J. Phys. Chem. A **2000,** *104,* 6622−6627

Ab Initio Investigation of Strain in Group 14 Polyhedrane Clusters (M_nH_n: $n = 4, 6, 8, 10, 12, 16, 20, 24$)

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Received: January 6, 2000; In Final Form: May 2, 2000

The results of ab initio calculations on a series of $[MH]_n$ polyhedral cages (M = C, Si, Ge, and Sn; $n = 4$, 6, 8, 10, 12, 16, 20, and 24) are presented. The energies are partitioned into contributions from each ring to obtain an estimate of how strain changes as a function of ring size for each of these elements. Results of these calculations indicate that three-membered rings are significantly strained for all of these elements, and five- and six-membered rings have similar stability. The relative strain in four-membered carbon rings appears to be significantly higher than the strain in four-membered rings of heavier Group 14 elements. These partitioned ring energies can be applied to predict the relative stability of other cages.

Introduction

Regular polyhedral clusters have long been the subject of scientific curiosity. Prismane (C_6H_6),[1] cubane (C_8H_8),[2] pentaprismane ($C_{10}H_{10}$),[3] and dodecahedrane ($C_{20}H_{20}$)[4] have all been synthesized and fully characterized, and simple derivatives of tetrahedrane (C_4H_4) are also known. The smaller members of this series are highly strained due to the presence of three- and four-membered rings. However, dodecahedrane, which contains only five-membered rings, is significantly less strained. Paquette's group has determined the experimental value for the strain in dodecahedrane to be 61.4 kcal/mol,[5] which is significantly smaller than the strain in tetrahedrane (140.0 kcal/mol) or cubane (154.7 kcal/mol).[6]

While a large number of regular organic polyhedral clusters and their derivatives have been synthesized, a more limited number of these types of clusters containing heavier Group 14 elements have been prepared.[7] These include[8] $[RSi]_4$ (R = ^{t}Bu$_3$Si[9]), $[RSi]_6$ (R = DIPP[10]), $[RSi]_8$ (R = ^{t}BuMe$_2$Si,[11] ^{t}Bu,[12] 1,1,2-trimethylpropyl,[13] and DEP[14]), the germanium cages $[RGe]_6$ (R = $(Me_3Si)_2CH$[15] and DIPP[10]) and $[RGe]_8$ (R = DEP[14]), and the tin compounds $[RSn]_8$[16] and $[RSn]_{10}$[17] (R = DEP).

Polyhedral cages have been the subject of a large number of theoretical investigations. Some of these results are summarized in Table 1. The results of ab initio calculations using double-ζ basis sets which include polarization functions are generally in good agreement with experimental results. For example, the calculated heat of formation of cubane (at RHF/6-31G*)[18] is 133.2 kcal/mol, which compares very well with the experimental value of 148.7 kcal/mol.[19] Disch and Schulman[20] have calculated (at RHF/6-31G*) the heat of formation of dodecahedrane to be 18.9 kcal/mol, in excellent agreement with the experimental value of 18.2 kcal/mol.[5] A high-level G2 calculation[21] on tetrahedrane predicts a $\Delta H_f^\circ = 535$ kJ/mol (128 kcal/mol) and a strain energy of 571 kJ/mol (136 kcal/mol). Since the successful isolation of C_{60}, a number of workers have reported results of calculations on pure carbon clusters. For example, Jones has reported results of a density functional study[22] of carbon clusters C_{2n} ($2 \leq n \leq 16$).

TABLE 1: Summary of Previously Calculated Strain Energies (kcal/mol) of Polyhedral Clusters

	C	Si	Ge	Sn	Pb
tetrahedrane	141.4[a]	22,[b] 140.3[a]	140.3[a]	128.2[a]	119.3[a]
prismane	145.3[a]	11,[b] 118.2[a]	109.4[a]	93.8[a]	65.2[a]
cubane	158.6[a]	99.1[a]	86.0[a]	70.1[a]	59.6[a]
(D_5h) $M_{10}H_{10}$	136.0[c]	82.8[d]			
(D_6h) $M_{12}H_{12}$	172.2[c]	102.1[d]			

[a] Nagase, S. *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 329. [b] Sax, A. F.; Kalcher, J. *J. Chem. Soc., Chem. Commun.* **1987**, 809. [c] Reference from Nagase, S. *Polyhedron* **1991**, *10*, 129. [d] Nagase, S. *Polyhedron* **1991**, *10*, 129.

