Table II. Yields (%) of 2:1 Inclusion Complexes of the Racemic Cis Acid 1 (X = Cl or Br) with Aromatic Solvents

	X			X	
aromate	Cl	Br	aromate	Cl	Br
benzene	92	94	furan[a]	83	89
fluorobenzene	92	91	2-methylfuran	49	69
thiophene	93	91	pyrrole	82	85

[a] Dissolved at 80 °C under pressure.

cooled to 0 °C in an ice bath (solutions in benzene were cooled to 8–10 °C). The crystals that deposited were filtered and washed with a small amount of the cool solvent. Yields and amounts of solvents used are given in Table II.

Separation of the Racemic Cis Acid 1 (X = Cl) from the Corresponding Cis–Trans Isomeric Mixture Using an Inclusion Complex with Thiophene. A 9.93-g portion of the racemic cis–trans mixture of the acid 1 (X = Cl) containing ca. 20% of the trans isomer was dissolved under reflux in thiophene (50 mL). Cooling in an ice bath afforded a crystalline inclusion complex, which upon desolvation (100 °C, 4 h, 1 Torr) yielded 7.89 g of the racemic cis acid (98% of theoretical based on the content of the cis isomer in the original isomeric mixture). The isolated cis acid contained less than 1% of the trans isomer. Replacement of thiophene by other appropriate aromatic compounds leads to similar results.

Separation of the Racemic Cis Acid 1 (X = Cl) from the Corresponding Optically Active (1*S*)-Cis Isomer Using an Inclusion Complex with Benzene. A 36.3-g portion of the laevorotatory cis acid 1 (X = Cl), $\alpha_D = -9.8°$ ($c = 1.21$, $CHCl_3$), i.e. 29% ee, was dissolved under reflux in benzene (44 mL). The crystalline complex which deposited upon cooling (ca. 10 °C) was filtered, washed with a small amount of the cool solvent, and thermally desolvated (80 °C, 24 h, 10 Torr). This yielded 21.6 g of the racemic cis acid $\alpha_D = 0.0°$ ($c = 1.20$, $CHCl_3$). Evaporation of the mother liquor yielded 13.1 g of the optically enriched (1*S*)-cis acid, $\alpha_D = -27.22°$ ($c = 1.20$, $CHCl_3$), which corresponds to ca. 81% ee.

Separation of the Racemic Cis Acid 1 (X = Cl) from the Corresponding Optically Active (1*S*)-Cis Isomer Using an Inclusion Complex with Thiophene. A procedure analogous to that described above using 18.0 g of the cis acid 1 (X = Cl), $\alpha_D = -12.4°$ ($c = 1.20$, $CHCl_3$), i.e. 37% ee, and thiophene (18 mL) afforded 10.18 g of the racemic cis acid and 7.30 g of the enriched (1*S*)-cis isomer, $\alpha_D = -29.17°$ ($c = 1.20$, $CHCl_3$), i.e. 87% ee.

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Calculated Properties of the 22 Carbon/Nitrogen Cubanoids

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Some properties of the 22 possible carbon/nitrogen cubanoids (i.e., $(CH)_{8-n}N_n$ $0 \le n \le 8$) have been calculated and are presented here. By use of the AM1 and PM3 semiempirical models, all the C/N cubanoids are shown to correspond to stationary points on the appropriate energy hypersurfaces. These stationary points are demonstrated to be local stable points via vibrational frequency calculations. The AM1 and PM3 models yield significantly different ΔH_fs, and this disparity increases as the amount of nitrogen in the cubanoid increases. The AM1 and PM3 ΔH_fs are compared with MNDO values and, in a few high-symmetry cases, with RHF/6-31G*// results. The potential of the C/N cubanoids as energetic materials is examined by prediction of two detonation properties of the condensed-phase materials. In order to make these predictions, condensed phase mass densities (ρ_o) are calculated with Stine's method. Then, by use of the ρ_o values and the calculated ΔH_fs, Chapman–Jouguet detonation pressures and velocities are determined. The calculations indicate that any of the C/N cubanoids that contain four nitrogens or more would be high-performance energetic materials. One highly symmetric nitrated cubanoid structure (T_d symmetry $C_4(NO_2)_4N_4$) is also examined using the same approach.

I. Introduction and Background

In this paper, a theoretical study is reported of the 22 cubanoid structures with chemical formulas $(CH)_{8-n}N_n$ with $0 \le n \le 8$. The limiting structures (i.e., $(CH)_8$ and N_8) are true cubes (i.e., O_h point group). Replacement of CH groups by nitrogen in the $(CH)_8$ structure breaks the O_h symmetry and results in structures with reduced symmetry (see Tables I and II) and similarly for N_8 cubane. Note that the CH group and nitrogen atom are isoelectronic and therefore the C/N cubanoids form an isoelectronic set of structures.

