5378 *Inorg. Chem.* **1996,** *35,* 5378−5386

Strain Energies of Silicon Rings and Clusters

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Received September 26, 1995⊗

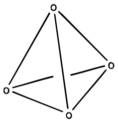
Strain energies of silicon ring and cluster compounds can be calculated as energy changes of homodesmotic reactions that convert cyclic structures into acyclic molecules. The energy changes of these reactions can be calculated by taking differences between *ab initio* energies of products and reactants. Since homodesmotic reactions conserve bond types and preserve atomic valence environments, one can anticipate cancellation of much of basis set and electron correlation errors in individual molecular energies when energy differences are taken. This study involved *ab initio* geometry-optimized calculations at both the RHF and MP2 levels using the 6-31G** basis set. Calculated strain energies of the cyclosilanes $(SiH_2)_n$ can be compared with experimental estimates and with the well established strain energies of the cycloalkanes $(CH_2)_n$. Strain energies of the polyhedral silanes $(SiH)_{2n}$ can be compared with those of the isostructural hydrocarbons. Except for tetrahedral $(SiH)_4$ and $(CH)_4$, which have large and comparable strain energies, and cyclooctatetraene structures, which have negligible strain energies, the silicon clusters have uniformly smaller strain energies than do the related hydrocarbons. These differences can be rationalized using the rule of additivity of individual ring strain energies. The resonance energy of planar hexagonal $(SiH)_6$ is less that that for benzene $(CH)_6$, but both of these quantities are modest stabilizing influences compared to the destabilizing strain energies associated with isomeric structures. The relative energies of the sila analogs of the valence isomers of benzene can be interpreted as resulting from differences in numbers of single and double bonds, the average energies associated with these bonds, and resonance energies and strain energies. These considerations allow an estimate of the energy of the Si═Si double bond: 101 kcal/mol.

Introduction

In this paper we report strain energies of cyclosilanes $(SiH_2)_n$, several silapolyhedranes $(SiH)_{2n}$, and related monocyclic and bicyclic molecules as calculated from energy changes of homodesmotic reactions using total molecular energies from *ab initio* molecular orbital calculations. We compare these results with quantities similarly obtained by ourselves and others for the related cycloalkanes $(CH_2)_n$ and polyhedranes $(CH)_{2n}$. The comparisons illuminate some fascinating similarities and differences between isoelectronic, isostructural compounds of elements of group 14 of the periodic table. Strain energies of individual rings can be used to rationalize strain energies of polycyclic and polyhedral molecules. Strain energies and average bond energies give insight into the relative energies of isomers.

Considerable thermochemical data exist for the cycloalkanes, allowing a detailed evaluation of the accuracy of our calculated strain energies. Spectroscopic data provide experimental strain energy comparisons for the cyclosilanes. Although the parent compound tetrahedrane, $(CH)_4$ (**1**), has long been a goal of synthetic organic chemists, the tetrahedral carbon core has been achieved only by stabilization with large protecting *tert*-butyl groups.[1] A comparable tetrasilatetrahedrane has never been reported. Of course, the isoelectronic molecules P_4, As_4, and Sb_4 have long been known to be tetrahedral.[2]

The five valence isomers of benzene, $(CH)_6$, **4**−**8**, have all been prepared and characterized. Their relative stabilities are implied in their synthetic history. Planar hexagonal benzene (**4**) was identified in the early 19th century and its cyclic structure was recognized in 1866. Benzvalene (**5**) and Dewar benzene (**6**) were first prepared in the 1960s.[3,4] Triangular prismane (**7**) was synthesized in 1973, and bicyclopropenyl (**8**) was finally realized in 1989.[5,6] *Ab initio* calculations by Schulman and Disch confirm this order of increasing isomer energies.[7] Our education as chemists has prepared us to accept these results. Benzene (**4**), with its system of six π-electrons delocalized around the ring, is said to be stabilized by resonance.[8−10] The other structures **5**−**8** contain small rings and conformations requiring substantial deviations from preferred bond angles around carbon and torsional angles around C−C bonds, and they are said to be destabilized by strain.[11,12]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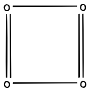
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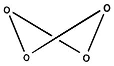
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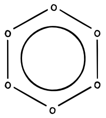
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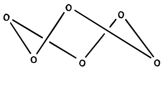
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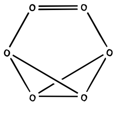
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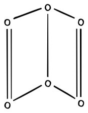
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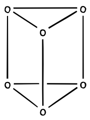
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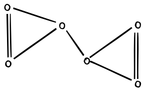
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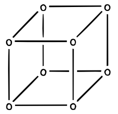
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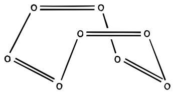
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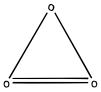
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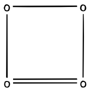
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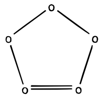
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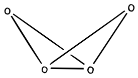
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The hexasila analogs $(SiR)_6$ (R = aryl) of the benzene valence isomers triangular prismane (**7**) and Dewar benzene (**6**) have recently been prepared, as has the octasila analog $(SiR)_8$ of cubane (**9**).[13−15] The hydrocarbon cubane, first prepared in 1964, is far from being the most stable of the $(CH)_8$ valence isomers, which include cyclooctatetraene (**10**) among many others.[16] A derivative of tetrasilabicyclobutane, Si_4R_6 (**14**), was prepared about 10 years ago;[17] its X-ray structure has been reported.[18]

