demonstrate that the bent structures of some monomeric barium and strontium dihalides[3-5] are not exceptional. But the first-row substituent effects are not monotonous. The smallest XMX angle is predicted for $Ba(CH_3)_2$ (115.9°), a value even lower than that for BaF_2 (125.6°). $P_\pi \rightarrow d_\pi$ donor interactions for X = NH_2, OH, F tend to widen the XMX angles. These π-contributions also may lead to significant rotational barriers in heavy alkaline earth amides. This conclusion receives some support from experimentally observed conformational preferences in some amide X-ray structures.[20-22] The availability of metal d-orbitals to act both as σ- and as π-acceptors offers an explanation for the similarities of the heavy alkaline earth structural organometallic chemistry to that of early transition-metal and f-block elements. Covalent contributions are important for the molecular geometries even though they constitute only a minor fraction of the total bonding energy in most of the highly ionic alkaline earth compounds (estimates of the heterolytic bonding energies of the dihalides based purely on coulombic considerations usually approximate the experiment closely[27]). A similar conclusion was

(27) Hildenbrand, D. L. *J. Electrochem. Soc.* **1979**, *126*, 1396.

reached regarding the significance of $p_\pi \rightarrow d_\pi$ bonding contributions for the more covalent early transition-metal amides, based on thermochemical and structural data.[25] Further computational studies will help assess the importance of the covalent d-orbital contributions, e.g., in the bioinorganic chemistry of Ca, Sr, and Ba.

Registry No. $CaLi_2$, 12013-43-3; $Ca(BeH)_2$, 137668-54-3; $Ca(BH_2)_2$, 137668-51-0; $Ca(CH_3)_2$, 19180-99-5; $Ca(NH_2)_2$, 23321-74-6; $Ca(OH)_2$, 1305-62-0; CaF_2, 7789-75-5; $SrLi_2$, 137718-23-1; $Sr(BeH)_2$, 137668-55-4; $BaLi_2$, 137718-22-0; $Ba(OH)_2$, 17194-00-2; BaF_2, 7787-32-8; $Ba(NH_2)_2$, 20253-29-6; $Ba(CH_3)_2$, 84348-36-7; $Ba(BeH)_2$, 137668-56-5; $Ba(BA)_2$, 137668-52-1; $Sr(OH)_2$, 18480-07-4; $Sr(BH_2)_2$, 137668-53-2; $Sr(CH_3)_2$, 108899-22-5; SrF_2, 7783-48-4; $Sr(NH_2)_2$, 23731-24-0.

Finite T_d Symmetry Models for Diamond: From Adamantane to Superadamantane ($C_{35}H_{36}$)

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Abstract: Seven clusters based on the diamond lattice, ranging in size from cyclohexane (C_6H_{12}, D_{3d}) to the "adamantane-of-adamantanes" (or superadamantane-5, $C_{35}H_{36}$, T_d), have been computed by molecular mechanics (MM2 and MM3), semiempirical self-consistent-field (SCF) (MINDO/3, MNDO, AM1, and PM3) methods, and ab initio SCF (with the minimal STO-3G, DZ, and DZP basis sets) theory. Molecular geometries are fully optimized under appropriate symmetry constraints in the MM2, MM3, and ab initio SCF methods, and by using Cartesian coordinates using semiempirical methods. Particular attention has been paid to the carbon–carbon bond lengths, total energies, and heats of formation. The largest cluster studied here is still far from the infinite diamond lattice. Comparisons among the computational methods reveal the merits and shortcomings of each.

Introduction

Owing to its composition, crystal structure, and mechanical, thermal, and electromagnetic properties, the diamond is unique. Its exceptional and favorable mechanical, thermal, and electromagnetic properties lead to wide-ranging industrial and engineering applications. Diamond research, particularly that involving thin films, continues to reveal new and important uses.[1-6]

Many physical properties of crystalline diamond are well established.[3,7,9] Each carbon atom in the diamond crystal is coordinated to four other carbons, with a carbon–carbon bond length of 1.5445 Å (X-ray).[8] The lattice is comprised of six-membered rings in chair conformations.[9]

Theoretical studies of diamond naturally fall into two broad categories: The first treats the diamond as an infinite lattice, while the second employs the finite cluster approximation. Sauer[10] analyzes these models from a chemist's point of view, emphasizing the crystal orbital and related solid-state physics approaches. Crystal orbital theory has been reviewed comprehensively by Pisani, Dovesi, and Roetti[11] recently.

The finite molecular approximation to infinite structures is frequently adopted by chemists.[10] In particular, fragments of the

diamond lattice may be saturated by hydrogen atoms. This approach may be used to investigate the convergence behavior of

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(2) Berman, R. *Physical Properties of Diamond*; Oxford University Press: Oxford, England, 1965.

(3) Fields, J. E., Ed. *The Properties of Diamond*; Academic Press: London, 1979. This book has chapters on research in theoretical and experimental solid-state physics, surface science, mechanics, artificial growth, geology, and industrial applications and a table of the properties of diamond.

(4) Guyer, R. L.; Koshland, D. E. Diamond: glittering prize for materials science. *Science* **1990**, *250*, 1640. Diamond (including diamond films) is featured in this news article as the molecule of the year 1990. The runners-up include the C_{60} buckminsterfullerene molecule.

(5) Whitesides, G. M. What will chemistry do in the next twenty years? *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1209. In this review, "very large" chemistry, of which the diamond chemistry is representative, is featured as one of the limits to be explored in the future, along with "very small" and "very fast" chemistry.

(6) Anthony, T. R.; Banholzer, W. F.; Fleischer, J. F.; Wei, L.; Kuo, P. K.; Thomas, R. L.; Pryor, R. W. *Phys. Rev.* **1990**, *42B*, 1104.

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Table I. Theoretical Geometry of Cyclohexane, C_6H_{12}, D_{3d}[a]

	MM2	MM3	MINDO/3	MNDO	AM1	PM3	STO-3G	DZ	DZP	exptl[c]
energy[b]	−29.5 kcal/mol	−30.0 kcal/mol	−37.0 kcal/mol	−34.8 kcal/mol	−38.5 kcal/mol	−31.0 kcal/mol	−231.482 67 au	−234.134 70 au	−234.253 99 au	−29.5 kcal/mol
CC	1.536	1.536	1.519	1.538	1.515	1.521	1.544	1.540	1.532	1.536
CH_e	1.117	1.115	1.119	1.114	1.121	1.107	1.088	1.086	1.089	1.121 (av)
CH_a	1.116	1.115	1.121	1.114	1.122	1.108	1.088	1.088	1.091	1.121 (av)
CCH_e	109.9	109.9	109.8	108.9	109.6	110.1	109.8	110.1	110.1	
CCH_a	109.5	109.5	108.7	109.4	109.4	109.8	109.3	109.2	109.2	
CCCC	56.4	55.3	35.2	46.3	55.2	56.0	55.4	54.9	54.8	54.9

[a] AB is the bond length (Å), ABC the bond angle (deg), with B being the apex, and ABCD the torsional angle in (deg) viewed along the BC bond. [b] Shown are heats of formation from molecular mechanics and the semiempirical SCF methods (kcal/mol) and total energy from the ab initio SCF method with three basis sets (au); 1 au = 627.51 kcal/mol. The MM2 and MM3 bond distances are thermally averaged internuclear distances (r_g); the ab initio bond distances are equilibrium internuclear distances (r_e). [c] Geometry is from ref 38. For the CH_e (equatorial) and CH_a (axial) bond lengths, an average (av) distance is given. Note that the experimental values cited here are thermally averaged internuclear distances (r_g) as determined by gas-phase electron diffraction techniques. Heat of formation is from ref 53.

the properties of the clusters toward the properties of the bulk. While this approximation is somewhat naive, there are distinct advantages. Molecular clusters of reasonably large sizes may be examined by modern ab initio quantum mechanical computations, which have been tested extensively and have reliability and limitations that are well documented.[12–14] Moreover, advantage can be taken of the symmetry inherent in some diamond lattice clusters (as those studied in the present paper), since high-symmetry ab initio computations, particularly at the self-consistent-field (SCF) level, can be carried out less expensively in terms of computer hardware. This allows larger molecules to be treated.