The C/N cubanoids are interesting for a number of reasons. For example, the pure carbon form $(CH)_8$ has been synthesized and studied extensively by Eaton and his co-workers.[2] In spite of the high strain energy (ca. 166 kcal/mol) present in carbon cubane, it is quite stable.[3] Carbon cubane slowly decomposes when heated to 200 °C.[4] The high thermal stability of this very strained structure is thought to result from the symmetry forbiddeness of the reactions that can take it to smaller/less strained structures.[5] Because the C/N cubanoids are isoelectronic with $(CH)_8$, it is possible these structures will show analogous stability. Secondly, ab-initio theoretical results for N_8 indicate it is a stable entity in which large amounts of energy can be stored.[6] If it could be synthesized, it is likely that N_8 would be the most powerful chemical explosive in existence.

In the light of these comments, the molecular stability and potential of the C/N cubanoids as energetic materials are examined here. In particular, we examine the question of how the energetic properties of the cubanoid are en-

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Table I. Definition of the C/N Cubanoid Structures (See Figure 1)[a]

site[b] no.	group for structure no.													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	CH	N	N	N	N	N	N	N	N	N	N	N	N	N
2	CH	CH	N	CH	CH	N	N	CH	N	N	N	N	N	CH
3	CH	CH	CH	N	CH	N	CH	N	N	N	N	N	CH	N
4	CH	CH	CH	CH	CH	CH	CH	CH	N	CH	CH	CH	CH	CH
5	CH	CH	CH	CH	CH	CH	CH	CH	CH	CH	CH	CH	CH	CH
6	CH	CH	CH	CH	CH	CH	CH	N	CH	CH	CH	N	CH	N
7	CH	CH	CH	CH	N	CH	N	CH	CH	CH	N	CH	N	CH
8	CH	CH	CH	CH	CH	CH	CH	CH	CH	N	CH	CH	N	N

[a] Note that structures 9–14 transform into themselves under the substitution CH ↔ N. We *define* structures 15–22 as those resulting from structures 1–8 when CH groups are replaced by N atoms and vice versa, i.e., 1 ↔ 22, 2 ↔ 21, 3 ↔ 20, 4 ↔ 19, 5 ↔ 18, 6 ↔ 17, 7 ↔ 16, and 8 ↔ 15, under these replacements. [b] Sites numbers are as shown in Figure 1.

Table II. C/N Cubanoid Predicted Properties[a]

struct. no.	stoichiometry	point group	AM1 ΔH_f	PM3 ΔH_f	MNDO ΔH_f	mass density	AM1 CJ pressure	AM1 CJ det. vel.	AM1 $-\Delta H_{det}$
1	$(CH)_8$	O_h	151.1	113.8	99.1	1.374	17.4	7.72	1.10
2	$(CH)_7N$	C_{3v}	187.6	126.0	115.7	1.468	20.3	7.74	1.37
3	$(CH)_6N_2$	C_{2v}	235.4	154.5	142.7	1.574	28.5	8.13	1.78
4		C_{2v}	224.1	138.1	131.0	1.574	27.8	8.05	1.67
5		D_{3d}	229.9	139.6	133.7	1.574	28.2	8.09	1.73
6	$(CH)_5N_3$	C_s	286.0	182.0	168.3	1.694	37.4	8.90	2.29
7		C_s	274.5	167.1	159.3	1.694	36.6	8.83	2.18
8		C_{3v}	263.3	147.3	145.2	1.694	35.7	8.76	2.08
9	$(CH)_4N_4$	C_{4v}	349.1	226.3	204.0	1.832	50.4	9.91	2.92
10		C_s	327.2	193.5	183.9	1.832	48.7	9.79	2.72
11		C_2	338.6	211.1	195.3	1.832	49.5	9.85	2.82
12		C_{3v}	339.0	208.5	192.8	1.832	49.7	9.85	2.83
13		D_{2h}	327.1	196.0	186.7	1.832	48.7	9.79	2.72
14		T_d	304.5	156.1	158.4	1.832	47.0	9.66	2.51
15	$(CH)_3N_5$	C_{3v}	382.2	218.9	207.8	1.990	64.1	10.91	3.27
16		C_s	393.7	239.2	221.6	1.990	65.0	10.97	3.38
17		C_s	404.3	254.4	230.2	1.990	65.8	11.02	3.48
18	$(CH)_2N_6$	D_{3d}	471.2	284.1	258.5	2.175	86.5	12.44	4.13
19		C_{2v}	462.2	281.7	255.9	2.175	85.8	12.40	4.05
20		C_{2v}	473.0	299.6	266.9	2.175	86.6	12.45	4.15
21	$(CH)N_7$	C_{3v}	547.0	344.0	303.4	2.393	116.5	14.23	4.15
22	N_8	O_h	630.7	406.2	350.7	2.655	175.0	16.06	5.62

[a] Units are as follows: (1) ΔH_f are in kcal/mol, (2) mass density in g/cm^3, (3) CJ pressure and detonation velocity in GPa and mm/μs, respectively, and (4) heat of detonation in kcal/g.