Differences in the order and range of stabilities of hydrocarbon and silicon polyhedral structures are striking. Nagase and co-workers have reported the results of *ab initio* calculations for $(SiH)_6$ in the forms of the valence isomers of benzene **4−7** (omitting the bicyclopropenyl structure **8**).[19] Their results show that the relative energies of the hexasilapolyhedranes differ by only 15 kcal/mol or so, with the planar hexagon **4** not being the structure of lowest energy. Comparable calculations for the $(CH)_6$ hydrocarbons show a range of 120 kcal/mol for the same isomeric structures.[7]

The polyhedral structures **5**, **6**, and **8** contain individual rings **11−13** that include one double bond, and the benzvalene structure **5** contains a butterfly-shaped bicyclobutane fragment **14** that consists of two noncoplanar three-membered rings which share a common edge. Because they occur as components of larger structures, **11−14** will be of interest here as well.

Calculations

We have used the GAUSSIAN 92 program package[20] to perform *ab initio* molecular orbital calculations geometry optimized at both the RHF and MP2 levels with the 6-31G** basis set for $(SiH_2)_n$ rings, n = 3−6, $(SiH)_{2n}$ polyhedral clusters, n = 2−4 (**1−10**), the double bond containing rings Si_nH_{2n-2}, n = 3−5 (**11−13**), and tetrasilabicyclobutane Si_4H_6 (**14**), as well as for a number of branched and unbranched acyclic structures that serve as unstrained reference structures for the calculation of strain energies. Total energies in hartrees (and for isomers, relative energies in kcal/ mol) are compiled in Tables 1, 3, and 4. The double asterisks in 6-31G** indicate that this basis set includes a set of d-type polarization functions for each carbon or silicon atom and a set of p-type polarization functions on each hydrogen. The symbol 31 denotes the use of double-ζ valence shell orbitals.[21] For comparisons with the cyclosilanes, we have performed parallel calculations for $(CH_2)_n$ rings, n = 3−6, and appropriate C_nH_{2n+2} chains, and these results appear in Table 2. Conformations of the cycloalkanes and cyclosilanes turned out to be the same.

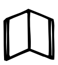
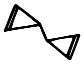
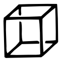
Table 1. Total Energies (hartrees) of $(SiH_2)_n$ Rings and Si_nH_{2n+2} Chains

structure	RHF	MP2
Si_3H_6 (D_{3h})	−870.19096	−870.47037
Si_4H_8 (D_{2d})	−1160.30917	−1160.68143
Si_5H_{10} (C_s)	−1450.41267	−1450.87609
Si_5H_{10} (C_2)	−1450.41267	−1450.87609
Si_6H_{12} (D_{3d})	−1740.50380	−1741.06062
SiH_4 (T_d)	−291.23084	−291.33900
Si_2H_6 (D_{3d})	−581.31357	−581.51249
Si_3H_8 (C_{2v})	−871.39775	−871.68912
Si_4H_{10} (C_{2h})	−1161.48209	−1161.86625
Si_4H_{10} (C_2)	−1161.48189	−1161.86631

Table 2. Total Energies (hartrees) of $(CH_2)_n$ Rings and C_nH_{2n+2} Chains

structure	RHF	MP2
C_3H (D_{3h})	−117.06906	−117.49714
C_4H_8 (D_{2d})	−156.10818	−156.68279
C_5H_{10} (C_s)	−195.17887	−195.89709
C_5H_{10} (C_2)	−195.17887	−195.89709
C_6H_{12} (D_{3d})	−234.22625	−235.09016
CH_4 (T_d)	−40.20170	−40.36463
C_2H_6 (D_{3d})	−79.23824	−79.54340
C_3H_8 (C_{2v})	−118.27616	−118.72538
C_4H_{10} (C_{2h})	−157.31395	−157.90745
C_4H_{10} (C_2)	−157.31244	−157.90645

Table 3. Total Energies (hartrees) of Polyhedral $(SiH)_{2n}$ (with Relative Energies Among Isomers in kcal/mol) and Number of Imaginary Vibrational Frequencies (iv) at Both Levels of Theory

Structure		E (RHF)	iv	E (MP2)	iv
1: T_d		−1157.82773 (10.9)	0	−1158.17924 (40.9)	2
2: D_{2h}		−1157.83423 (6.8)	2	−1158.18890 (34.8)	3
3: D_{2d}		−1157.84512 (0.0)	0	−1158.24354 (0.0)	0
4: D_{6h}		−1736.87444 (13.7)	1	−1737.40686 (11.9)	1
4': D_{3d}		−1736.87466 (13.6)	0	−1737.41359 (7.6)	0
5: C_{2v}		−1736.87939 (10.6)	0	−1737.41640 (5.9)	1
6: C_{2v}		−1736.87343 (14.4)	0	−1737.40906 (10.5)	1
7: D_{3h}		−1736.89634 (0.0)	0	−1737.42578 (0.0)	0
8: C_{2h}		−1736.79721 (62.2)	0	−1737.33530 (56.8)	0
9: O_n		−2315.95420 (0.0)	0	−2316.65044 (0.0)	0
10: D_{2d}		−2315.79809 (98.0)	0	−2316.50755 (89.7)	4