We report the energetics and optimized molecular geometries of seven molecular clusters (1–7) taken from the diamond lattice. The smallest is cyclohexane (1), and the largest the "adamantane-of-adamantanes"[15] (7) with the composition $C_{35}H_{36}$. Two obvious questions appear to be to what extent the theoretical CC bond lengths in such clusters approach the diamond lattice value 1.5445 Å, and whether the theoretical energies of the carbon atoms in the clusters approach that of a carbon atom in the infinite diamond lattice. We use several theoretical methods, including molecular mechanics (MM2 and MM3), semiempirical methods (MINDO/3, MNDO, AM1, and PM3), and the ab initio direct SCF method with three basis sets, and compare the results.

Theoretical Details

A. Ab Initio SCF Methods. The direct SCF method was first proposed by Almlöf.[16] In the direct SCF strategy, all or a large fraction of the two-electron integrals are computed as needed. The direct SCF method allows one to treat molecules of larger sizes than the conventional SCF method. Here we used the TURBOMOLE direct SCF program package[17] from Ahlrichs' group as implemented on a DECstation 3100 Unix platform at the University of Georgia. For the two largest molecules (6 and 7) at the DZP

SCF level of theory, the programs were modified slightly.

The STO-3G minimal basis set was developed by the Pople group.[18] The Dunning[20] double-ζ (DZ) contraction of the Huzinaga[19] primitive Gaussian basis sets was also used. Orbital exponents of all Gaussian hydrogen s functions in the DZ basis set were multiplied by a factor of 1.44. The addition of a set of five d basis functions for the carbon atoms, and three p basis functions for the hydrogen atoms to the DZ basis set, gives the DZ plus polarization (DZP) basis set.[21] The orbital exponents of the polarization functions are $\alpha(C) = 0.75$ and $\alpha(H) = 0.75$. The DZP basis set for $C_{35}H_{36}$ contains 705 basis functions.

Full geometry optimizations were carried out using analytic energy gradients and internal coordinates within the point group symmetries reasonably assumed for each molecule. Ab initio SCF computation of harmonic vibrational frequencies was not feasible for the larger molecules with all the basis sets. In choosing independent internal coordinates to optimize, we found the recipes recommended by Pulay, Fogarasi, Pang, and Boggs[22] to be very useful. The threshold energy change was set to be 10^{-7} au, and the threshold on the maximum absolute gradient was set to be 10^{-5} au.

B. Semiempirical SCF Methods. The semiempirical SCF program package (MOPAC 5.0) used in the present study[23] is implemented on the IBM 3090 supercomputers at the Cornell National Supercomputer Facility (CNSF). We used the MINDO/3,[24] MNDO,[25] AM1,[26] and PM3[27] Hamiltonians provided in MOPAC 5.0. Cartesian coordinate optimizations were used, with more precise control of threshold tests. The optimized geometries all have the expected point group symmetry to within 0.0001 Å and 0.01°.

C. Molecular Mechanics. The MM2 and MM3 program systems developed by the Allinger group[28–35] (implemented on the

(8) Lonsdale, K. *Philos. Trans. R. Soc. London* **1946**, *A240*, 219.

(9) Greenwood, N. N.; Earnshaw, A. *Chemistry of the Elements*; Pergamon Press: New York, 1984; pp 304–305. (i) CC distance in diamond 1.5445 Å; (ii) cubic unit cell $a_0 = 3.5668$ Å, each unit cell has eight carbon atoms; (iii) heat of sublimation to monoatomic gas is ~710 kJ/mol which is ~170 kcal/mol and which is ~7.36 eV; (iv) band gap is ~580 kJ/mol which is ~6.01 eV.

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(13) Schaefer, H. F. *Quantum Chemistry. The Development of Ab Initio Methods in Molecular Electronic Structure Theory*; Oxford University Press: Oxford, England, 1984.

(14) Hehre, W. J.; Radom, L.; Schleyer, P. von R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(15) Schleyer, P. von R. My thirty years in hydrocarbon cages: from adamantane to dodecahedrane. In *Cage Hydrocarbons*; Olah, G. A., Ed.; Wiley: New York, 1990; pp 1–38.

(16) Almlöf, J.; Faegri, K.; Korsell, K. *J. Comput. Chem.* **1982**, *3*, 385.

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(23) Stewart, J. J. P. *MOPAC (Molecular Orbital package)* Version 5.0x; Frank J. Seller Research Laboratory, U.S. Air Force Academy, Colorado Springs, CO 80840. In geometry optimization, Cartesian coordinates were used, because we became frustrated trying to provide the program with an appropriate number of symmetrized internal coordinates. Therefore, geometry optimizations were carried out without symmetry constraints.

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(25) (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899; 4907.

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(28) Allinger, N. L. *Molecular Mechanics. Operating Instructions for MM2 program. 1987 Force Field. December 1987*; Department of Chemistry, The University of Georgia, Athens, GA 30602.

Table II. Molecular Structure of Adamantane, $C_{10}H_{16}$, T_d^a

	MM2	MM3	MINDO/3	MNDO	AM1	PM3	STO-3G	DZ	DZP	exptl[c]
energy[b]	-31.5 kcal/mol	-32.0 kcal/mol	2.1 kcal/mol	-26.4 kcal/mol	-43.2 kcal/mol	-34.6 kcal/mol	-383.515 36 au	-387.902 52 au	-388.097 24 au	-31.8 kcal/mol
C_cC_s (Å)	1.539	1.540	1.549	1.555	1.526	1.531	1.548	1.545	1.537	1.540
C_tH (Å)	1.118	1.116	1.121	1.113	1.122	1.115	1.090	1.085	1.089	1.12 (av)
C_sH (Å)	1.116	1.114	1.118	1.112	1.120	1.107	1.088	1.087	1.090	1.12 (av)
C_sC_tH (deg)	109.5	109.8	109.7	109.4	109.5	109.5	109.5	109.6	109.6	
HC_sH (deg)	106.8	106.5	101.8	105.1	108.0	106.2	107.6	106.9	106.9	

^{a} The molecular structure for adamantane is shown in Figure 1. ^{b} See footnote b in Table I. ^{c} Geometry is from ref 42a,b. See footnote c in Table I. See ref 43 for three selected papers reporting X-ray crystallographic studies on the adamantane crystal, which turned out to be very complex. Heat of formation is from ref 55.

DECstation 3100 Unix platform) were used. We note that MM3 can predict harmonic vibrational frequencies. The fact that these frequencies for 1–7 were all computed to be real verifies the symmetry of the clusters in the MM3 approximation.

We stress that the MM2 and MM3 programs used here are parameterized to fit experimental geometries determined by gas-phase electron diffraction, rather than the equilibrium geometries. In particular, the bond lengths determined by gas-phase electron diffraction are thermally averaged internuclear distances, and are usually denoted by r_g (cf. ref 33b). For a particular bond, the difference between r_g and r_e values is determined by the anharmonicity of the stretching vibrational motion: The more anharmonic the stretching vibration, the greater the difference. For saturated hydrocarbons like those in the present study, r_g(CH) are greater than r_e(CH) bond lengths by roughly 0.03 Å. On the other hand, differences in r_g and r_e CC bond lengths are much less. For a recent experimental and theoretical study of these bond distances for cubane, see ref 36.

Results and Discussions

A. Cyclohexane, D_{3d}, C_6H_{12}. As a starting point, we applied all the theoretical methods to cyclohexane (1), D_{3d}, C_6H_{12}. Its equilibrium geometries, as computed by the various theoretical models, are compared in Table I. While the cyclohexane literature, including investigations of its conformations,[37] is very rich, our only concern here is the chairlike form found in the diamond lattice.

In Table I, ab initio total energies and molecular mechanics and semiempirical heats of formation are provided together with the structural parameters. Obviously these energies cannot be compared directly, but they are provided as useful energetic information.

Figure 1. Adamantane, $C_{10}H_{16}$, T_d symmetry; structure **2**. C–C and C–H bond distances from the ab initio SCF method with the DZP basis set are shown. Predictions by other theoretical methods and comparison with experiment are given in Table II.

Figure 2. Diamantane, $C_{14}H_{20}$, D_{3d} symmetry; structure **3**. C–C and C–H bond distances from the ab initio SCF method with the DZP basis set are shown. Geometries predicted by other theoretical methods and comparison with experiment are given in Table III, where the same atom labels (numbers) are used.

As seen from Table I, the cyclohexane carbon–carbon bond lengths given by MM2 and MM3, as well as ab initio SCF methods with all three basis sets, agree quite well with gas-phase electron diffraction experiment.[38] Since the MM2 and MM3

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(35) Lii, J.-H.; Allinger, N. L. *J. Am. Chem. Soc.* **1989**, *111*, 8566.