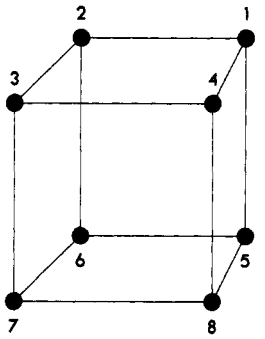

Figure 1. Numbering scheme used to define the carbon/nitrogen cubanoid structures. See the information in Table I to identify a particular structure.

hanced as nitrogens are substituted for CH groups.

The effect of nitration on a carbon-containing cubanoid's explosive performance is studied by calculating properties of the fully nitrated form of T_d symmetry $(CH)_4N_4$. Nitration is predicted to increase the Chapman–Jouguet (CJ) pressure by ca. 30% relative to the unnitrated species.

Because it was desired to investigate all 22 C/N cubanoid structures and because of the number of heavy atoms present in these structures, the AM1 (Austin Model 1)[7] and PM3 (Parameter Method 3)[8] semiempirical methods were the primary methods used for the calculations. To gauge the quality of the semiempirical energies, ab-initio RHF/6-31G*//RHF/6-31G* ΔH_fs were computed for four of the highest symmetry cubanoids. ΔH_f comparisons are also made with previously published MNDO values. All the AM1 and PM3 structures were shown to be stable points by calculation of their vibrational frequencies. Stine's method[9] was used to estimate the crystalline mass densities of the C/N cubanoids. These densities and the calculated heats of formation were then used to calculate Chapman–Jouguet detonation pressures and velocities.[10]

II. The Calculational Methods

A. The Quantum-Mechanical Calculations. The AM1 and PM3 methods are current variants of MNDO; these methods are used for most of the calculations reported here.[7,8] The primary differences between AM1 and MNDO are as follows: (1) in AM1 the core-repulsion functions have been modified to reduce the interatomic repulsions at ca. the van der Waal separations, and (2) an improved minimum has been found on the parameter-space error hypersurface. Dewar and his co-workers note

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that one reason for introducing the first type of modification is to improve the method's performance on structures that contain four-membered rings. This is an important consideration for calculations of cubanoids. The AM1 calculations were done using the GAUSSIAN-88 set of codes on a VAX-8600 computer.[11]

The PM3 method is another improvement of MNDO in which improved numerical algorithms were used to further refine the quality of the parameter determination. Stewart states that the PM3 parameters probably correspond to either a global minimum on the error hypersurface or are very near to it. The PM3 calculations were done with the MOPAC set of codes on a CRAY X-MP computer.[8]

To test the quality of the semiempirical results, ab-initio calculations were done on four high-symmetry cubanoids. These were done with the CADPAC set of codes on a CRAY X-MP computer.[12] The RHF/6-31G*//RHF/6-31G* model was used in these calculations. In locating the stationary points, the largest component of the energy space gradient was reduced to less than 10^{-5} hartree/bohr. Analytic second derivatives of the energy were used to determine the vibrational frequencies.

Due to space limitations, only the AM1 results are discussed in detail in this paper. Complete information on the geometries, energies, and frequencies obtained with the PM3 and RHF/6-31G*//RHF/6-31G* models are available from the author.

B. Mass Density Calculations. Stine[9] has developed a group-additivity method for computing the crystalline mass density of organic compounds. This method is based on the premise that the molar volume of an organic crystal is a linear combination of the volumes of the organic molecule's constituent parts. These constituent volumes are a function of the type of atoms in the organic molecule and their bonding configuration. To obtain the constituent volumes, Stine did least-squares regressions between measured and calculated densities with the constituent volumes as the fitting parameters. He used 34 different types of "atoms" in various bonding situations in his regression analysis.

An example of a particular constituent volume is a nitrogen completely σ-bonded in ring systems. This nitrogen entity has a volume of 8.759 ± 0.705 Å^3 in Stine's procedure. The error bar is a standard deviation; note that it is roughly 8% as large as the parameter estimate. Given this "atom" value one can predict, e.g., the crystal density of N_8 cubane.

Stine's error analysis indicates that the constituent volume parameters predict crystal densities of "normal" molecular species within ca. ±3% of their experimental values. Density predictions are usually desired for exotic compounds. Since the bonding configurations characteristic in such cases may be underrepresented in the volume–parameter–regression data set, the density predictions could have larger errors. Since any cubanoid is somewhat exotic, it is of interest to examine how well the method performs of them. Two examples are carbon cubane $(CH)_8$ and 1,3,5,7-tetranitrobutane. The experimental[13] (predicted) densities for these structures are as follows: for $(CH)_8$, 1.29 (1.37) g/cm^3, and for $C_8H_4(NO_2)_4$, 1.81 (1.92) g/cm^3. In both cases, Stine's method predicts approximately 6% higher than the measured density. These measured cubane values and the error bar on the nitrogen "atom" parameter indicate that the nitrogen-rich cubanoid densities presented below are accurate to ca. 5–10% and that the density estimates are probably high.