While strain in hydrocarbons has been widely studied, much less is known about strain in heavier elements. It is expected that strain should change, perhaps dramatically, as one descends a column of the periodic table. To pick a common example, the H−N−H bond angles in NH_3 are 106.6°, while the H−P−H bond angles in PH_3 are 93.8°.[23] This tendency can be attributed to the larger separation of s- and p-orbital energies, giving rise to an inert ns^2 pair.

The goal of the present investigation is to examine a series of Group 14 clusters using a consistent level of theory in order to determine factors that influence relative stability. It is hoped that these results will prove to be a useful guide to further synthesis of heavier polyhedral clusters. For example, all of the heavier polyhedral compounds synthesized to date contain bulky substituents. While these groups undoubtedly provide steric hindrance to help protect the heavy atom centers from further attack during synthesis, Nagase has performed ab initio calculations[24] that suggest that substituents can also decrease the strain in smaller silicon clusters ($[RSi]_n$, $n = 4, 8$). These calculations suggest that R = SiH_3 groups should give rise to less strained clusters than either R = CH_3 or R = H.

Earlier investigations on smaller clusters have indicated that inclusion of polarization functions is necessary. For example, Sax et al.[25] have performed calculations that would suggest that persilabenzene is more stable than persilaprismane. However, upon addition of *d*-type polarization functions, this conclusion is reversed, with the prismane analogue being calculated as 41 kJ/mol more stable than the benzene analogue. Calculations on silicon cages using either a 6-31G* basis set or an effective core potential appear to be in excellent agreement. For example, Nagase's group has calculated the strain in the series $[HSi]_n$