The three-membered rings are, of course, planar D_{3h}. The four-membered rings are puckered squares, D_{2d}. For the five-membered

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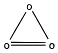
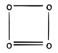
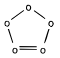
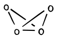
Table 4. Total Energies (hartrees) of Acyclic Reference Structures and Cyclic Fragments (in Parentheses, Relative Energies (kcal/mol) of Various Rotational Conformers)

Structure		RHF	MP2
$H_2Si{=}SiH_2$ — D_{2h}		−580.08277 (0.01)	−580.26921 (0.8)
$H_2Si{=}SiH_2$ — C_2		−580.08277 (0.01)	−580.26921 (0.8)
$H_2Si{=}SiH_2$ — C_{2h}		−580.08279 (0.0)	−580.27049 (0.0)
$H_2Si{=}SiH{-}SiH{=}SiH_2$ — C_{2h}		−1159.03471 (0.03)	−1159.39563 (2.0)
$H_2Si{=}SiH{-}SiH{=}SiH_2$ — C_i		−1159.03475 (0.0)	−1159.39883 (0.0)
$H_2Si{=}SiH{-}SiH{=}SiH_2$ — C_2		−1159.03388 (0.5)	−1159.39809 (0.5)
$H_3Si{-}SiH{=}SiH{-}SiH_3$ — C_2		−1160.26369 (0.6)	−1160.63691 (0.5)
$H_3Si{-}SiH{=}SiH{-}SiH_3$ — C_i		−1160.26461 (0.0)	−1160.63772 (0.0)
$HSi(SiH_3)_3$ — C_{3v}		−1161.48320	−1161.86891
11: C_{2v} — SiH_4		−868.96913	−869.24253
12: C_{2v} — Si_4H_6		−1159.09611	−1159.45850
13: C_s — Si_5H_8		−1449.19776	−1449.65174
14: C_{2v} — Si_4H_6 "open"		−1159.09029 (0.0)	−1159.46759 (0.0)
14: C_2 — Si_4H_6 "closed"		−1159.08624 (2.5)	

rings, two conformations, C_2 and C_s, have identical energies. The six-membered rings are chair-form, D_{3d}.

For $(CH)_4$ and N_4, the calculated frequencies of tetrahedrane (**1**) and cyclobutadiene (**2**) structures are all real at both RHF and MP2 levels, indicating that these two structures correspond to relative minima on their respective energy surfaces.[22,23] $(SiH)_4$ is different. Yates, Clabo, and Schaefer found that while tetrahedral $(SiH)_4$ is a minimum at the RHF level, it is not a minimum on the MP2 surface. $(SiH)_4$ cyclobutadiene (**2**) is not a minimum for either the RHF or MP2 approximations. However, $(SiH)_4$ in the form of a puckered square **3** is a minimum at both levels of theory.[24] Nagase and Nakano have also studied the relative stabilities of $(SiH)_4$ in structures **1**−**3**.[25]

At the RHF/6-31G** level, calculated vibrational frequencies for the hexasila polyhedra **5**−**8** are all real, but those for the planar D_{6h} hexagon **4** include one imaginary frequency. This situation has been thoroughly studied by Janoschek[26] and Nagase[27] who note that, at higher levels of theory, the D_{6h} structure of $(SiH)_6$ is a transition state between two equivalent chair-form D_{3d} minima **4′**. Our results confirm those conclusions. But deviations from planarity and D_{6h} symmetry are slight and the energy of the D_{3d} minimum is only a fraction of a kcal/mol below that of the D_{6h} transition state at the RHF level. With MP2 calculations, structures **7** and **8** correspond to real minima while **4**, **5**, and **6** each have a single imaginary vibrational frequency, indicating that these structures are transition states. By including the effects of electron correlation to the MP2 level, the energy of the chair-form D_{3d} minimum **4′** falls to a little more than 4 kcal/mol below the energy of the planar D_{6h} transition state. The saddle point status of **6** is disconcerting because experimentalists have claimed to have observed the Dewar benzene form (**6**) of $(SiR)_6$.[14] Removing all symmetry constraints for **6** (to C_1) led to rapid geometry convergence with a structure virtually identical to **6** (C_{2v}). Therefore, we conclude that the single imaginary frequency for **6** is the result of a computational artefact. Lowered symmetry constraints for **5** (to C_2) and subsequent attempts at reoptimization did not give geometry optimized convergence after many cycles. This result suggests that the energy surface is very flat in the vicinity of **5** (C_{2v}). We have used the energies of **5** and **6** in calculating strain energies of the hexasila polyhedra.