(36) Hedberg, L.; Hedberg, K. W.; Eaton, P. E.; Nodari, N.; Robiette, H. G. *J. Am. Chem. Soc.* **1991**, *113*, 1514. This paper reports a gas-phase electron diffraction (GED) study (r_g) on the cubane compound. Also various corrections based on microwave and multiple scattering experiments are made and an estimation of the equilibrium geometry (r_e) of the cubane molecule is reported. The values of interest here are r_g(CH) = 1.114 (6) Å, r_e(CH) = 1.096 (13) Å, r_g(CC) = 1.573 (2) Å, and r_e(CC) = 1.562 (4) Å. The $r_g - r_e$ difference is 0.02 Å for CH and 0.011 Å for CC. Of course, one would expect the CC bonds in cubane to be much different than the CC bonds in the clusters in this study, although the CH bonds in cubane and in the adamantane clusters here should not be too dissimilar.

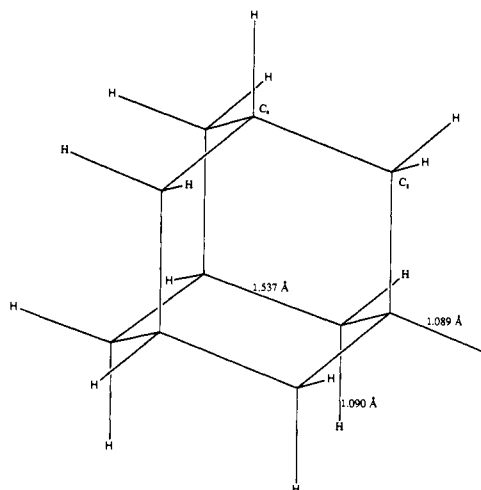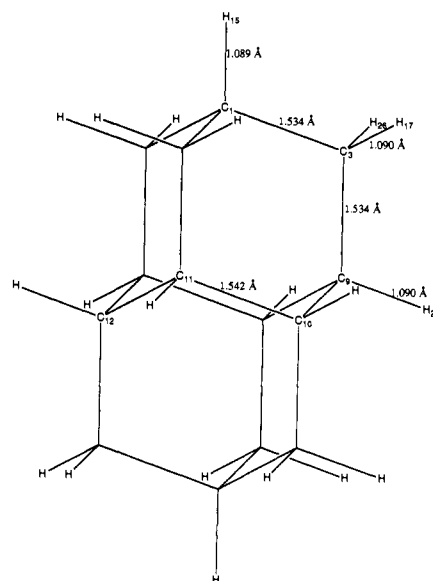(37) E.g. Dixon, D. A.; Komornicki, A. *J. Phys. Chem.* **1990**, *94*, 5630.

(38) Bastiansen, O.; Fernholt, L.; Seip, H. M.; Kambara, H.; Kuchitsu, K. *J. Mol. Struct.* **1973**, *18*, 163.

Table III. Molecular Structure of Diamantane, $C_{14}H_{20}$, D_{3d}[a]

	MM2	MM3	MINDO/3	MNDO	AM1	PM3	STO-3G	DZ	DZP	exptl[c]
energy[b]	-34.3 kcal/mol	-35.0 kcal/mol	29.2 kcal/mol	-23.4 kcal/mol	-48.7 kcal/mol	-38.5 kcal/mol	-535.55034 au	-541.67375 au	-541.94355 au	-34.9 kcal/mol
C_1C_3	1.537	1.538	1.545	1.551	1.525	1.529	1.546	1.542	1.534	1.538 ± 0.005
C_3C_9	1.538	1.539	1.543	1.551	1.523	1.528	1.546	1.542	1.534	1.535 ± 0.005
C_9C_{10}	1.541	1.545	1.580	1.568	1.534	1.539	1.552	1.550	1.542	1.532 ± 0.005
C_1H_{15}	1.118	1.116	1.121	1.113	1.122	1.115	1.090	1.085	1.089	1.00 ± 0.10
C_3H_{17}	1.116	1.114	1.118	1.112	1.120	1.107	1.088	1.087	1.090	1.01 ± 0.10
C_9H_{29}	1.118	1.116	1.122	1.113	1.123	1.116	1.089	1.087	1.090	0.98 ± 0.10
$H_{17}C_3H_{26}$	106.8	106.5	101.9	105.1	108.0	106.2	107.6	106.9	106.9	
$C_1C_3H_{17}$	110.1	110.0	111.3	110.6	109.8	110.2	110.0	110.1	110.1	
$C_9C_{10}C_{11}C_{12}$	61.7	61.3	66.4	63.6	61.5	61.4	61.9	62.3	62.4	
$C_3C_9C_{10}$	110.2	109.9	112.0	110.9	110.0	109.9	110.3	110.4	110.4	110.2 ± 0.4
$C_3C_9H_{29}$	108.8	109.1	107.9	107.8	109.5	109.5	109.2	109.3	109.3	

[a] The molecular structure of diamantane is shown in Figure 2. Bond lengths are in angstroms; bond angles and torsional angles are in degrees. [b] See footnote b in Table I. [c] Geometry is from ref 48. Note that the cited values are determined by X-ray diffraction techniques. Heat of formation is from ref 55. In comparing bond lengths from the X-ray experiment and our theoretical results here, note that C–H bond lengths from X-ray diffraction experiments are usually underestimated.
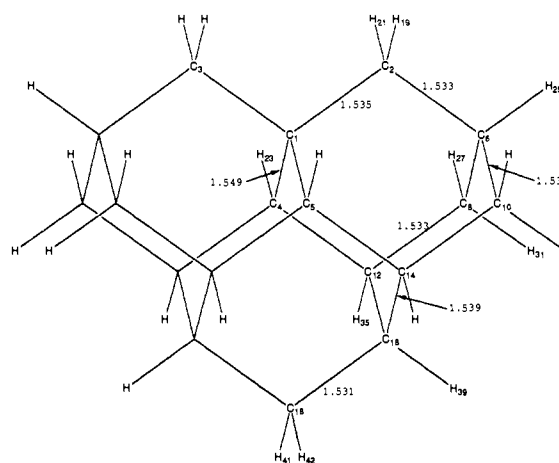
programs are parameterized to give r_g values, these may be compared directly with the Bastiansen and Kuchitsu results. The CCCC torsional angles, given by MM2 and MM3 and ab initio SCF methods, are also in good agreement with experiment.

B. Adamantane, T_d, $C_{10}H_{16}$. The theoretical geometries for adamantane[39-41] are presented in Table II. This table and all subsequent ones are organized in the same format as that for cyclohexane (Table I). Adamantane (2) is well known, but for reference its molecular structure is depicted in Figure 1.

Comparisons between theoretical and experimental geometries for adamantane are similar to those for cyclohexane. The MM2, MM3, and ab initio SCF CC bond lengths agree very well with the experimental results of Hargittai and Hedberg.[42] See also ref 43.

We are aware of two previous ab initio SCF studies of adamantane (2). Schulman and Disch[44] included 2 in their systematic ab initio study of the heats of formation of medium-sized hydrocarbons with STO-3G, 4-31G (near equivalent of DZ), and 6-31G* (approaching DZP) basis sets. Their energies and geometries are quantitatively similar to ours. Almlöf and Lüthi[45] also included adamantane in their study of large carbon clusters. Because of their interest in larger systems, they used a simplified approach, and did not refine the molecular geometries completely. For each molecule in their study, only one average CC bond length was optimized at the DZ SCF level.

C. Diamantane, D_{3d}, $C_{14}H_{20}$. The next larger diamondoid molecule, diamantane (3; see Figure 2), was first synthesized in 1965 (and given a more figurative name, congressane, emphasizing its historical connection) by Cupas, Schleyer, and Trecker.[47] The

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(42) Gas-phase electron diffraction studies on the adamantane crystal: (a) Nowacki, W.; Hedberg, K. W. *J. Am. Chem. Soc.* **1948**, *70*, 1497. (b) Hargittai, I.; Hedberg, K. W. *J. Chem. Soc., Chem. Commun.* **1971**, 1499.