10.1021/jp000090u CCC: $19.00

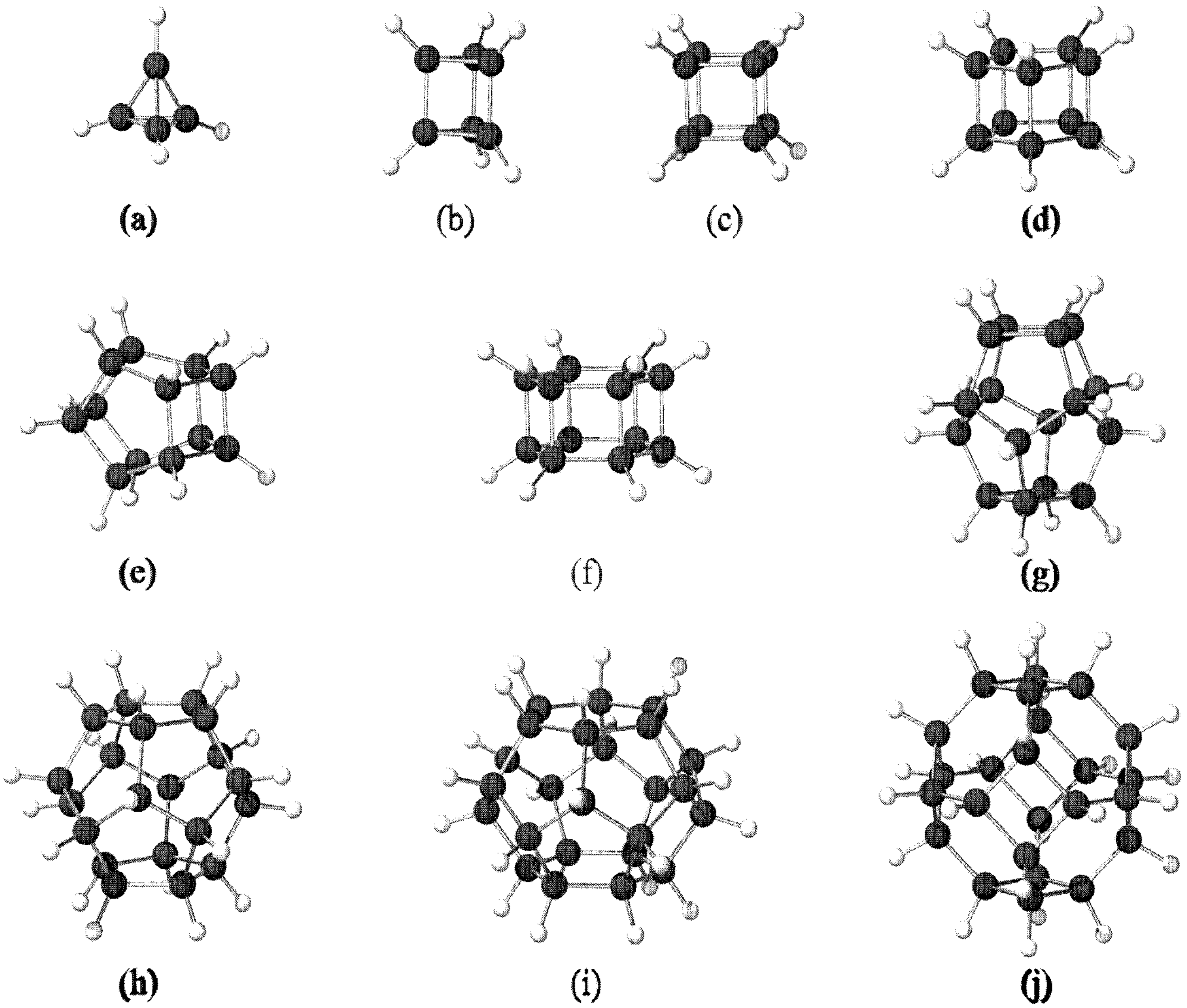

Figure 1. Representative structures of molecules included in this study: (a) T_d M_4H_4, (b) D_{3h} M_6H_6, (c) O_h M_8H_8, (d) D_{5h} $M_{10}H_{10}$, (e) D_{2d} $M_{12}H_{12}$, (f) D_{6h} $M_{12}H_{12}$, (g) D_{4d} $M_{16}H_{16}$, (h) D_{5d} $M_{20}H_{20}$, (i) D_{6d} $M_{24}H_{24}$, and (j) O_h $M_{24}H_{24}$.

($n = 4$, 6, and 8) using both a 6-31G* basis set[26] and an effective potential.[27] In all cases, the results agree within 6% (<6 kcal/mol, see Table 1).

Calculations using density functional theory have been somewhat inconsistent. Grimme performed calculations using density functional theory to determine strain[28] in some of the smaller carbon clusters (tetrahedrane, prismane, and cubane) and obtained results in excellent agreement with experiment. However, Ball has reported[29] somewhat surprising results which suggest that density functional calculations do a relatively poor job of predicting ΔH_f for both tetrahedrane and cubane. Comparing results using a variety of basis sets (6-31G* to 6-31+G**) and exchange functionals (SVWN, BP, BLYP, and B3LYP), calculated values for ΔH_f for cubane ranged from 108.5 to 170.8 kcal/mol. For comparison, reported values for HF/STO-3G, HF/4-31G, HF/6-31G*, and MP2/6-31G*//HF/6-31G* range from 137.9 to 149.9, with the experimental value reported as 148.7 kcal/mol.

In the present study, a series of polyhedral clusters having the general formula (M_nH_n: M = C, Si, Ge, and Sn; $n = 4$, 6, 8, 10, 12, 16, 20, and 24) are examined using ab initio electronic structure calculations. Representative structures are shown in Figure 1. All of the compounds in this series contain tetrahedral, tertiary heavy atom centers with a single M−H bond. Several of these compounds (D_{2d} $M_{12}H_{12}$, $M_{16}H_{16}$, and D_{6d} $M_{24}H_{24}$) contain rings that are not required by symmetry to be planar, and thus are expected to have reduced torsional strain. Results from those molecules that contain strictly planar rings are emphasized so that rings in different molecules can be compared directly. By performing calculations on the same types of cages for each element in this series, it should be possible to make realistic comparisons of how angle strain changes for heavier elements.