As anticipated by the work of Nagase and co-workers,[19] we find the hexasilapolyhedranes **4**−**7** to be close in energy, within 10 to 15 kcal/mol of each other. The isomer with the lowest energy is the triangular prism **7**. The bicyclopropenyl structure **8** is 55 to 60 kcal/mol higher. Figure 1 compares the relative energies of the valence isomers of $(SiH)_6$ to those of $(CH)_6$.

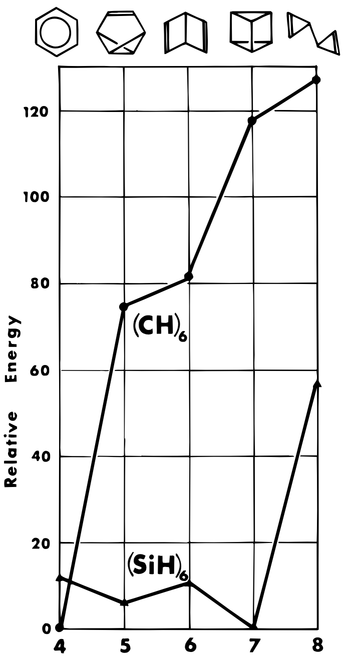


Figure 1. Relative energies (kcal/mol) of valence isomers $(XH)_6$.

Calculated vibrational frequencies of octasilacubane (**9**) indicate that this structure is a real minimum on both the RHF and the MP2 energy surfaces. For octasilacyclooctatetraene (**10**), vibrational frequencies are all real at the RHF level, but four imaginary values occur in the MP2 spectrum. There are many other examples of silicon structures that differ only slightly from the corresponding benchmark hydrocarbons. Lowering symmetry restrictions from D_{2d} to C_2 led back to a structure indistinguishable from the D_{2d} form of **10** and with an energy only 10^{-7} h lower. The MP2 result must be quite close to the minimum because we find (next section) that the strain energy of **10** is negligible. We therefore use **10** for comparisons in this series. For $(SiH)_8$, the energy of **9** is far below that of **10**—just the reverse of the order for the corresponding hydrocarbons.

Figure 2 displays the SiSi bond distances and selected bond angles of the cluster cores of **1**−**10** as obtained from 6-31G**/MP2 calculations. Si−Si single bonds range from 2.2807 (**10**) to 2.3851 Å (**9**). A total of 52 single bonds in 14 different structural sites average 2.3392 Å. Si═Si double bonds show a somewhat narrower range, from 2.1211 (**8**) to 2.1754 Å (**5**). A total of 11 double bonds among 5 different positions average 2.1554 Å. The planar hexagon (**4**, D_{6h}; 2.2122 Å) and the puckered hexagon (**4′**, D_{3d}; 2.2345 Å) each contain six equivalent SiSi bonds of lengths intermediate between single and double bonds. Classical structures cannot be drawn for either the puckered square **3** or the puckered hexagon **4′**. It is interesting to note that the Si−Si bonds in the puckered square are short but otherwise well within the norms of other Si−Si single bonds, while the bonds of the puckered hexagon are only slightly longer than those of the planar hexagon. Not appearing in Figure 2 are Si−H bond distances, which range from 1.4670 to 1.4892 Å, with an average of 1.4776 Å among 58 bonds in 14 different locations.

The substituted tetrasilabicyclobutane Si_4R_6 (**14**) has been prepared and an X-ray structure is available.[17,18] Several groups have reported *ab initio* calculations for **14**, initiating a controversy concerning bond stretch isomerism.[28−33] Schoeller, Dabisch, and Busch found two

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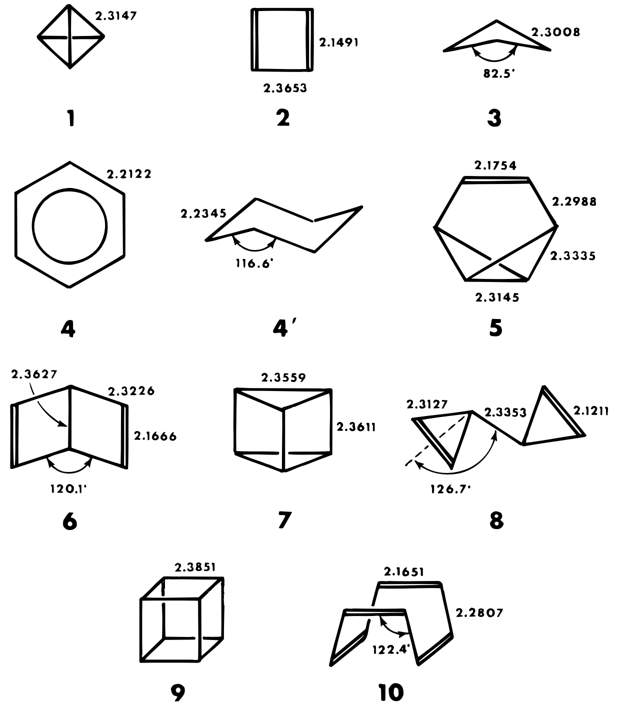

Figure 2. Selected structural parameters for $(SiH)_{2n}$ clusters obtained from *ab initio* calculations at the 6-31G**/MP2 level. All structures were optimized under symmetry constraints. Structures **1**, **2**, **4**, **5**, **6**, and **10** have one or more imaginary vibrational frequencies, indicating that these structures do not correspond to relative minima on their energy surfaces.

