indicates that the C/N cubanoids only become competitive with the O_2–H_2 mixture when there are six or more nitrogens in the cubanoid. However, N_8 cubanes appears to be an interesting propellant candidate with $I_{sp} = 529$ s, when the MP2/6-31G*//RHF/6-31G* model is used to predict ΔH_f. A point of interest concerning the more carbon/hydrogen heavy cubanoids (i.e., $0 \leq n \leq 4$) is that if they were burned with O_2 as an oxidizer very low energy products would be obtained (e.g., H_2O, CO, and CO_2); used in this way they might also be valuable propellants.

IV. Conclusions

A uniform set of ab initio calculations is reported for 10 of the 22 possible C/N cubanoids (see structures **1** to **10**). The geometries were optimized using the RHF/6-31G*// model and shown to be stable points by vibrational frequency analyses in the harmonic approximation. Judging by the lowest vibrational frequencies obtained, one infers that these structures are fairly rigorously defined by their energy hypersurfaces.

Correlation effects on the energy are taken into account via the MP2/6-31G*//RHF/6-31G* model. Estimates of the ΔH_f of the structures are made by use of appropriate isodesmic reactions. All the structures are found to have high heats of formation. The structures that contain many N–N bonds are particularly energy rich. For example, for N_8 cubane, the MP2 model gives a predicted ΔH_f of 443 kcal/mol.

Perhaps the most interesting result obtained is that the high-energy content of the nitrogen-rich cubanoids is not primarily due to strain, but rather is associated with the high-energy content of the NN single bond. This judgment is made by use of bond separation energies. Arguments are given that the error in the calculated ΔH_f's are ca. ±10 kcal/mol.

Because the energy content of the nitrogen-rich C/N cubanoids is very high, we also predict values for their mass densities and some of their properties as condensed-phase explosives and propellants. It appears these materials are very interesting in this sense. In particular, N_8 cubane would probably be the most powerful condensed-phase chemical explosive in existence, if it could be synthesized and has reasonable kinetic stability. It is also predicted to be a valuable propellant.

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(18) Fickett, W.; Davis, W. C. *Detonation*; University of California Press: Berkeley, CA, 1979.

(19) Cowperthwaite, M.; Zwisler, W. H. Stanford Research Institute Publication No. Z106, 1973.

(20) Mader, C. L. *Numerical Modeling of Detonation*; University of California Press: Berkeley, CA, 1979; pp 412–448.

(21) Dobratz, B. M.; Crawford, P. C. *LLNL Explosive Handbook*; Lawrence Livermore National Laboratory: Livermore, CA, 1985; pp 19–56.

(22) Rosen, G. *Current Status of Free Radicals and Electronically Excited Metastable Species as High Energy Propellants*, NASA-JPL Contract 953623, Aug 1973.