Computational Methodology

All calculations were performed using the Gamess[30] program. Calculations were performed primarily on personal computers running under the Linux operating system (Linux−Mandrake version 6.0), although a few calculations were performed on a Digital Equipment Corporation ALPHA AXP-3000. For carbon, the 6-31G(*d*) basis set of Pople et al. was used,[31] while for silicon, Gordon's 6-31G(*d*) basis set[32] was used. For silicon, germanium, tin, and lead, the CEP-31G(*d*) basis set was used. This is the effective core potential basis set of Stevens, Basch, and Krauss,[33] which is a double-ζ valence description augmented by a set of five *d*-type polarization functions. All calculations were performed using direct SCF procedures.[34]

Molecular geometries were fully optimized within the indicated symmetry constraints by optimization of Cartesian coor-

TABLE 2: Summary of Calculated Bond Distances (Å) in Cages Containing Only Planar Rings

		6-31G(d)		effective core calculations		
$[MH]_n$		C	Si	Si	Ge	Sn
T_d $[M_4H_4]$	M−M (3R)	1.463	2.320	2.322	2.459	2.838[a]
D_{3h} $[M_6H_6]$	M−M (3R)	1.507	2.366	2.365	2.493	2.867
	M−M (4R)	1.549	2.382	2.382	2.489	2.850
O_h $[M_8H_8]$	M−M (4R)	1.559	2.402	2.400	2.505	2.867
D_{5h} $[M_{10}H_{10}]$	M−M (4R)	1.558	2.400	2.399	2.503	2.866
	M−M (5R)	1.552	2.398	2.398	2.497	2.858
D_{6h} $[M_{12}H_{12}]$	M−M (4R))	1.554	2.398	2.397	2.502	2.865
	M−M (6R)	1.551	2.397	2.398	2.498	2.858
D_5d^b $[M_{20}H_{20}]$	M−M (5R)	1.548	2.391	2.392	2.482	2.841
O_h $[M_{24}H_{24}]$	M−M (4R)	1.557	2.397	2.397	2.497	2.858
	M−M (6R)	1.531	2.381	2.385	2.476	2.834
T_d $[M_4H_4]$	M−H	1.063	1.469	1.476	1.524	1.694[a]
D_{3h} $[M_6H_6]$	M−H	1.074	1.481	1.489	1.543	1.712
O_h $[M_8H_8]$	M−H	1.081	1.482	1.490	1.538	1.706
D_{5h} $[M_{10}H_{10}]$	M−H	1.082	1.484	1.492	1.542	1.710
D_{6h} $[M_{12}H_{12}]$	M−H	1.083	1.486	1.494	1.544	1.712
$D_{5d}{}^b$ $[M_{20}H_{20}]$	M−H	1.084	1.487	1.495	1.544	1.713
O_h $[M_{24}H_{24}]$	M−H	1.083	1.488	1.497	1.548	1.717

[a] Results reported for transition state containing one triply degenerate imaginary frequency. [b] The full symmetry of this molecule is actually I_h.

dinates using Baker's method.[35] The convergence criteria used with the Gamess program required that both the maximum and RMS gradient components be less than 10^{-4} and $^1/_3 \times 10^{-4}$ au, respectively (default values). Force calculations were performed on MH_4, M_2H_6, M_4H_4, M_4H_{10}, M_6H_6, and M_8H_8 (M = C, Si, Ge, Sn) to characterize the stationary points obtained. For all but Sn_4H_4 (see results) the Hessian matrixes were positive definite, which verified that these optimizations had converged to local minima on the potential energy surface. Due to computational restraints, force calculations have not been completed on the larger molecules. Since frequency calculations were not performed on all molecules, the total energies reported do not include in any corrections for zero-point vibrational energy.

Strain energies were calculated using the homodesmotic reaction:[36]

$$[HM]_n + {}^3/_2 n H_3M{-}MH_3 \rightarrow n(MH_3)_3MH$$

Using the total energies calculated for each of the molecules in this reaction, the change in energy of the above reaction is calculated, which is assumed to be equal to the strain energy of the cluster.

Results and Discussion

Calculated geometries for all compounds included in this study that contain only planar rings are summarized in Table 2. These results are in excellent agreement with previous calculations, and are generally in good agreement with experimental results.

The experimentally determined Si−Si bond lengths in the tetrahedral core of the $Si_4(^tBu_3Si)_4$ molecule[9] range from 2.315 to 2.341 Å, compared with the theoretical value of 2.320 Å. In the prismane analogue $Si_6(DIPP)_6$,[10] the Si−Si bonds in the three-membered rings (3R) range from 2.374 to 2.387 Å (av 2.380 Å) and range from 2.365 to 2.389 Å (av 2.373 Å) in the four-membered rings (4R). The calculated values in Si_6H_6 are comparable in magnitude (2.366 Å in the 3R and 2.382 Å in the 4R), but show the opposite trend with bond lengths in 4R greater than those in 3R. A number of $[RSi]_8$ silacubanes have been characterized crystallographically. For R = ^{t}Bu,[12] the Si−Si bond distances range from 2.374 to 2.400 Å, for R = DEP,[14] the average Si−Si bond distance is 2.399 Å, and for R = 1,1,2-trimethylpropyl,[13] the average Si−Si bond distance is 2.421 Å. The calculated Si−Si bond distances in Si_8H_8 of 2.402 Å compare favorably with these values.