minima for **14**: one, referred to as the "closed" form, with a Si−Si single bond of normal length (~2.3 Å) forming the shared edge between the two triangles; the other, an "open" form, with a much elongated bond (~2.8 Å) along the shared edge.[30] The "open" form was a few kcal/mol lower in energy than the "closed" form. These conclusions were affirmed by Schleyer and co-workers, who also noted that the energy barrier between the two isomers is small, ~1 kcal/mol.[31] The known substituted compound Si_4R_6 has the "closed" structure.[18] Calculations with various model substituents show that substituents can reverse the relative energies of "closed" and "open" forms, perhaps explaining nature's preference for the "closed" isomer.[30] Other groups report calculations that locate an energy minimum for the "closed" form only.[32,33] At the RHF/6-31G** level we find minima for both forms, with the "open" isomer 2.5 kcal/mol lower than the "closed" form. With MP2/6-31G** calculations we locate a minimum for the "open" form only. All of this evidence suggests a flat energy surface for rather large displacements of the shared edge Si−Si bond in **14**—a conclusion consistent with a low activation barrier to inversion of the nonplanar "closed" structure that has been invoked to interpret the ^{1}H-NMR spectrum of Si_4R_6.[17]

Silicon is notorious for the different structures its compounds prefer to take compared to their hydrocarbon analogs,[34,35] and these differences occur among the acyclic reference compounds we need for calculation of strain energies. The lowest energy structure of Si_2H_4 is not planar D_{2h} like ethylene but instead it has a nonplanar, trans, C_{2h} shape. But the energy difference between D_{2h} and C_{2h} is small—less than 1 kcal/mol at the MP2/6-31G** level. Another important reference structure is tetrasilabutadiene $H_2Si{=}SiH{-}HSi{=}SiH_2$. At the MP2/6-31G** level, the nonplanar C_i structure is 2 kcal/mol lower in energy than the planar, trans, C_{2h} structure expected in analogy to the butadiene hydrocarbon.

Several *ab initio* calculations of silane strain energies have already appeared. Kitchen, Jackson, and Allen[33] and Nagase, Nakano, and Kudo[36] have reported calculated strain energies of the cyclosilanes, n = 3 and 4. Nagase and co-workers have studied relative energies and strain energies of $(SiH)_6$ in forms **4**−**7** but not **8**.[19] Janoschek *et al.* have calculated the strain energy of **5**. The strain energy of tetrasilatetrahedrane **1** has been calculated by Schoeller, Dabisch, and Busch.[30] Nagase has reported the calculated strain energies of **1**, **7**, and **9**.[36−38] Several authors give calculated strain energies of tetrasilabicyclobutane **14**.[28−30,33] Compared with the work we report here, none of the previous studies has surveyed as many different structures at the same level of theory and, with the exception of Nagase's investigation of the relative energies of structures **4** and **4′** for hexasilabenzene,[27] no calculations have been reported at a level as high as geometry optimized MP2/6-31G**.

We rely heavily on the results of Schulman and Disch[7] for relative energies and strain energies of the valence isomers of benzene $(CH)_6$ **4**−**8** and the calculated strain energy of tetrahedrane $(CH)_4$ (**1**) by Schulman and Venanzi.[39] Nagase has compared strain energies of the polyhedral hydrocarbons tetrahedrane (**1**), prismane (**7**), and cubane (**9**).[19,36−38] Hess and Schaad[40] must be acknowledged for a significant study of the resonance energy of $(CH)_6$ benzene (**4**).

Strain Energies of the Cyclosilanes

Several methods have been proposed for the definition and calculation of strain energies.[11,12,41−43] The scheme we use here is particularly convenient for the application of *ab initio* calculated energies of strained molecules. The unstrained reference comparison is the bond additivity model, which assumes average values of energies for different kinds of bonds without regard for structural context and therefore contains nothing about strain.

Equation 1 establishes a general process from which ring strain energies of the cyclosilanes can be estimated as functions of the homodesmoticity parameter s. This parameter specifies the lengths of unbranched and presumably unstrained acyclic reference structures. In eq 1, the $(SiH_2)_n$ ring is dismantled into

$$(SiH)_n \text{ (ring)} + nH(SiH_2)_{s+1}H \text{ (chain)} \rightarrow nH(SiH_2)_{s+2}H \text{ (chain)} \quad (1)$$

n SiH_2 units, each of which is then inserted into a chain $H(SiH_2)_{s+1}H$, the length of which is thereby increased to $H(SiH_2)_{s+2}H$. At the $s = +1$ level, eq 1 describes a *homodesmotic* process which has two significant features.[44] First, the numbers of Si−Si and Si−H bonds are the same on both sides of the equation, thereby establishing an energy change of zero as calculated from average values of bond energies. We recognize, however, that the process converts rings into chains, thereby releasing any strain produced by the structural constraints of the ring. Therefore, we can interpret any reaction energy change as the strain energy of the ring. We expect such reactions to be exothermic, but we will express the corresponding strain energies as positive quantities. The second feature of a homodesmotic reaction is that it preserves the valence environment around each atom in reactants and products. In