C. Detonation Performance Calculations. Two important measures of an energetic material are its detonation-wave velocity and the pressure the detonation generates. Knowledge of these values allows one to compare the relative potential of two explosives. For steady-laminar detonation, the characteristic values of these parameters are called the Chapman–Jouguet (CJ) detonation velocity (D_{CJ}) and pressure (P_{CJ}) of the material. D_{CJ} and P_{CJ} *are* dependent on the initial mass density of the explosive, the heat of detonation, and the equation of state of the reaction products; see ref 10 for further discussion.

The AM1 detonation performance results presented below assume that the reaction products can be described by a Becker–Kistiakowsky–Wilson (BKW) equation of state (EOS). This EOS is designed and calibrated to represent the behavior of condensed-phase organic explosives. Given this EOS assumption, the heat of formation and initial density of the reactants, and a set of reaction products, one can compute the equilibrium chemical composition of the detonation products at the CJ state and D_{CJ} and P_{CJ}; we used the TIGER code to do this; see ref 14.

For the $(CH)_{8-n}N_n$ cubanoids, the assumed reaction products were N_2, CH_4, H_2, NH_3, HCN, and solid carbon. For the one nitrated cubanoid examined $(C_4(NO_2)_4N_4)$, the assumed reaction products were N_2, CO_2, CO, NO, NO_2, and solid carbon.

Such calculations usually produce D_{CJ} and P_{CJ} estimates within ca. 5% and 10%, respectively, of the experimental values. For HMX (octahydro-1,3,5,7-tetranitrotetrazocine), the best performing explosive in common use, the TIGER code predicts D_{CJ} and P_{CJ} values of 9.14 mm/μs and 40.5 GPa at density of 1.90 g/cm^3, while the experimental values are 9.11 mm/μs and 39.4 GPa at density 1.89 g/cm^3.[15]

TIGER detonation calculations were done with the AM1 ΔH_fs for all 22 cubanoids. Rather than repeating this somewhat tedious process with the PM3, MNDO, and ab-initio ΔH_fs, a scaling procedure can be used, with the AM1 results, to estimate the corresponding D_{CJ} and P_{CJ} values. Kamlet[16] has generated a method that can be used to show that for two materials with values of q_2 and q_1 (and identical in all other respects) $P_{CJ}(2)/P_{CJ}(1) = (q_2/q_1)^{1/2}$ and $D_{CJ}(2)D_{CJ}(1) = (q_2/q_1)^{1/4}$, where $q = \Delta H_{det}$. These relations allow one to approximately correct the P_{CJ} and D_{CJ} values found with the AM1 ΔH_fs to the corresponding ΔH_fs found with the other methods. D_{CJ} and P_{CJ} have weak dependence on the q values because of the square and fourth root dependencies in the above equations.

III. Results

A. The Geometries. The first stage of the calculations was to optimize the C/N cubanoid geometries. Standard C–C, C–N, and N–N bond lengths were used to start the optimizations. The angle guesses usually presumed a

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highly symmetric structure. Such presumptions and, also, a priori symmetry constraints built into the geometry files were not worrisome, since the character of all the stationary points was checked via frequency calculations.

To conserve space we only discuss the AM1-optimized structure bond lengths. Typical experimental C–C, C–N, and N–N bond lengths for sp^3-hydridized atoms in unstrained systems are 1.54 (C_2H_6), 1.47 (CH_3NH_2), and 1.45 Å (N_2H_4), respectively. The same values as calculated by AM1 are 1.501, 1.432, and 1.379 Å, i.e., shorter than experiment by 2.5, 2.6, and 4.9%, respectively. The AM1 C–C and N–N optimized bond lengths for $(CH)_8$ and N_8 are 1.577 and 1.496 Å, respectively; i.e., ca. 5% and 8.5% longer than the AM1 values for unstrained C–C and N–N bonds. This bond lengthening results from inefficient orbital overlap due to strain in the cubanoid structures.

There is a roughly monotonic increase in the cubanoid C–C, C–N, and N–N bond lengths as one increases the nitrogen content. This effect is not a strong one, consisting of increases of ca. 0.013, 0.020, and 0.034 Å for C–C, C–N, and N–N bonds, respectively, as n increases from 0 to 8. This bond lengthening pattern as n increases is consistent with the ΔH_f trends presented in Section III.C; i.e., longer bonds correspond to higher ΔH_fs. There is a significant dispersion of the C–C, C–N, N–N bond lengths, at fixed n, as the structural isomer is varied—this dispersion is ca. ± 0.01 Å for $3 \leq n \leq 6$. For the $(CH)_4N_4$ isomers, typical C–C, C–N, and N–N bond lengths are 1.585, 1.555, and 1.472 Å, respectively. The cubanoids with n = 1, 2, 7, and 8 violate these simple trends somewhat. Bond lengths of a particular type (e.g., C–C) in these structures show greater variations; a dispersion of ±0.015 Å is not atypical.

In all cases, the AM1 CH bond lengths have typical values; i.e., 1.100 ± 0.005 Å.