(43) Selected X-ray crystallographic studies on the adamantane solid: (a) Nowacki, W. *Helv. Chim. Acta* **1945**, *28*, 1233. This paper reports a carbon–carbon bond distance of 1.541 ± 0.016 Å. (b) Nordman, C. E.; Schmitkons, D. L. *Acta Crystallogr.* **1965**, *18*, 764. This paper reports a carbon–carbon bond distance of 1.52 ± 0.03 Å. Notice the large uncertainty. (c) Amoureux, J. P.; Foulon, M. *Acta Crystallogr.* **1987**, *B43*, 470. This paper reports a carbon–carbon bond distance of 1.529 ± 0.003 Å, and a carbon–carbon bond angle of 109.5 ± 0.4°.

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

(45) (a) Almlöf, J.; Lüthi, H. P. Theoretical methods and results for electronic structure calculations on very large systems. In *Supercomputer Research in Chemistry and Chemical Engineering*; ACS Symposium Series 353; Jensen, K. F., Truhlar, D. G., Eds.; American Chemical Society: Washington, DC, 1987; pp 35–48. The DZ basis set used was carbon = 7s3p/4s2p, hydrogen = 3s/2s. Almlöf, J.; Lüthi, H.-P. Electronic and molecular structure of carbon grams. University of Minnesota Supercomputer Institute Research Report, UMSI 90/206; October 1990.

(46) Orlando, R.; Dovesi, R.; Roetti, C.; Saunders, V. R. *J. Phys.: Condens. Matter* **1990**, *2*, 7769–7789.

Figure 3. Triamantane, $C_{18}H_{24}$, C_{2v} symmetry; structure **4**. The C–C bond distances from the ab initio SCF method with the DZP basis set are shown. Geometries predicted by other theoretical methods are presented in Table IV. The C_2 axis passes C_1–C_{18}, the σ_{xz} plane passes C_4–C_1–C_5, and the σ_{yz} plane passes C_2–C_1–C_3.

compound was characterized by the usual elemental and mass, NMR, IR, and Raman spectral analyses. Karle and Karle[48] determined the crystal and molecular structure of diamantane using X-ray diffraction.

The theoretical geometries for diamantane are presented in Table III. The agreement between the experimental and MM2 and MM3 and ab initio SCF carbon–carbon bond lengths and the one available experimental bond angle is good. The ab initio SCF CH bond lengths agree with the X-ray values. Note that the predicted heats of formation obtained from the four semiempirical models begin to exhibit big differences. Heats of formation are relative quantities, and similar theoretical methods or levels should give comparable predictions.

D. Triamantane, C_{2v}, $C_{18}H_{24}$. Triamantane (**4**; see Figure 3) is the next polymantane leading from adamantane to the diamond lattice. Triamantane was first synthesized via isomerization in 1966 by Williams, Schleyer, Gleicher, and Rodewald.[49] Mass, IR, and proton NMR spectra are available, but no X-ray diffraction analysis has been reported.

Triamantane (Figure 3) is the first cluster in this paper which has a carbon atom directly bonded to four other carbon atoms. Of course, in the diamond lattice all carbon atoms are directly bonded to four other carbons. We may call such atoms "bare"

(47) Cupas, C.; Schleyer, P. von R.; Trecker, D. J. *J. Am. Chem. Soc.* **1965**, *87*, 917.

(48) Karle, I. L.; Karle, J. *J. Am. Chem. Soc.* **1965**, *87*, 918.

(49) Williams, V. Z.; Schleyer, P. von R.; Gleicher, G. J.; Rodewald, L. B. *J. Am. Chem. Soc.* **1966**, *88*, 3862.

Table IV. Molecular Structure of Triamantane, $C_{18}H_{24}$, C_{2v}[a]

	MM2	MM3	MINDO/3	MNDO	AM1	PM3	MBS	DZ	DZP
energy[b]	−38.4 kcal/mol	−39.6 kcal/mol	62.0 kcal/mol	−17.4 kcal/mol	−52.7 kcal/mol	−42.6 kcal/mol	−687.585 57 au	−695.446 37 au	−695.790 69 au
C_1C_2	1.541	1.542	1.560	1.559	1.527	1.534	1.550	1.542	1.535
C_1C_4	1.544	1.548	1.614	1.584	1.543	1.547	1.557	1.558	1.549
C_2C_6	1.537	1.538	1.545	1.552	1.524	1.529	1.546	1.541	1.533
C_6C_8	1.537	1.537	1.544	1.550	1.524	1.529	1.546	1.542	1.534
C_8C_{12}	1.537	1.539	1.543	1.551	1.523	1.528	1.546	1.541	1.533
$C_{16}C_{12}$	1.540	1.543	1.575	1.565	1.533	1.538	1.551	1.547	1.539
$C_{16}C_{18}$	1.536	1.537	1.539	1.547	1.522	1.527	1.544	1.539	1.531
C_2H_{19}	1.115	1.114	1.119	1.113	1.120	1.108	1.088	1.087	1.090
C_4H_{23}	1.117	1.116	1.124	1.114	1.123	1.117	1.089	1.088	1.091
C_6H_{25}	1.118	1.116	1.121	1.113	1.123	1.115	1.090	1.085	1.089
C_8H_{27}	1.116	1.114	1.118	1.112	1.120	1.107	1.088	1.087	1.090
C_8H_{31}	1.116	1.114	1.118	1.112	1.120	1.107	1.088	1.087	1.090
$C_{12}H_{35}$	1.118	1.116	1.122	1.114	1.123	1.116	1.089	1.087	1.090
$C_{16}H_{39}$	1.118	1.116	1.122	1.114	1.123	1.116	1.089	1.087	1.090
$C_{18}H_{41}$	1.116	1.114	1.118	1.113	1.120	1.107	1.088	1.087	1.090
$C_2C_1C_3$	110.5	110.6	114.7	111.7	110.6	110.6	110.8	111.0	111.1
$C_4C_1C_5$	107.9	108.3	103.5	106.5	108.2	108.4	107.8	107.3	107.2
$C_1C_2C_6$	110.1	110.5	112.2	110.5	110.0	110.0	110.3	110.6	110.7
$C_{14}C_{16}C_{12}$	108.7	108.9	106.5	107.8	108.8	108.9	108.6	108.4	108.4
$C_{16}C_{12}C_8$	110.2	109.9	112.1	111.0	110.0	110.0	110.3	110.5	110.5
$C_{12}C_8C_6$	109.4	110.1	110.1	109.5	109.7	109.7	109.5	109.6	109.7
$C_8C_6C_{10}$	109.4	109.0	109.0	109.3	109.3	109.3	109.3	109.3	109.2
$C_{14}C_{16}C_{12}C_8$	59.4	59.3	56.5	58.3	59.1	59.2	59.2	58.9	59.0
$C_{16}C_{12}C_8C_6$	60.1	60.0	60.0	60.1	60.0	60.0	60.1	60.0	60.1
$C_{12}C_8C_6C_{10}$	59.9	59.5	59.6	60.0	60.0	59.9	59.8	59.7	59.7
$H_{19}C_2H_{21}$	106.8	106.6	101.9	105.2	108.0	106.2	107.5	106.9	106.8
$C_1C_2H_{19}$	110.1	110.1	110.6	110.7	109.6	110.1	109.7	109.6	109.6
$C_1C_4H_{23}$	109.4	109.4	108.5	109.9	109.0	109.1	108.9	108.6	108.6
$C_8C_6C_2$	109.4	109.1	109.5	109.7	109.5	109.5	109.4	109.3	109.2
$C_2C_6H_{25}$	109.6	109.9	109.3	109.2	109.4	109.4	109.5	109.6	109.6
$H_{27}C_8H_{31}$	106.8	106.5	101.9	105.0	108.0	106.2	107.6	107.0	106.9
$C_6C_8H_{27}$	110.1	110.0	111.4	110.7	109.8	110.3	110.0	110.1	110.1
$C_6C_8H_{31}$	110.2	110.0	111.3	110.6	109.8	110.2	110.0	110.2	110.2
$C_{12}C_8H_{27}$	110.2	110.0	111.0	110.5	109.8	110.2	109.9	110.0	110.0
$C_{12}C_8H_{31}$	110.1	110.0	110.9	110.4	109.7	110.2	109.9	110.0	110.0
$C_{16}C_{12}H_{35}$	109.4	109.5	109.2	109.6	109.2	109.3	109.2	109.2	109.2
$C_8C_{12}H_{35}$	108.8	109.1	108.0	107.8	109.5	109.5	109.3	109.3	109.3
$H_{18}C_{16}H_{39}$	108.9	109.2	108.2	108.0	109.6	109.5	109.4	109.4	109.4
$H_{41}C_{18}H_{42}$	106.8	106.5	102.0	105.1	107.9	106.2	107.6	107.0	106.8

[a] The molecular structure of triamantane is shown in Figure 3. Bond lengths are in angstroms; bond angles and torsional angles are in degrees.
[b] See footnote *b* in Table I.

carbon atoms (because they have no hydrogen atoms attached). Triamantane is also the most complicated molecule in this study in terms of geometry optimization, because of its relatively low (C_{2v}) symmetry. There are 35 totally symmetric internal coordinates to be optimized.