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Table 5. Strain Energies (kcal/mol) for Cyclosilanes, $(SiH_2)_n$, and Cycloalkanes, $(CH_2)_n$, n = **3**−**6**, Obtained as Energy Differences Following Eq 1 at *ab Initio* RHF/MP2 Levels

	$(SiH_2)_n$			$(CH_2)_n$		
n	$s = 0$	$s = +1$	$s = +2$	$s = 0$	$s = +1$	$s = +2$
3	35.9/31.4	38.6/37.4	38.9/38.3	25.4/24.6	28.1/30.6	27.8/30.8
4	13.7/7.9	17.3/15.8	17.7/17.0	23.8/20.3	27.3/28.3	27.0/28.5
5	0.6/−5.4	5.2/4.4	5.7/6.0	2.4/−2.0	6.8/8.1	6.3/8.3
6	−4.6/−12.4	0.8/−0.5	1.4/1.4	4.4/−11.0	0.8/1.1	0.3/1.4

Table 6. Strain Energies of Cycloalkane $(CH_2)_n$ Rings (kcal/mol) from eq 1, $s = +2$, Based on *ab Initio* Total Energies and MM3 and Experimental Heats of Formation

n	*ab initio* (MP2)	MM3	exptl
3	30.8	27.8	28.7
4	28.5	26.1	28.1
5	8.3	5.8	7.9
6	1.4	0.3	2.6

eq 1, for $s = +1$ (and larger), the number of silicon atoms connected to two hydrogens and two other silicons is the same on both sides of the equation—a balance that also holds for the numbers of silicons bonded to one other silicon and to three hydrogens. Reactions that conserve both bond types and atomic valence environments give us hope that basis set and electron correlation errors inherent in the calculation of molecular electronic structures might largely cancel when differences are taken between total energies of products and reactants to obtain energy changes for eq 1.[45]

We have had considerable experience in the calculation of strain energies for O_n, S_n, $(NH)_n$, and $(PH)_n$ rings using the s-homodesmotic analogs of eq 1.[46] Using the 6-31G** basis set, we have found that strain energies, whether obtained at RHF or MP2 levels, are essentially the same for $s \geq +1$. Our calculated strain energies for the cyclosilanes $(SiH_2)_n$ with $s = 0$, $+1$, and $+2$ and at both RHF and MP2 levels appear in Table 5. For comparison, Table 5 also contains strain energies for the cycloalkanes $(CH_2)_n$ as obtained by the same procedure.

In Table 6 we show $(CH_2)_n$ strain energies following eq 1 with $s = +2$ but based on experimental[11] and MM3[47] heats of formation for comparison with strain energies from our MP2/6-31G** results. Naturally, the parameters for the MM3 force field were originally chosen to make calculated properties such as heats of formation, bond distances, and bond angles match those from experiment for a set of hydrocarbons that included the alkanes and cycloalkanes. The *ab initio* strain energies are essentially in quantitative agreement with those obtained from MM3 and experimental heats of formation.

For the cyclosilanes, at least one set of experimental strain energies is available for comparison with *ab initio* values. Watanabe and co-workers proposed that strain energies should be the differences in UV absorption transition energies for $Me(SiMe_2)_nMe$ chains and $(SiMe_2)_n$ rings for the same n.[48] Table 7 compares our calculated strain energies for the cyclosilanes (MP2, $s = +2$) with the spectroscopic values obtained by Watanabe *et al.* The agreement between the two sets of strain energies is startling.

Table 7. Strain Energies of Cyclosilane $(SiH_2)_n$ Rings (kcal/mol) from Experiment and from *ab Initio* (MP2) Results, eq 1, $s = +2$

n	*ab initio* (MP2)	exptl[a]
3	38.3	41
4	17.0	23
5	6.0	6
6	1.4	0

[a] Reference 44.

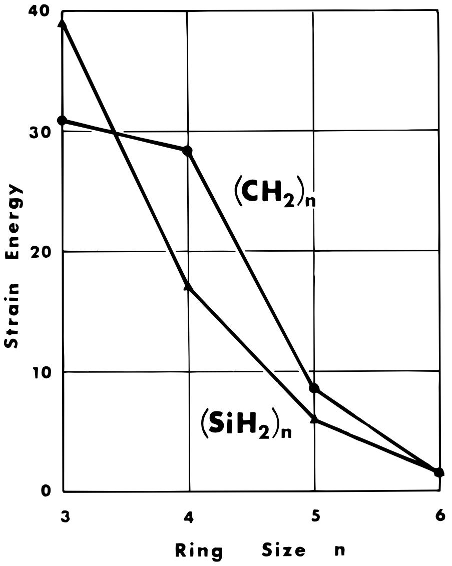
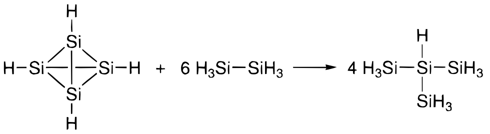


Figure 3. Strain energy trends with ring size for cycloalkanes and cyclosilanes.