B. The Vibrational Frequencies. Vibrational frequencies were calculated with the AM1 and PM3 models to demonstrate that the stationary point geometries are stable points. In all cases, the frequencies are real and the lowest frequencies are quite large. This is an indication that the C/N cubanoid stable point geometries are fairly rigorously defined by the energy hypersurfaces. Again, to conserve space we discuss only the AM1 frequencies. For the cubanoids, the frequencies break into three classes. These are as follows: two normals modes at ca. 630 ± 60 cm^{-1}, $(8 - n)$ CH stretches at ca. 3200 cm^{-1}, and $2(16 - n)$ modes in the 800–1300 cm^{-1} range.

The AM1 zero-point energies are accurately represented by

$$\mathrm{ZPE}(n) = An + B \quad (1)$$

where n is the number of nitrogens in the cubanoid, A and B equal −7.80 ± 0.02 and 87.8 ± 0.2 kcal/mol, respectively, and the error bars are standard deviations. Since $A < 0$, the ZPE decreases as the number of nitrogens is increased. The ZPE's vary from 87.8 kcal/mol (for $(CH)_8$) to 25.4 kcal/mol (for N_8). There are only small changes in the ZPE as a function of structural isomer; the largest range in ZPE's being 0.5 kcal/mol for the six $(CH)_4N_4$ structures.

C. The Heats of Formation. The AM1 and PM3 calculations produce ΔH_fs for the optimized structures. ΔH_f is an energy quantity of interest when studying whether a molecular structure may be a useful energetic material. The ΔH_fs are given in Table II and Figure 2.

The AM1[PM3] ΔH_fs vary from 151[114] kcal/mol for $(CH)_8$ to 631[406] kcal/mol for N_8. As is seen from Figure 2, these ΔH_fs vary nonlinearly with nitrogen content. The nonlinear contribution to N_8's ΔH_f is quite large, being, e.g., ca. 150 kcal/mol out of the total 480 kcal/mol increase in going from $(CH)_8$ to N_8, when AM1 is used. This

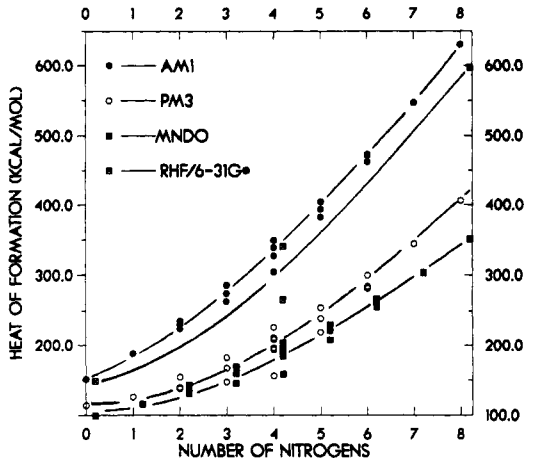

Figure 2. C/N cubanoid ΔH_fs calculated with the AM1, PM3, MNDO, and RHF/6-31G*//RHF/6-31G* models as a function of nitrogen content. Note that the MNDO and RHF/6-31G* values have been displaced 0.2 units to the right to prevent overlap of the symbols.

nonlinearity is attributable to the addition of *more* than one N–N bond to a C/N cubanoid when one nitrogen is added.

A linear least-squares regression was carried out between the AM1 cubanoid ΔH_fs and the pattern of atomic neighbors to examine how the AM1 ΔH_fs depend on the bonding configuration. Bonding configuration numbers were assigned to a structure by viewing the structure from a particular nuclear center, e.g., site 1 of Figure 1. There are three nearest neighbors, three second nearest neighbors, and one third nearest neighbor for any such site. Consequently, one can compose a list of whether the first, second, and third nearest neighbors are nitrogen or carbon centers. This generates a set of numerical values that characterize the site. In our regression analysis five such numbers were used. These were three values that counted the number of C–C, C–N, and N–N bonds and two numbers that counted the number of nitrogen–nitrogen second and third nearest neighbors. This counting process was done for all eight sites and the numbers of each type summed; this double counts the number of bonds and second nearest neighbors, so these sums were halved. Using these values, one can do the regression

$$\Delta H_f(m) = \alpha \mathrm{CC}(m) + \beta \mathrm{CN}(m) + \gamma \mathrm{NN}(m) + \delta \mathrm{N_2}(m) + \epsilon \mathrm{N_3}(m) \quad (2)$$

In eq 2, m is the structure number (see Table I), $\mathrm{CC}(m)$, $\mathrm{CN}(m)$, and $\mathrm{NN}(m)$ are the number of CC, CN, and NN bonds in structure m, $\mathrm{N_2}(m)$ and $\mathrm{N_3}(m)$ are the number of N–N second and third nearest neighbors for structure m, and $\alpha,\ldots,\epsilon$ are the fitting parameters. The regression yields the values α = 12.7 ± 1.4, β = 24.3 ± 1.4, γ = 49.0 ± 4.0, δ = 2.2 ± 0.4, and ϵ = 2.1 ± 0.4 kcal/mol, where error bars are one standard deviation. The α, β, and γ parameters show the effect on the ΔH_fs of nitrogen loading. A CH group bonded to a CH group in a C/N cubanoid contributes ca. 12.7 kcal/mol to the AM1 ΔH_f, while a nitrogen bonded to a CH group or to another nitrogen contributes 24.2 or 49.0 kcal/mol, respectively. The relative values of α, β, and γ shows that there is a rapid increase in the AM1 ΔH_f as many nitrogens are added. There are small contributions to the AM1 ΔH_f from second and third nitrogen–nitrogen nearest neighbors as shown by the parameters δ and ϵ.