Theoretical geometries for triamantane (**4**) are collected in Table IV. We list the complete optimized internal coordinates for completeness. Many CH bond lengths and many angles in Table IV are identical to the prevision reported (0.001 Å, 0.1°), although they were independently optimized.

As with **1–3**, the geometries predicted by MM2 and MM3 are very similar. The bond and torsional angles predicted by the ab initio SCF methods are insensitive to basis sets employed. Comparing the MM3 and DZP SCF predictions, we find that the MM3 bond lengths are generally larger than DZP SCF by about 0.005 Å (with one exception; the MM3 C_1C_4 bond length is shorter by 0.001 Å than the DZP SCF).

E. Isotetramantane, C_{3v}, $C_{22}H_{28}$. There are three diamondoid $C_{22}H_{28}$ isomers, iso- (**5**; see Figure 4), *anti*-, and *skew*-tetramantane.[15] Burns, McKervey, Mitchell, and Rooney[50,51] synthesized *anti*-tetramantane, but we have chosen to apply the various theoretical methods to isotetramantane (**5**) because of its higher symmetry.

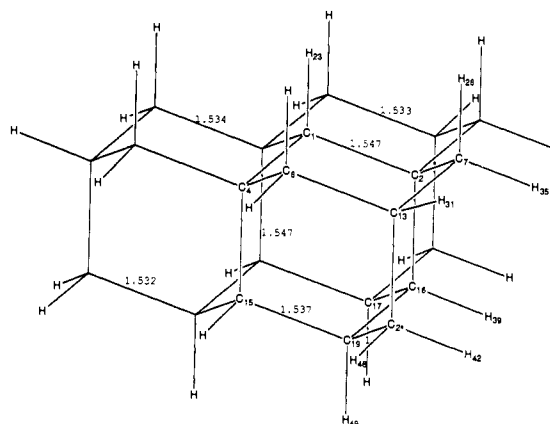The molecular structure of isotetramantane (**5**) is shown in Figure 4. Theoretical geometries for isotetramantane (**5**) are

(50) Burns, W.; Mitchell, T. R. B.; McKervey, M. A.; Rooney, J. J. *J. Chem. Soc., Chem. Commun.* **1976**, 893.
(51) Burns, W.; McKervey, M. A.; Mitchell, T. R. B.; Rooney, J. J. *J. Am. Chem. Soc.* **1978**, *100*, 906.

Figure 4. Isotetramantane, $C_{22}H_{28}$, C_{3v} symmetry; structure **5**. C–C bond distances from the DZP SCF method are shown here. Geometries predicted by other theoretical methods are given in Table V. The C_3 axis passed C_1–H_{23}.

presented in Table V. The ab initio geometry with the DZP basis set is very similar to that given by MM3. The bond angles predicted by MM2, MM3, and all the ab initio SCF basis sets are also quite similar.

The long MINDO/3 bond lengths are the most noticeable features in Table V. Note especially the values 1.606 Å for C_1–C_2 and 1.610 Å for C_2–C_{16} (defined in Figure 4), where C_2 is the bare carbon. Note also the short AM1 distances 1.524 Å for

Table V. Molecular Structure of Isotetramantane, $C_{22}H_{28}$, C_{3v}[a]

	MM2	MM3	MINDO/3	MNDO	AM1	PM3	STO-3G	DZ	DZP
energy[b]	−43.8 kcal/mol	−45.8 kcal/mol	100.5 kcal/mol	−8.5 kcal/mol	−54.8 kcal/mol	−47.1 kcal/mol	−839.621 09 au	−849.220 40 au	−849.638 66 au
C_1C_2	1.544	1.547	1.606	1.579	1.540	1.545	1.556	1.555	1.547
C_2C_7	1.540	1.541	1.559	1.559	1.527	1.534	1.549	1.542	1.534
$C_{13}C_7$	1.537	1.538	1.544	1.551	1.524	1.529	1.545	1.541	1.533
C_1H_{23}	1.116	1.116	1.126	1.115	1.123	1.118	1.089	1.090	1.093
C_7H_{26}	1.115	1.114	1.119	1.113	1.120	1.108	1.088	1.087	1.090
C_7H_{35}	1.115	1.114	1.119	1.113	1.120	1.108	1.088	1.088	1.090
$C_{13}H_{31}$	1.118	1.116	1.121	1.114	1.123	1.115	1.090	1.086	1.089
$C_4C_1C_2$	110.3	110.0	112.0	110.7	110.0	109.9	110.3	110.5	110.6
$C_1C_2C_7$	109.6	109.4	109.1	109.4	109.3	109.3	109.5	109.5	109.5
$C_2C_7C_{13}$	110.0	110.4	112.0	110.3	110.0	109.0	110.2	110.5	110.6
$C_7C_{13}C_8$	109.5	109.2	109.9	110.0	109.7	109.9	109.4	109.3	109.3
$C_4C_1C_2C_7$	58.3	58.7	53.5	57.1	58.8	58.9	58.2	57.7	57.6
$C_1C_2C_7C_{13}$	59.1	59.3	56.7	58.4	59.3	59.4	59.1	58.8	58.7
$C_2C_7C_{13}C_8$	60.0	59.6	60.3	60.4	60.1	60.2	60.0	59.8	59.8
$H_{26}C_7H_{35}$	106.8	106.6	101.8	105.1	108.0	106.2	107.5	106.8	106.8
$C_2C_7H_{26}$	110.2	110.1	110.7	110.8	109.6	110.1	109.7	109.6	109.7
$C_{13}C_7H_{26}$	109.8	109.8	110.6	109.9	109.8	110.3	109.9	110.1	110.0
$C_2C_7H_{35}$	110.2	110.1	110.7	110.7	109.6	110.1	109.7	109.6	109.7
$C_{13}C_7H_{35}$	109.8	109.8	110.6	109.9	109.8	110.3	109.9	110.1	101.0
$H_{31}C_{13}C_8$	109.5	109.8	109.2	109.1	109.4	109.3	109.5	109.6	109.6
C_2C_{16}	1.543	1.546	1.610	1.580	1.542	1.546	1.556	1.555	1.547
$C_{19}C_{21}$	1.537	1.539	1.542	1.550	1.523	1.528	1.545	1.540	1.532
$C_{19}C_{16}$	1.538	1.542	1.568	1.560	1.531	1.536	1.549	1.544	1.537
$C_{16}H_{39}$	1.117	1.116	1.124	1.114	1.123	1.117	1.089	1.088	1.091
$C_{19}H_{49}$	1.118	1.116	1.123	1.114	1.123	1.116	1.090	1.087	1.090
$C_{21}H_{42}$	1.116	1.114	1.118	1.112	1.120	1.107	1.088	1.087	1.090
$H_{46}C_{21}H_{42}$	106.8	106.6	101.9	105.0	108.0	106.2	107.6	106.9	106.9
$H_{42}C_{21}C_{19}$	110.2	110.1	111.0	110.5	109.8	110.2	109.9	110.0	110.0
$C_{16}C_{19}C_{21}$	110.1	109.8	111.7	110.6	109.8	109.8	110.2	110.3	110.4
$C_{16}C_{19}H_{49}$	109.5	109.5	108.9	109.5	109.2	109.2	109.1	109.0	109.3
$C_{21}C_{19}H_{49}$	108.8	109.1	108.2	107.9	109.5	109.5	109.3	109.3	109.3
$C_2C_{16}H_{39}$	109.5	109.5	108.7	110.0	109.1	109.2	109.0	108.8	108.8
$C_{15}C_{19}C_{16}C_{17}$	59.3	59.4	56.3	57.9	59.1	59.1	59.1	58.8	58.8
$C_{19}C_{16}C_2$	109.5	109.5	109.2	109.2	109.4	109.4	109.4	109.4	109.4
$C_{19}C_{16}H_{39}$	108.8	109.0	107.6	108.2	109.3	109.3	109.1	109.0	109.0