Figure 3 compares strain energies of the cyclosilanes and the cycloalkanes. The strain energy of the 3-membered silicon ring is almost 10 kcal/mol greater than that for cyclopropane. At $n = 4$ and 5, the cyclosilane strain energies fall below those of the cycloalkanes, with both series approaching zero for $n = 6$.

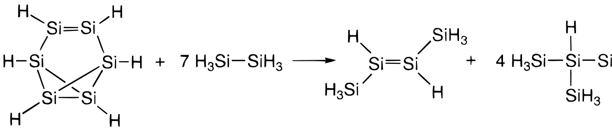
Strain Energies of Polyhedral Clusters

Equation 2 is a homodesmotic reaction (conserving bond types and atomic valence environments) that releases the strain energy of tetrasilatetrahedrane **1**, $(SiH)_4$.



(2)

Similar reactions can be written involving the silicon analogs of the benzene valence isomers prismane (**7**) and cubane (**9**). Equation 3 is the homodesmotic reaction with hexasilabenzvalene **5** showing the disposition of the Si═Si double bond. Analogous reactions involve **2**, **6**, **8**, and **10**.



(3)

We interpret the energy changes for such reactions as strain energies, although we recognize that the acyclic reference structures used here—particularly tetrasilaisobutane—may themselves involve strain. Strain energies of the silapolyhedranes **1**−**10** appear in Table 8. For comparison, we include estimates of the strain energies of the corresponding polyhedral alkanes

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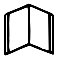
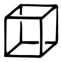
Table 8. Strain Energies (kcal/mol) of $(SiH)_n$ and $(CH)_n$[a]

Structure			$(SiH)_n$[b] — RHF/MP2	$(CH)_n$
1	Tetrahedrane		140.3 / 139.0	129-137[c] 129.2[d] 140[e] 141[f]
2	Cyclobutadiene		42.6 / 38.7	
3	Puckered Square		37.0 / 8.3	
4	Benzene		−13.3 / −15.1	−24.7[g]
5	Benzvalene		77.2 / 68.7	81.3[g]
6	Dewar Benzene		34.1 / 26.2	63.6[g]
7	Prismane		113.4 / 110.0	148.9[g] 145.3
8	Bicyclopropenyl		81.9 / 72.5	107.2[g]
9	Cubane		93.2 / 94.5	154.7[e] 158.6[f] 165.1[h]
10	Cyclooctatetraene		+4.0 / −4.2	2.1

[a] Negative values indicate resonance stabilization energy. [b] This work. [c] Reference 35. [d] Reference 1. [e] Reference 39. [f] References 32−34. [g] Reference 7. [h] Reference 11.

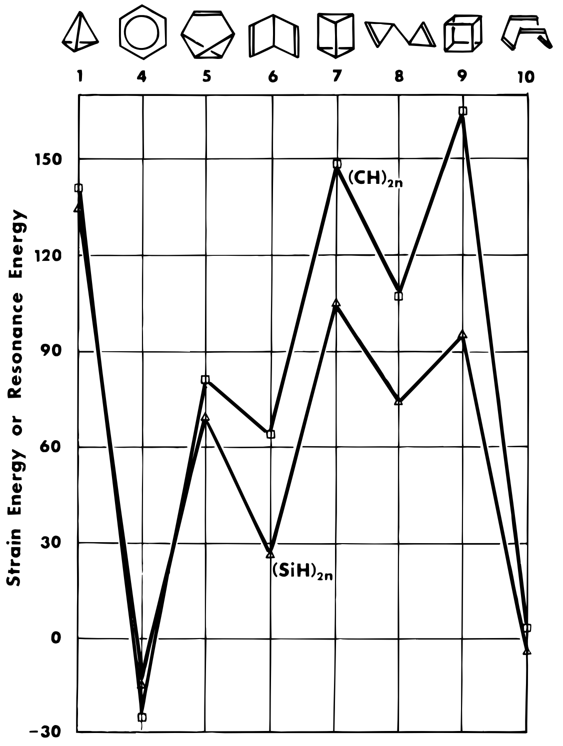
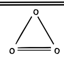
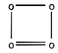
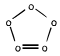
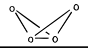


Figure 4. Comparison of strain energies (kcal/mol) of the polyhedral silanes $(SiH)_{2n}$ and the corresponding hydrocarbons $(CH)_{2n}$.

obtained from a number of sources. Strain energies calculated at RHF and MP2 levels differ by less than 10 kcal/mol—generally a small value compared to the sizes of the strain energies themselves. This observation gives support to the assumption that electron correlation errors in *ab initio* total energies largely cancel when product and reactant energy differences are taken. Figure 4 gives a visual comparison of strain energies of the polyhedral silanes and hydrocarbons.

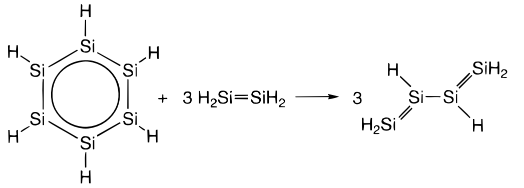
Table 9. Strain Energies (kcal/mol) of Structures that Occur as Fragments in Larger Silapolyhedranes

Structure		Silicon[a] — RHF/MP2	Carbon[b]
11		41.5 / 37.2	54.5
12		14.6 / 12.6	30.6 34.0
13		3.6 / 2.1	6.8 6.9
14		65.1 / 54.0	66.5

[a] This work. [b] Reference 12.