The experimental Ge−Ge bonds in the prismane cage $Ge_6[(Me_3Si)_2CH]_6$[15] average 2.58 and 2.52 Å in the 3R and 4R, respectively. In $Ge_6(DIPP)_6$, the Ge−Ge bond lengths average 2.503 Å (3R) and 2.468 Å (4R). These compare reasonably well with the 2.493 Å (3R) and 2.489 Å (4R) bond lengths obtained in the present work. In the cubane analogue $Ge_8(DEP)_8$, the average Ge−Ge bond distance is 2.490 Å, which is slightly shorter than the 2.505 Å calculated for Ge_8H_8. The lengthening of the Ge−Ge bonds in $Ge_6[(Me_3Si)_2CH]_6$ and the fact that the bonds within the three-membered rings are longer than those in 4R can be attributed to steric repulsion.

The Sn−Sn bonds in the tin cubane analogue Sn_8(2,6-diethylphenyl)$_8$[16] range from 2.839 to 2.864 Å (av 2.854 Å), which is slightly shorter than the 2.867 Å calculated for Sn_8H_8. For Sn_{10}(2,5-diethylphenyl)$_{10}$,[17] the Sn−Sn bonds average 2.856 Å in both 4R and 5R, which is shorter than the 2.866 Å (4R) and 2.858 Å (5R) calculated in this work. Nagase[27] also obtained slightly longer calculated bond lengths in Sn_8H_8 (2.887 Å) using a different pseudopotential.

Examination of calculated geometries given in Table 2 reveals a few significant trends. In all cases, the shortest M−M bonds were found in the tetrahedranes. This presumably occurs to allow maximum overlap of the bonding orbitals in these highly strained compounds. For carbon and silicon, this trend carries over into the prismane structures, which contain shorter M−M bonds within the three-membered rings and slightly longer M−M bonds within the four-membered rings. However, for germanium and tin, the opposite trend is observed. In all molecules, the longest M−M bonds are found in the cubanes.

For all of the smaller cages ($n \leq 8$), calculations of the force constant matrix were performed to verify that the stationary points obtained were minima on the potential energy surface. For the Sn_4H_4 tetrahedral cluster, a single triply degenerate imaginary frequency was obtained, corresponding to motion of the terminal hydrogen atoms toward bridging positions. All attempts to locate a true ground state containing nonbridging hydrogen atoms failed (even in the absence of any symmetry constraints). While it was originally intended to include lead clusters in the present investigation, force calculations on Pb_4H_4, Pb_6H_6, and Pb_8H_8 all resulted in imaginary frequencies being obtained.

While other workers[7b,24,27] have reported results of theoretical investigations on both Sn_4H_4 and Pb_4H_4, there are several indications in the literature that these highly strained molecules are not expected to be stable. Srinivas and Jemmis[37] reported results of ab initio calculations using both the LANL1DZ and a quasirelativistic pseudopotential basis set on various hydrogen-bridged isomers of M_4H_4 clusters. In several cases, the tetrahedral geometry was found to be transition state by one method, but a ground state by a different method (changing basis set or addition of correlation). More significantly, these workers found that triply or quadruply η^2 hydrogen-bridged structures were more stable than the corresponding tetrahedranes for Si, Ge, Sn, and Pb clusters.[38] Lead showed the strongest preference for H-bridging structures. Nagase and Nakano[39] have performed calculations (at the MP2/6-31G*//RHF/6-31G* level) on Si_4H_4 that suggest that the barrier to dissociation of one of the Si−Si bonds is near zero. While no attempt was made to

TABLE 3: Summary of Theoretical Strain Energies (kcal/mol) for Polyhedral Cages Calculated from Homodesmotic Reactions[a]