[a] The molecular structure of isotetramantane is shown in Figure 4. Bond lengths are in angstroms; bond angles and torsional angles are in degrees.
[b] See footnote *b* in Table I.
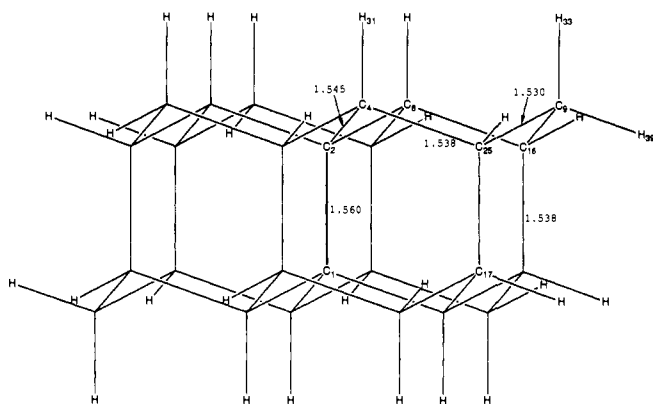
Figure 5. Cyclohexamantane, $C_{26}H_{30}$, D_{3d} symmetry; structure **6**. The C–C bond distances from the DZP SCF method are shown in the figure. Other theoretically predicted geometries are given in Table VI. The C_3 axis passes through C_1–C_2.

C_7–C_{13} and 1.523 Å for C_{19}–C_{21}. However, in the absence of an experimental structure, dogmatism should probably be avoided on whether AM1 was underestimating these bond lengths.

F. Cyclohexamantane, D_{3d}, $C_{26}H_{30}$. Cyclohexamantane (**6**; see Figure 5) differs from other polymantanes considered above. The other polymantanes (**2–5**) are chainlike combinations of adamantane units, whereas cyclohexamantane is "cyclic". Applying graph theory, one can use a point to represent the center of each adamantane cage. Two such points are connected by a line when the two adamantane cages are face-fused. The "graphs" for polymantanes **3–5** are "trees" (no cycles), while the graph for the cyclohexamantane molecule is a cycle. The graphs for **2–7**

are shown below, where VIa and VIb and VIIa and VIIb are isomorphic.
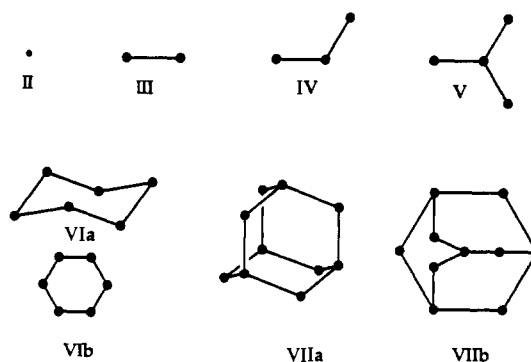
The molecular structure of cyclohexamantane (Figure 5) is composed of six adamantane cages face-fused in a cyclic manner; also recognizeable are two tiers supported by six "columns" on the circumference and a central bare carbon–bare carbon bond. The bond between the two bare carbon atoms (shown by the darker line in **6**) is the first considered in this paper.

The theoretical geometry of cyclohexamantane is presented in Table VI. The ab initio SCF CC bond lengths generally become shorter as bigger basis sets are used, with one exception. The central DZ SCF CC bond length is longer than the STO-3G SCF bond length by 0.004 Å. The MM3 CC bonds are generally longer than the ab initio SCF CC bonds as expected, with one important exception. The central MM3 C_1–C_2 bond length is shorter than the ab initio DZP SCF value by 0.011 Å. MINDO/3 gave a longest length for the central CC bond (1.660 Å).

Besides the central CC bond, the six column CC bonds in this

Table VI. Molecular Structure of Cyclohexamantane, $C_{26}H_{30}$, $D_{3d}{}^a$

	MM2	MM3	MINDO/3	MNDO	AM1	PM3	STO-3G	DZ	DZP
energy[b]	−34.3 kcal/mol	−37.2 kcal/mol	146.3 kcal/mol	0.7 kcal/mol	−50.0 kcal/mol	−40.5 kcal/mol	−990.513 92 au	−1001.832 60 au	−1002.323 10 au
C_1C_2	1.547	1.549	1.660	1.602	1.553	1.556	1.562	1.566	1.560
C_2C_4	1.543	1.547	1.598	1.574	1.538	1.543	1.555	1.552	1.545
C_4C_{25}	1.539	1.542	1.571	1.563	1.531	1.537	1.550	1.545	1.538
C_9C_{16}	1.535	1.536	1.539	1.547	1.522	1.527	1.544	1.538	1.530
C_4H_{31}	1.117	1.116	1.124	1.115	1.123	1.117	1.089	1.089	1.092
$C_{16}H_{47}$	1.118	1.116	1.123	1.114	1.123	1.116	1.089	1.087	1.090
C_9H_{33}	1.116	1.114	1.118	1.113	1.120	1.108	1.088	1.087	1.090
C_9H_{39}	1.116	1.114	1.118	1.113	1.120	1.107	1.088	1.087	1.090
$C_4C_2C_8$	110.1	110.0	112.3	110.8	110.1	110.0	110.2	110.4	110.5
$C_2C_8C_{16}$	109.6	109.6	109.3	109.4	109.4	109.4	109.6	109.6	109.6
$C_8C_{16}C_9$	110.0	109.7	111.6	110.6	109.8	109.8	110.1	110.2	110.2
$C_{16}C_9C_{25}$	109.4	110.0	110.4	109.8	110.0	110.0	109.5	109.6	109.6
$C_4C_2C_8C_{16}$	58.4	58.8	53.2	56.8	58.7	58.8	58.2	57.7	57.5
$C_2C_8C_{16}C_9$	59.2	59.1	56.2	58.3	59.1	59.2	59.0	58.8	58.7
$C_8C_{16}C_9C_{25}$	59.9	59.9	60.3	60.1	60.1	60.1	59.9	60.1	60.0
$C_2C_4H_{31}$	109.4	109.4	108.5	109.9	109.1	109.2	108.9	108.6	108.5
$C_8C_{16}H_{47}$	109.6	109.6	108.8	109.5	109.2	109.2	109.2	109.1	109.1
$H_{56}C_{25}C_4C_2$	178.8	179.0	175.6	177.2	179.3	179.2	179.2	178.9	178.8
$H_{33}C_9C_{25}C_4$	61.3	61.5	63.4	62.1	60.7	61.5	61.0	61.2	61.2
$H_{33}C_9H_{39}$	106.8	106.6	102.0	105.0	107.9	106.2	107.6	106.9	106.9
$C_{25}C_{17}$	1.538	1.541	1.572	1.562	1.533	1.537	1.549	1.546	1.538

[a] The molecular structures of cyclohexamantane is shown in Figure 4. Bond lengths are in angstroms; bond angles and torsional angles are in degrees. [b] See footnote b in Table I.

Table VII. Molecular Structure of the Adamantane-of-Adamantanes (7), $C_{35}H_{36}$, $T_d{}^a$

	MM2	MM3	MINDO/3	MNDO	AM1	PM3	STO-3G	DZ	DZP
energy[b]	−27.7 kcal/mol	−33.4 kcal/mol	261.0 kcal/mol	29.0 kcal/mol	−38.9 kcal/mol	−34.5 kcal/mol	−1330.881 04 au	−1346.086 22 au	−1346.738 30 au
C_1C_2	1.546	1.549	1.639	1.591	1.548	1.552	1.561	1.562	1.555
C_2C_9	1.542	1.545	1.595	1.573	1.537	1.543	1.554	1.550	1.543
$C_{12}C_{21}$	1.537	1.540	1.567	1.559	1.531	1.536	1.548	1.543	1.535
$C_{30}C_{21}$	1.535	1.536	1.538	1.547	1.522	1.528	1.544	1.537	1.530
C_9H_{39}	1.117	1.116	1.124	1.115	1.123	1.117	1.089	1.089	1.092
$C_{27}H_{57}$	1.118	1.116	1.123	1.114	1.123	1.116	1.089	1.087	1.090
$C_{30}H_{60}$	1.116	1.114	1.118	1.113	1.120	1.108	1.088	1.087	1.090
$H_{60}C_{30}H_{66}$	106.8	106.6	102.0	105.0	107.9	106.2	107.6	106.9	106.9
$C_{21}C_9H_{39}$	108.8	109.0	107.7	108.2	109.3	109.3	109.1	109.0	109.0
$C_{30}C_{27}H_{57}$	108.8	109.1	108.2	108.0	109.5	109.5	109.4	109.5	109.5
$C_{21}C_{30}C_{27}$	109.2	110.0	110.4	109.7	110.0	110.0	109.4	109.4	109.5
$C_2C_9H_{39}$	109.5	109.5	108.5	110.0	109.1	109.2	108.9	108.7	108.6

[a] This molecule may also be called superadamantane-5. The molecular structure of adamantane-of-adamantanes is shown in Figure 5. Bond lengths are in angstroms; bond angles and torsional angles are in degrees. [b] See footnote b in Table I.

molecule are also of interest. They have the same length by symmetry. All theoretical methods predicted a shorter CC bond length for the columns than the central one.