If the small δ and ϵ contributions are neglected, one can obtain α, β, and γ values from the $(CH)_8$, N_8, and T_d $(CH)_4N_4$ ΔH_fs. Using this procedure with the AM1 and

PM3 ΔH_fs, one finds for the (α,β,γ) triplet the values (12.6,23.4,52.6) and (9.5,13.0,33.9), respectively. The AM1 method predicts significantly larger ΔH_f contributions from the CN and NN bonds in the cubanoids than does PM3.

D. The Mass Densities. For the $(CH)_{8-n}N_n$ cubanoid structures, Stine's[9] procedure for the crystal mass density gives

$$\rho_o(n) = \frac{\rho_o(0)}{1 - |D|n} + \frac{Cn}{1 - |D|n} \quad (3)$$

where n is the number of nitrogen nuclei present, $\rho_o(0) = (M_C + M_H)/(V_C + V_H)$, $C = (M_N - M_C - M_H)/8(V_C + V_H)$, and $D = (V_N - V_C - V_H)/8(V_C + V_H)$. Here M_C, M_H, M_N and V_C, V_H, V_N are, respectively, the atomic masses and Stine's volume parameters for carbon, hydrogen, and nitrogen in the cubanoid bonding configuration. Note that $\rho_o(0)$ is the estimated density of $(CH)_8$ cubane. The right side of eq 3 is written as two terms as this will be useful below. Stine's volume parameters are $V_C = 9.755 \pm 0.351$, $V_H = 5.981 \pm 0.298$, and $V_N = 8.759 \pm 0.705$ Å^3.

The densities calculated from eq 3 are given in Table II. The limiting densities are 1.374 g/cm^3 for $(CH)_8$ and 2.655 g/cm^3 for N_8. There is a nonlinear dependence of density on the nitrogen content. As one replaces CH groups by N's in a cubanoid, the structures become more compact and more massive. The two terms on the right side of eq 3 show the relative importance of these two effects. The first term, $[\rho_o(0)/(1 - |D|n)]$, measures the increase in density of a *fixed mass* structure as the nitrogen content is increased. This density increase results from the relative compactness of a nitrogen "atom" relative to a CH group. The second term in eq 3, $[Cn/(1 - |D|n)]$, occurs both because of the molecular mass increase as N's replace CH groups and because the molecular structure becomes more compact under this replacement. If one evaluates the two right-hand terms of eq 3 for $(CH)_8$, the values are 1.374 and 0.0 g/cm^3, respectively. For N_8, these two values are 2.47 and 0.19 g/cm^3. The *dominant* factor in producing the large density changes as nitrogen is added is the relative size of V_N and $(V_C + V_H)$. The cubanoid-type nitrogen "atom" is the smallest of all Stine's volume parameters for normally valent C, N, O, or F "atoms". Thus, *provided* these parameters approximate reality, the mass densities of the very nitrogen-rich cubanoids may be near the *highest densities possible* for organic molecules. A substantial part of the remarkable detonation performance predicted for the nitrogen-rich cubanoids can be traced to the high predicted mass densities.

E. The Detonation Results. The AM1 detonation performance predictions (D_{CJ} and P_{CJ}) are presented in Table II and Figure 3. As is seen from Figure 3, *all* the C/N cubanoids are predicted to be reasonably-energetic to very-energetic explosives.

Note the arrows on the left and right ordinates of Figure 3 labeled "HMX". HMX is the best performing explosive in common use; it will be used as the standard for gauging the explosive performance of the C/N cubanoids.

As shown in Figure 3, the calculations predict that $(CH)_8$ at its crystal density is an explosive with $D_{CJ} = 7.72$ mm/μs and $P_{CJ} = 17.4$ GPa. Thus, carbon cubane is predicted to have explosive performance markedly inferior to HMX. As nitrogens are substituted into the cubanoid structure, the comparison vs HMX becomes more favorable to the C/N cubanoids. The results on Figure 3 indicate that cubanoids containing four or more nitrogens will outperform HMX. As one exceeds four nitrogens in the cubanoid structure, both the CJ detonation velocity and pressure rise very rapidly as a function of nitrogen content.