$[MH]_n$		6-31G(d)		effective core calculations		
n	symmetry	C	Si	Si	Ge	Sn
4	T_d	141.5	140.2	141.3	145.3	133.7[b]
6	D_3h	145.4	112.8	113.7	109.3	97.0
8	O_h	158.7	91.4	91.6	84.4	71.0
10	D_5h	135.9	81.2	82.5	73.3	60.1
12	D_6h	172.2	99.5	101.6	91.9	75.0
12	D_2d	109.7	70.3	72.9	65.2	52.6
16	D_4d	71.2	50.1	55.3	47.3	35.2
20	D_5d[c]	43.7	32.0	40.0	32.2	19.5
24	D_6d	75.7	42.0	51.6	43.1	26.5
24	O_h	205.4	106.1	114.7	104.2	77.4

[a] See text for details. [b] Results reported for transition state containing one triply degenerate imaginary frequency. [c] The full symmetry of this molecule is actually I_h.

account for electron correlation in the present study, it appears that this could be a significant factor for some of the heavier, more highly strained systems.

While ring strain is predicted to be somewhat smaller in the heavier cages (see below), the bonds are also expected to be significantly weaker. Both previous efforts and the present calculational study suggest that ring strain in the heaviest (particularly tin and lead) hydride clusters is sufficiently large enough to overcome the metal−metal bond strengths, and alternate structures are preferred. However, isolation of compounds containing these tetrahedral cores may still be possible under the appropriate conditions. Compounds containing Si_4 and Ge_4 cores have already been isolated experimentally in clusters containing bulky ligands, and calculations suggest[24] that electron-withdrawing substituents can help stabilize these clusters. Thus, the most reasonable synthetic strategy for isolation of these compounds would appear to involve use of bulky, electropositive substituents and trapping the cluster as a kinetic product.

Calculated strain energies for all compounds included in this study are given in Table 3. These results are in excellent agreement with previous calculations. In all cases, the icosahedral petagonal dodecahedrane ($M_{20}H_{20}$) was calculated to be the most stable. The D_{6d} $M_{24}H_{24}$ structure also appears to be a viable synthetic target, especially for elements heavier than carbon. For all elements heavier than carbon, the tetrahedrane (M_4H_4) structure was calculated to have the most strain.

A quick examination of the calculated strain energies for carbon cages does not reveal any obvious trends. An estimate of the strain per heavy atom is more informative, and can be found by dividing the strain energies by the number of atoms in each cage. These results are shown in Table 4. In all cases, tetrahedrane analogues are calculated to contain the most strain per atom, followed by the prismanes and the cubanes. Of all of the structures considered, the icosohedral $M_{20}H_{20}$ is calculated to be the least strained, although the strain in the D_{6d} $M_{24}H_{24}$ cages also appears to be relatively low. Finally, the double five-ring (D_{5h} $M_{10}H_{10}$) is always found to have less strain than the double six-ring (D_{6h} $M_{12}H_{12}$). This leads to the rather unremarkable conclusion that the strain (per atom) decreases in the order 3R > 4R > 6R > 5R. This conclusion appears to be valid for all Group 14 elements, although the strain is generally smaller in the heavier elements. To quantify these results, an alternate energy partitioning scheme was examined.

TABLE 4: Calculated Strain Energies Normalized by the Number of Atoms in Each Cage (kcal mol^{-1} $atom^{-1}$)

$[MH]_n$		6-31G(d)		effective core calculations		
n	symmetry	C	Si	Si	Ge	Sn
4	T_d	35.38	35.06	35.32	36.34	33.42[a]
6	D_3h	24.24	18.80	18.94	18.22	16.16
8	O_h	19.83	11.42	11.45	10.55	8.87
10	D_5h	13.59	8.12	8.25	7.33	6.01
12	D_6h	14.35	8.29	8.47	7.66	6.25
12	D_2d	9.14	5.86	6.08	5.43	4.38
16	D_4d	4.45	3.13	3.46	2.96	2.20
20	D_{5d} (I_h)	2.18	1.60	2.00	1.61	0.97
24	D_6d	3.15	1.75	2.15	1.80	1.11
24	O_h	8.56	4.42	4.78	4.34	3.22

[a] Results reported for transition state containing one triply degenerate imaginary frequency.