G. The Adamantane-of-Adamantanes, T_d, $C_{35}H_{36}$. The last molecule (7; see Figure 6) we considered has the chemical formula $C_{35}H_{36}$, point symmetry group T_d, and has been given as a descriptive name "the adamantane-of-adamantanes".[15] One can identify ten adamantane cages which are face-fused in the same manner as the carbon atoms in an adamantane molecule are bonded. The graph (see above, VIIa and VIIb) for the adamantane-of-adamantanes is isomorphic to the "chemical graph" of adamantane, which is usually constructed by simply taking the carbon atoms as vertices and carbon–carbon bonds as edges.

In 7 four bare carbon atoms are directly bonded tetrahedrally to a fifth bare carbon atom; these bonds are shown by darker lines. In other words, the carbon skeleton of neopentane is completely enclosed by other carbon atoms (or the neopentane skeleton is directly bonded only to other carbon atoms). In this sense, one can name 7 "superadamantane-5" (5 for five bare carbon atoms). This nomenclature scheme may be extended to even larger systems by changing the trailing numeral.

Due to its high symmetry (T_d), this much larger diamondoid molecule is actually much simpler than cyclohexamantane (**6**), isotetramantane (**5**), and triamantane (**4**) as far as the ab initio SCF geometry optimization is concerned.

Theoretical geometries for the adamantane-of-adamantanes are presented in Table VII. A more detailed comparison among the theoretical methods follows. MM3 CC bond lengths are longer
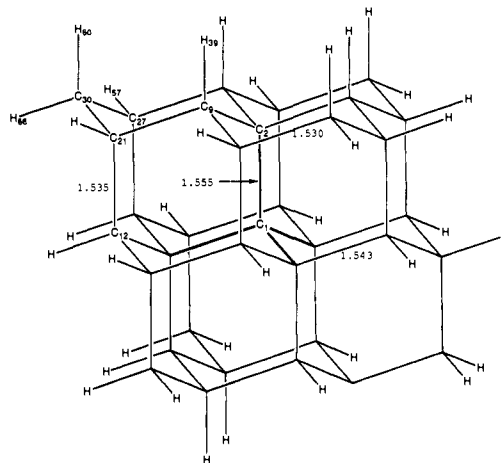

Figure 6. The adamantane-of-adamantanes, $C_{35}H_{36}$, T_d symmetry; structure 7. The predicted C–C bond lengths from the DZP SCF method are shown in the figure. Other theoretically predicted geometries are given in Table VII. The center of all symmetry elements rests with carbon C_1, and each symmetry C_3 axis passes through carbon C_1 and a carbon–carbon bond emanating from C_1.

than the MM2 values by a small amount, 0.003 Å. The MM3 CH bond lengths are shorter than the MM2 distances by 0.002 Å. The MM3 and MM2 bond angles are very close, differing by no greater than 0.8°. The DZP SCF CC bond lengths are

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shorter than the DZ SCF values by 0.007 Å. (However, the DZP SCF CH bond lengths are longer than the DZ SCF distances by 0.003 Å.) The DZP and DZ SCF bond angles are virtually identical. The behaviors of the MM2 and MM3 methods and that of the ab initio SCF method with different basis sets are all well expected. However, if we compare the MM3 (r_g) and DZP SCF (r_e) CC bond lengths, we find that all but one of the CC bond lengths fall within the expectation that r_g should be larger than r_e. The exceptional bond is the central C_1C_2 bond, with r_g(MM3) = 1.549 Å and r_e(DZP SCF) = 1.555 Å. MINDO/3 produced some very long CC bond lengths [e.g., C_1C_2(MINDO/3) = 1.639 Å], and some of its bond angles are far from other theoretical values. MNDO shows a considerable improvement over MINDO/3 in bond angles and bond lengths, although its bond lengths are still quite long [e.g., C_1C_2(MNDO) = 1.591 Å]. AM1 no longer produces long bonds, but some of its CC bond lengths seem to be too short [e.g., $C_{30}C_{21}$(AM1) = 1.522 Å]. Finally the PM3 method performed in a manner comparable to AM1, but its short CC bond problem is less severe.

The one earlier ab initio SCF study of this molecule is by Almlöf and Lüthi.[45] As discussed earlier (for adamantane), Almlöf and Lüthi were aiming at large carbon grains, and without analytic energy gradient techniques implemented, they did not completely optimize the molecular geometry. For this molecule in T_d symmetry, 12 symmetrized internal coordinates should be optimized, whereas Almlöf and Lüthi only optimized an overall CC bond length, assuming that all CC bonds had equal length. Also, due to the less complete DZ basis sets (Almlöf and Lüthi,[45] carbon = 7s3p/4s2p, hydrogen = 3s/2s, compared to the Huzinaga–Dunning[19,20] DZ used in the present study, carbon = 9s5p/4s2p, hydrogen = 4s/2s), the ab initio SCF total energy for this molecule reported by Almlöf and Lüthi[45] is −1344.906 65 au, while our result (in Table VII) is −1346.082 22 au.

Almlöf and Lüthi also considered a much larger T_d diamond cluster, $C_{84}H_{64}$, which may be thought of as encompassing the entire adamantane carbon skeleton, with additional carbon atoms to prevent any pair of hydrogen atoms from having too short an internuclear distance. One could call Almlöf and Luthi's molecule superadamantane-10, analogous to superadamantane-5.

H. Convergence toward the Diamond Lattice? i. Bond Lengths between Directly Bonded Bare Carbon Atoms. There is one pair of directly bonded bare carbon atoms in cyclohexamantane (6), the C_1–C_2 bond (Figure 5). Notice that the MINDO/3 prediction for this bond length is strikingly long (1.660 Å, Table VI), and the MNDO prediction is very long (1.602 Å). There are four bonds between bare carbon atoms in the adamantane-of-adamantanes (7; Figure 6), all of which are equivalent by symmetry. The MINDO/3 and MNDO carbon–carbon distances are again very long (Table VII). The AM1, PM3, MM2, and MM3 predictions are quite close. MM2 and MM3 predictions are smaller than the ab initio SCF values, even though the opposite is expected.

All theoretical methods used here predict at least somewhat longer lengths for these bare CC bonds than the CC distance in the diamond lattice, 1.5445 Å. It may be difficult to duplicate the bare carbon–carbon bond length in diamond using ab initio SCF methods with STO-3G, DZ, and DZP basis sets applied to diamondoid clusters. Clearly, crystal structures for the larger polymantane molecules would be of great value in clarifying this point.

ii. Total Energy of Bare Carbon Atoms by the ab Initio SCF Method. Our analysis of the ab initio SCF total energies for the clusters employs the well-known energy partition method.[52-54] The ab initio SCF total energy (E_{total}) is approximated by a sum of the energy of bare carbon atoms, and CH and CH_2 groups.

$$E_{total} = n_C E_C + n_{CH} E_{CH} + n_{CH_2} E_{CH_2} \qquad (1)$$

where n_C is the number of bare carbon atoms, and E_C is the energy

of the bare carbon atoms, etc. We may determine the energies of the groups by a standard linear multivariate least-squares fit. Here we only show the energies and estimated standard deviation for the STO-3G, DZ, and DZP results. With the estimated energy of a carbon atom in diamond, we may have an estimated cohesive energy (E_{coh}) of diamond using the following equation:[45]

$$E_{coh} = E_0 - E_C \qquad (2)$$

where E_0 is the energy of a free carbon atom determined at the same ab initio SCF level of theory (i.e., using the same basis set). The above defined cohesive energy is equal to the heat of sublimation at some finite temperature, if the zero-point vibrational energy of diamond and the change of the enthalpies with respect to temperature is properly taken into account. The experimental heat of sublimation of the diamond lattice is ∼710 kJ/mol, or ∼7.36 eV.[9] The results of the least-squares fittings are

	STO-3G	DZ	DZP
E_C, au	−37.437 97	−37.865 43	−37.882 19
E_0, au	−37.198 39	−37.684 51	−37.684 62
E_{coh}, eV	9.81	4.92	5.38
σ, au	0.000 85	0.001 11	0.000 72

We see that the cohesive energy estimated above does not take into account the zero-point vibrational energy and the contribution of heat capacity. Deficiencies in basis sets and lack of electron correlation treatment may well contribute to the discrepancy. But it seems that DZP SCF estimation is better than DZ SCF. The DZP SCF estimate here agrees closely with the 6-21G* Hartree–Fock crystalline orbital result of Orlando, Dovesi, Roetti, and Saunders.[46]

iii. Heats of Formation for 1–7. With the exception of cyclohexane (1) the semiempirical SCF models give quite different heats of formation for 1–7. AM1 and PM3 agree with each other reasonably well. MM2 and MM3 also agree with each other reasonably well. AM1 and PM3, and MM2 and MM3, predict the expected trend, where the heat of formation has a minimum with respect to the size of the cluster.