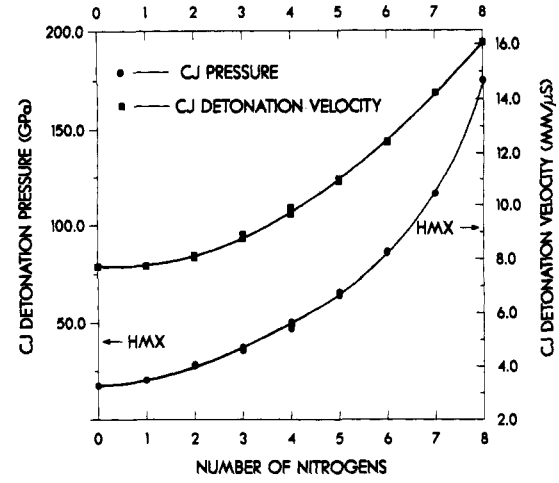

Figure 3. Chapman–Jouguet (CJ) detonation pressure and detonation velocity, computed with AM1 ΔH_fs, as a function of nitrogen content. The arrows near the left- and right-hand ordinates indicate CJ values for crystal density HMX (ρ_o = 1.90 g/cm^3). Note that the C/N cubanoids containing four or more nitrogens are predicted to have D_{CJ} and P_{CJ} values greater than crystalline HMX.

It is likely that the introduction of large amounts of nitrogen into the C/N cubanoid structures will *kinetically* destabilize them, in addition to increasing their thermodynamic metastability. For the cubanoid structures containing two or more nitrogens or (CH) groups, there are cubanoid structural isomers. As shown on Figure 2, the ΔH_fs for a particular C/N ratio do not vary widely. The higher energy structures are those with the largest number of N–N bonds; such structures are probably also the most kinetically unstable. As shown in Figure 3, the detonation performance *within* a set of structural isomers also does *not* vary radically; these isomers may have very *different* kinetic stabilities. One such case is structure 14 of Table I, which consists of a $(CH)_4$ tetrahedron juxtaposed with an N_4 tetrahedron. There are *no* N–N bonds in this structure. Because of this, structure 14 is probably more kinetically stable than (say) structure 9 of Table I. Structure 9 consists of a square of four N's bonded to a square of four (CH) groups; each nitrogen is bonded to two other nitrogens. The point of this is that, at given nitrogen content, one could choose the kinetically most stable structural isomer, while retaining most explosive performance.

F. AM1 Results for Nitrated $(CH)_4N_4$. The carbon-rich C/N cubanoid detonation products contain significant amounts of solid carbon, CH_4, and NH_3. The addition of oxygen, as carried by nitro groups, into such molecules allows reaction to much lower energy products, i.e., H_2O, CO_2, and CO. The extra energy release should produce improved detonation performance. To study this factor for the C/N cubanoids, the fully nitrated form of structure 14 (i.e., T_d symmetry $C_4(NO_2)_4N_4$) was studied with AM1.

We optimized the $C_4(NO_2)_4N_4$ structure within T_d symmetry. The AM1 bond lengths obtained were as follows: 1.560 (in-cube C–N), 1.515 (nitro-group C–N), and 1.189 Å (N–O). The in-cube C–N bond length of 1.560 Å is very slightly longer (0.005 Å) than that obtained for the unnitrated form; this indicates that the nitro groups do not significantly affect the character of the C–N bonds within the cubanoid.

The AM1 ΔH_f for the optimized structure is 378.6 kcal/mol; i.e., 74 kcal/mol larger than the unnitrated form. The corresponding D_{CJ} and P_{CJ} are 10.82 mm/μs and 63.7 GPa with N_2, CO_2, and CO as the major reaction products.

The predicted mass density is 2.198 g/cm^3.

G. Ab-Initio and MNDO Results. Ab-initio RHF/6-31G*//RHF/6-31G* calculations were carried out on four high-symmetry cubanoids. The computed structures were (#1) $(CH)_8$, (#9 and #14) $(CH)_4N_4$, and (#22) N_8, where # indicates a Table I structure. These calculations were done to gauge the accuracy of the semiempirical ΔH_fs. Stability of the structures was demonstrated by vibrational frequency calculations.

The absolute energies (hartree) so obtained were as follows: (#1) −307.407 754 6, (#9) −371.230 243 4, (#14) −371.348 948 9, and (#22) −434.949 162 9. These energies were converted to ΔH_fs by computing bond separation energies (BSE) in the isodesmic reaction

$$(CH)_8 + nN(CH_3)_3 \rightarrow (CH)_{8-n}N_n + nCH(CH_3)_3$$

The BSE's are given by

$$BSE = E[(CH_8)] + nE[N(CH_3)_3] - E[(CH)_{8-n}N_n] - nE[CH(CH_3)_3]$$

where the RHF/6-31G*//RHF/6-31G* absolute energies (hartree) for $N(CH_3)_3$ and $CH(CH_3)_3$ are −173.282 985 8 and −157.293 074 5, respectively. The BSE's (in kcal/mol) are as follows: (#1) 0.0, (#9) −86.1, (#14) −11.6, and (#22) −237.1. These BSE's can be used to obtain the ΔH_fs via

$$\Delta H_f[(CH)_{8-n}N_n] = \Delta H_f[(CH)_8] + n[\Delta H_f[N(CH_3)_3]] - \Delta H_f[HC(CH_3)_3] - BSE.$$

Measured values of ΔH_f in the above equation are $(CH)_8$ = 148.7 ± 1.0, $N(CH_3)_3$ = −5.7 ± 0.2, and $HC(CH_3)_3$ = −32 ± 0.2 (in kcal/mol).[17] These give the following heat of formation values: (#1) 148.7, (#9) 340.4, (#14) 265.9, and (#22) 597.0 (kcal/mol) (see Figure 3).