TABLE 5: Number and Type of Rings Present in Each of the Cages Containing Only Planar Rings

	symmetry	#3R	#4R	#5R	#6R
M_4H_4	T_d	4			
M_6H_6	D_3h	2	3		
M_8H_8	O_h		6		
$M_{10}H_{10}$	D_5h		5	2	
$M_{12}H_{12}$	D_6h		6		2
$M_{20}H_{20}$	D_{5d} (I_h)			12	
$M_{24}H_{24}$	O_h		6		8

TABLE 6: Partitioned Ring Energies (kcal mol^{-1} $atom^{-1}$) Relative to Calculated Energy of 3R[a]

	3R[b]	4R	5R	6R	av error[c]
C	−	−5.23	−11.02	−10.65	±0.10
Si[d]	−	−7.86	−11.11	−11.24	±0.08
Ge	−	−8.63	−11.51	−11.50	±0.12
Sn[e]	−	−7.33	−9.97	−10.09	±0.05[e]

[a] See text for details. [b] The partitioned ring energies for the 3R are C = −38.3997, Si = −289.4560, Ge = −4.2550, and Sn = −3.8430 au/ring. [c] Average error = $\sqrt{\sum(E_{RHF}-E_{rings})^2/n}$, where E_{RHF} is the ab initio total energy divided by the number of heavy atoms and E_{rings} is the energy calculated using the partitioned ring energies (also normalized by dividing by the number of heavy atoms). [d] Values given based on 6-31G(d) basis set. Values calculated using effective potential agree within 1%. [e] Energy of 3R calculated on the basis of energy of 3R in perstannaprismane since the T_d Sn_4H_4 structure was not a ground state.

While the normalized strain energies give an average contribution per atom to strain in these cages, these values do not give any real information of the source of this strain. To determine if the relative stability of the cages could be related in a simple manner to ring strain, the geometry of the seven polyhedranes containing planar rings is decomposed to show the number and type of each ring present. (See Table 5 and Figure 1). The calculated total energy of each cage was partitioned using a least-squares fitting procedure into contributions from each type of ring.[40] Dividing these estimated energies by the number of atoms in each ring gives a normalized value of strain per atom that allows comparison between different ring sizes. These results are summarized in Table 6 relative to the energy of an atom in a three-membered ring (3R). These values generally follow the expected trend. In all cases, atoms in three-membered rings are the least stable (most strained), while atoms in five- and six-membered rings are the most stable (least strained). Since the bond angle in a regular five-membered ring (108°) is closest to the ideal tetrahedral angle (109.47°), 5R is expected to be the most stable for planar rings. This is the observed result for carbon. However, for all of the heavier elements, the normalized energy of atoms in 5R indicates that these are approximately equally or even slightly less stable than atoms in 6R using this energy partitioning scheme.

The error in these partitioned ring energies is estimated by comparing the ab initio calculated total energy with the energy calculated using the ring energies. In all cases, the difference is

<0.65 kcal mol^{-1} $atom^{-1}$. For all molecules, the largest difference between the calculated RHF total energy and the total energy calculated on the basis of the partitioned ring energies is for the prismanes (M_6H_6). Comparing prismane ($[3R]^2$ $[4R]^3$) with tetrahedrane ($[3R]^4$) and cubane ($[4R]^6$), the total energy of prismane can be approximated as

$$E_{\text{prismane}} = {}^{1}/_{2}E_{\text{tetrahedrane}} + {}^{1}/_{2}E_{\text{cubane}}$$

In all cases the total energies from the ab initio calculations indicate that the prismane molecule is slightly more stable than this simple averaging method would predict. The difference between the full ab initio calculation and the simple average is 2.8 to 5.6 kcal/mol. This difference is believed to be due to extra stability associated with changes in bond strength. In all cases, the heavy atom bonds in the tetrahedranes are shorter than in the cubanes. In the prismanes, the bond lengths are all between these two extremes. The bonds in prismane are not of equal strength, and any weakening of bonds within three-membered rings (longer bonds, less overlap) appears to be more than offset by strengthening of bonds within four-membered rings. Smaller differences in bond lengths are found in larger rings, and the differences in rings (and thus the partitioned ring energies) found in difference cages are much smaller. For example, when the energy of $M_{10}H_{10}$ is estimated as a weighted average of the cubane and dodecahedrane structures,[41] the difference between this average and the ab initio total energy is about half of that observed for the prismanes. These conclusions about bonding in the prismane molecules are supported by analysis of bonding in cages using the “atoms in molecules” approach.[42] Grimme[28] performed an analysis of bonding in strained carbon cages and found that the C−C bonds in the three-membered rings in prismane are significantly less strained (and less bent) than the bonds in three-membered rings in tetrahedrane (21.0 vs 25.7 kcal/mol). Matsunaga and Gordon found[43] that the electron density at the bond critical points in the 3R bonds of Si_6H_6 is lower than the electron density in 4R, implying weaker bonds.