Ab initio SCF methods generally do not provide heats of formation directly, but several schemes can effectively relate the ab initio total energies to heats of formation of the compound, namely, the isodesmic and homodesmotic reaction schemes.[52-54] The isodesmic method gives heats of formation in general too positive. At the DZP SCF level of theory, the estimated heats of formation are −18.6, −2.7, +11.3, +24.7, +37.7, +65.1, and +114.3 kcal/mol for the molecules 1–7. Note that these estimates do not take into account the zero-point vibrational energy and heat capacity, both of which may have large effects.

The more sophisticated scheme of homodesmotic reactions recognizes the fact that ethane does not represent branching effects in hydrocarbon compounds. Therefore, instead of using ethane to simulate the clusters, branched molecules are used. For this purpose, we optimized the geometry for propane ($CH_3CH_2CH_3$, C_{2v}) which provides a secondary branch, isobutane [$CH(CH_3)_3$, C_3 symmetry was used] which provides a tertiary branch, and neopentane [$C(CH_3)_4$, T symmetry was used] which provides a four-way branch. As an example, the homodesmotic equation for the adamantane-of-adamantanes is

$$C_{35}H_{36} + 52C_2H_6 \leftrightarrow 5C_5H_{12} + 24C_4H_{10} + 6C_3H_8 \qquad (3)$$
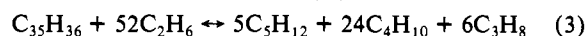
At the DZP SCF level of theory, the estimated homodesmotic heats of formation for 1–7 are −26.8, −32.2, −39.5, −47.9, −57.5, −58.6, and −71.7 kcal/mol, respectively. Note the monotonous trend, which is in contrast to MM2 and MM3, and AM1 and PM3. Comparing with available experimental data for cyclohexane,[53] adamantane,[55] and diamantane,[55] these homodesmotic estimations tend to be too negative.

While the scheme using homodesmotic equations is a big improvement over that using isodesmic equations, there are other effects it overlooks. One may construct a scheme to ensure balance

(52) Wiberg, K. B. *J. Comput Chem.* **1984**, *5*, 197.
(53) Ibrahim, M. R.; Schleyer, P. von R. *J. Comput. Chem.* **1985**, *6*, 157.
(54) Yala, Z. *J. Mol. Struct.*: THEOCHEM **1990**, *207*, 217.

(55) Clark, T.; Knox, T. M. O.; McKervey, M. A.; Mackle, H.; Rooney, J. J. *J. Am. Chem. Soc.* **1979**, *101*, 2404. The standard heat of formation for adamantane in the gas phase at 298 K is −31.76 ± 0.32 kcal/mol, and that for diamantane in the gas phase is −34.87 ± 0.64 kcal/mol.

of the cyclohexane rings, which would be "isocircular". Still more complicated schemes may be constructed to ensure balance of adamantane cages, giving rise to an "isonodal" scheme (with each adamantane cage thought of as a node).

There are two more problems associated with estimating the thermodynamics of the larger clusters. First, very large coefficients are involved in the hypothetical reactions and experimental errors are greatly amplified. For example, in the homodesmotic reaction for the adamantane-of-adamantanes (7), the estimated error for the heat of formation for the adamantane-of-adamantanes is

$$52\Delta H(\text{ethane}) + 5\Delta H(\text{neopentane}) + 24\Delta H(\text{isobutane}) + $$
$$6\Delta H(\text{propane})$$

Second, zero-point energies and the change of ethalpies with respect to temperature are not taken into account, because the ab initio SCF determination of all harmonic vibrational frequencies is not practical at this time for the larger clusters. In short, the estimation of highly accurate heats of formation from ab initio SCF total energies for the larger clusters here is not practical at the present time.

Schulman and Dish[44] estimated the heat of formation for adamantane using a homodesmotic reaction and another scheme which balances the cyclohexane rings (in the same spirit as the isocircular scheme). Good results were obtained for the relatively simple molecule adamantane.

Conclusions

We have applied molecular mechanics (MM2 and MM3), semiempirical SCF methods (including the MINDO/3, MNDO, AM1, and PM3 models as implemented by J. J. P. Stewart in the Package MOPAC 5.0), and ab initio direct SCF method with analytic energy gradients, as implemented by R. Ahlrichs and his group in the package TURBOMOLE, used here in conjunction with three standardized basis sets, STO-3G, DZ, and DZP, to seven clusters modeled on the diamond lattice. These clusters range in size from cyclohexane (C_6H_{12}, D_{3d}) (1) to the adamantane-of-adamantanes ($C_{35}H_{36}$, T_d) (7). All geometries are fully optimized, in the MM2 and MM3 and the ab initio SCF methods within the appropriate symmetry constraints using analytic energy gradients, and in semiempirical SCF methods (MOPAC) using Cartesian coordinates (without any symmetry constraints). Our general conclusion is that the clusters used here are still some distance from approaching the infinite diamond lattice. The bare carbon–carbon bond lengths predicted for the clusters are somewhat longer than diamond's 1.5445 Å. The energy of the bare carbon atom estimated using energy partition is quite a bit higher too. Larger clusters, larger basis sets, and presumably higher levels of ab initio theory incorporating electron correlation effects are required. For example, the use of larger basis sets is expected to yield SCF carbon–carbon bond distances closer to 1.5445 Å.

However, the present research does reveal many useful insights. From comparing the predictions of these widely differing theoretical approaches, their merits and shortcomings are apparent. Ab initio SCF methods with good basis sets (as good as DZ and DZP used here) give reasonably accurate molecular geometries in general and consistent total molecular energies. The ab initio SCF method is much more demanding on computational hardware than the other methods used here.

Within the group of semiempirical SCF models, PM3 and AM1 seem to be an improvement over the earlier models MINDO/3 and MNDO insofar as the carbon–carbon bond distances and the heats of formation are concerned. The MINDO/3 model greatly underestimates the thermodynamic stability of the clusters here; it also yields some long carbon–carbon bond distances, up to 1.6 Å. The carbon–carbon bond lengths predicted by AM1 and PM3 are in some cases shorter than normal expectations, giving as low as 1.52 Å for several bonds.

MM2 and MM3 molecular mechanics methods give very good molecular geometries, in good agreement with available experimental data and with the ab initio DZP SCF method, except for those bond distances between the bare carbons. The heats of formation predicted by MM2 and MM3 models first get progressively more negative and then progressively less negative (with the isotetramantane being the most thermodynamically stable compound of the seven). This parallels the predictions of the semiempirical AM1 and PM3 models.

With this research, theory is now well ahead of experiment with respect to understanding the approach to the diamond limit of hydrocarbon molecular structures. At this point it would be extremely valuable to have crystal structures and thermodynamic information for several of the important molecules studied here. To date there is no such experimental characterization for triamantane (4, $C_{18}H_{24}$), isotetramantane (5, $C_{22}H_{28}$), cyclohexamantane (6, $C_{26}H_{30}$), or the adamantane-of-adamantanes (7, $C_{35}H_{36}$). The theoretical methods employed here produce a rather wide range of predictions, and it may reasonably be concluded that the ab initio results are the most reliable. However, the availability of hard experimental facts for these prototypical large molecules would provide an unequivocal evaluation of the different theoretical approaches.