MNDO calculations on the C/N cubanoids have been reported by other workers;[18] see Figure 3 and Table II.

We can now compare the ΔH_fs as obtained from the AM1, PM3, MNDO, and RHF/6-31G*//RHF/6-31G* models. As shown in Figure 3, the PM3 and MNDO models give significantly lower values of ΔH_f than do the AM1 and ab-initio methods. The disparity in ΔH_f between the two groups of results grows with the amount of nitrogen present. For $(CH)_8$ it is ca. 50 kcal/mol, while for N_8 it is ca. 250 kcal/mol. There is good agreement between the AM1 ΔH_fs and those obtained with the ab-initio model. It is likely the RFH/6-31G*//RHF/6-31G* ΔH_fs are quite accurate, because an experimental $(CH)_8$ ΔH_f is known and because an isodesmic reaction involving it can be used to obtain the heats of formation for the other cubanoids.

These results indicate that AM1 is the semiempirical method of choice for nitrogen-loaded strained-ring systems and that PM3 and MNDO produce ΔH_f values that are serious underestimates for such systems.

IV. Discussion

AM1 and PM3 results were presented for all 22 $(CH)_{8-n}N_n$ ($0 \le n \le 8$) cubanoid structures. These results indicate that all these structures are *metastable* to rearrangement to smaller species. All the AM1 frequencies are greater than ca. 600 cm^{-1}; this is evidence that there are no low-energy distortions by which the C/N cubanoids can disintegrate.

Comparison of AM1, PM3, and MNDO ΔH_fs with those computed with the RHF/6-31G*//RHF/6-31G* model shows good agreement between the AM1 and ab-initio results, but poor agreement with PM3 and MNDO values. Thus, if a semiempirical method is to be used to compute energies of nitrogen-loaded strained-ring systems, it should be AM1.

The ΔH_fs are accurately represented by a simple linear function of the bonding configuration (see eq 2). This function shows that substitution of nitrogens into a C/N cubanoid causes a strong increase in ΔH_f, this is particularly true for the nitrogen-rich cubanoids. All the C/N cubanoids have high energy content. The AM1 ΔH_fs range from ca. 150 kcal/mol for $(CH)_8$ to 630 kcal/mol for N_8. There are structural isomers of the C/N cubanoids when $2 \le n \le 6$. For a given quantum-mechanical method, the isomer ΔH_fs are not radically different; however, it is possible that their kinetic stabilities are.

The predicted crystalline mass densities of the C/N cubanoids vary from 1.374 to 2.655 g/cm^3; i.e., it is likely that the high nitrogen C/N cubanoids have mass densities near the highest possible for organic molecules.

Detonation performance calculations predict that all the C/N cubanoids are explosives—*including* carbon cubane. While the C/N cubanoids high in carbon content are predicted to be low-to-average performance explosives, this changes with four or more nitrogens are present. For $n \ge 4$, the predictions state that the C/N cubanoids would be very high performance explosives—equal or superior to the highest performance explosives in existence. To the author's knowledge, there is no experimental data on the detonation properties of any C/N cubanoid.

A central question concerning the high-nitrogen-content cubanoids is whether any of them are kinetically stable enough to be practically interesting. Jolly[19] has made a comment in relation to this "...it is possible to prepare (nitrogen) compounds that are thermodynamically unstable but that decompose at a negligible rate". The possibility of this statement being true for the C/N cubanoids is supported by the symmetry forbiddeness of their dissociation to smaller entities. For example, concerted cycloreversion reactions leading from the C/N cubanoids to C_2H_2, N_2 and HCN are [4 + 4 + 4 + 4] Woodward–Hoffmann forbidden. In any attempt to synthesize nitrogen-rich C/N cubanoids, it will no doubt be important to use the latitude offered by the structural isomers in choosing a kinetically most stable synthetic target. This target should contain the minimum number of N–N bonds. Structure 14 (T_d symmetry $(CH)_4N_4$) would seem a likely first choice, if explosive performance is a consideration.

The effect of nitration on the explosive performance of the C/N cubanoids is examined by AM1 calculations on T_d symmetry $C_4(NO_2)_4N_4$. Nitration increases the predicted ΔH_f and ρ_o by 74 kcal/mol and 0.37 g/cm^3 over the unnitrated form. D_{CJ} and P_{CJ} are enhanced by 12% and 36%, respectively. The AM1 bond lengths do not indicate a substantial effect due to NO_2 presence on the within cube C–N bonds.

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