While the partitioning of ring energies in this manner is obviously a rather crude approximation, this scheme can be applied with some success to compounds not included in the present study. Disch and Schulman[20] reported results of 6-31G* calculations that indicate that the T_d isomer of $C_{12}H_{12}$ ($[3R]^4$ $[6R]^4$) is expected to be more stable than the D_{6h} (double six-ring, $[4R]^6$ $[6R]^2$) isomer. This appears to be a somewhat surprising result, given the large number of highly strained three-membered rings that would be present in this structure. The explanation for this appears to be due to the strain in four-membered rings. The partitioned ring energies indicate that the atoms in five- and six-membered rings are about 10−11.5 kcal mol^{-1} $atom^{-1}$ less strained than the atoms in three-membered rings for all Group 14 elements. However, the four-membered ring for carbon appears to contain significant strain. The presence of a large number of four-membered rings makes the D_{6h} isomer of $C_{12}H_{12}$ less stable than the T_d isomer.

Using the partitioned ring energies listed in Table 6, the T_d isomer of $C_{12}H_{12}$ is also predicted to be more stable than the D_{6h} isomer. However, the difference in energy between these two structures calculated by Disch and Schulman is significantly larger (∼60 kcal/mol) than that calculated using the partitioned ring energies (∼2 kcal/mol). Careful examination of the structure of the T_d molecule reveals that the C−C bonds are calculated to be unusually short. In particular, the bonds in the six-membered rings (1.501 Å) are slightly shorter than the bonds within the three-membered rings (1.505 Å). The C−H bonds are also somewhat shortened at 1.076 Å. These structural deviations appear to reduce the strain in this molecule, making it more stable than predicted on the basis of the simple ring partitioning scheme presented here.

The present partitioning scheme indicates that the four-membered ring for carbon is significantly more strained than it is in heavier elements. A similar conclusion was reached by Nagase.[27] When the partitioned ring energies are applied to heavier members of the $M_{12}H_{12}$ structure, the results are different than those obtained for $C_{12}H_{12}$. In all cases, the T_d isomer is predicted to be more strained (by ∼50−70 kcal/mol) than the D_{6h} isomer. This conclusion has been verified by full ab initio calculations on the T_d isomers. For these heavier molecules, the calculated energy differences ($E[D_{2d}] - E[T_d]$) using the partitioned ring energies are between 5 and 10 kcal/mol of the differences calculated using RHF/6-31G(*d*) total energies.[44]

Strain energies have also been calculated for the D_{2d} isomer of $M_{12}H_{12}$ ($[4R]^4$ $[5R]^4$). While this compound contains nonplanar rings, it is predicted to be significantly less strained than the D_{6h} isomer for all Group 14 elements. Calculated total energies[45] of $M_{12}H_{12}$ isomers indicate that the D_{2d} structures are less strained than the T_d isomers also. While the D_{2d} structure contains nonplanar rings, the partitioned ring energies can be applied to this molecule with reasonable success. For carbon, the calculated energy using the partitioned ring energies is within 9 kcal/mol of the RHF/6-31G*(d)* total energy. For the heavier elements, this difference is ∼1 kcal/mol.

Conclusion

Calculations on a series of M_nH_n polyhedral cages indicate that strain decreases as one descends Column 14 of the periodic table. However, since this is also accompanied by a decrease in bond strength, isolation of the most highly strained heavy atom cages is expected to be difficult. Strain in four-membered rings appears to be much less significant for heavier elements compared with C_4 rings, suggesting that the isolation of a variety of heavy cages containing four-membered rings (such as the already isolated R_8Sn_8) is promising. In this paper, an extremely simple approximation based on the number of atoms in a ring is presented that allows a crude approximation of the relative stability of cages.

Acknowledgment. Support for this project from the Kent State University−Stark Campus is gratefully acknowledged.

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(41) Since $M_{10}H_{10} = [4R]^5[5R]^2$, $E(M_{10}) = 5/6*E(\text{cubane}) + 2/12*E(\text{dodecahedrane})$.

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