Since structures **5**, **6**, and **8** include rings **11**−**13** that contain one double bond, we have calculated strain energies for these Si_nH_{2n-2} monocyles using homodesmotic reactions related to eq 3. The structures we chose for **11**−**13** are not their lowest energy conformations but are those that approximate structural arrangements in the polycyclic clusters **5**, **6**, and **8**. The benzvalene structure **5** contains a bicyclobutane butterfly structure **14**, the strain energy of which can be calculated from an analog of eq 1. Strain energies for **11**−**14** are given in Table 9.

Hexasilabenzene (**4**) requires special consideration. Equation 4 is the silicon analog of the homodesmotic reaction proposed by Hess and Schaad to give the resonance energy of benzene.[40] If the hexagonal reactant was a Kekulé structure composed of alternate single and double bonds, then eq 4 would be homodesmotic. But **4** (D_{6h}) and **4′** (D_{3d}) do not consist of single and double bonds. Instead, they have six equivalent Si⋯Si bonds of length intermediate between normal single and double bonds.



(4)

Therefore, the homodesmotic conservation of bond types and atomic valence environments cannot strictly apply to eq 4. Furthermore, the planar regular hexagon **4** is not a minimum on either the RHF or the MP2 energy surface with the 6-31G** basis set. Only slightly lower is the chair-form structure **4′**. We have used energies of both **4** and **4′** in calculating the energy change for eq 4. As mentioned earlier, the tetrasilabutadiene product in eq 4 has nonplanar C_i symmetry and lies less than 1 kcal/mol below the planar trans C_{2h} structure anticipated for the corresponding hydrocarbon.

The calculated energy changes for eq 4 are endothermic; the hexagonal $(SiH)_6$ structures, both **4** and **4′**, are more stable than expected from the bond additivity model. The D_{6h} structure **4** has bond angles of 120°, exactly appropriate for sp^2-hybridized ring atoms, and therefore we expect no strain energy for **4**. The endothermic energy change for eq 4 involving **4** is conventionally interpreted as resonance stabilization resulting from the delocalization of π electrons around the ring. For **4′**, the D_{3d} structure is not exactly planar, the SiSiSi bond angles are slightly less than 120°, separation of MOs into sets of σ and π symmetry breaks down, and the nonplanar structure **4′** is slightly more stable than the planar hexagon **4**. Traditionally and operationally, resonance energy is a measure of the chemist's surprise that a structure is more stable than average bond properties would predict. Therefore, the energy change of eq 4 involving the nonplanar D_{3d} hexagon **4′** we call the resonance energy of that structure and use a negative sign in Table 8 to indicate that it is a stabilizing quantity, in opposition to the destabilizing strain energies that we give as positive quantities. The

Table 10. Ring Strain Additivity Rule Estimates of Polyhedral Cluster Strain Energies (kcal/mol) as Sums of Monocycle or Fragment Energies Compared to Directly Calculated Polyhedral Strain Energies (in Parentheses)

no.	structure	(CH)$_n$	(SiH)$_n$
1	tetrahedrane	$4 \times 30.8 = 123.2$ (129.2)	$4 \times 38.3 = 153.2$ (139.0)
7	prismane	$2 \times 30.8 + 3 \times 28.5 = 147.1$ (148.9)	$2 \times 38.3 + 3 \times 17.0 = 127.6$ (120.3)
9	cubane	$6 \times 28.5 = 171.0$ (158.6)	$6 \times 17.0 = 102.0$ (94.5)
8	bicyclopropenyl	$2 \times 54.5 = 109.0$ (107.2)	$2 \times 37.2 = 74.4$ (72.5)
6	Dewar benzene	$2 \times 30.6 = 61.2$ (63.6)	$2 \times 12.6 = 25.2$ (26.2)
5	benzvalene	$2 \times (30.8 + 6.8) = 75.2$ (81.3) or $2 \times 6.8 + 66.5 = 80.1$ (81.3)	$2 \times (38.3 + 2.1) = 80.8$ (68.7) or $2 \times 2.1 + 54.0 = 58.2$ (68.7)

Table 11. Relative Energies (kcal/mol) of Valence Isomers (XH)$_6$ at the Bond Additivity Level

	silanes[a]				hydrocarbons[b]			
isomer	A[c]	B	$A - B$	$A - B + C$	A	B	$A - B$	$A - B + C$
1	40.9	139.0	−98.1	0				
2	34.8	38.7	−3.9	94.2				
3	0	8.3	−8.3	85.8				
4	11.9	−15.1	27.0	137.0	0	−24.7	+24.7	56.1
4'	7.7	−19.3	27.0	137.0				
5	5.9	68.7	−62.9	47.1	74.8	81.3	−6.5	24.9
6	10.5	26.2	−15.7	94.3	81.0	63.6	+17.4	48.8
7	0	110.0	−110.0	0	117.5	148.9	−31.4	0
8	56.8	72.5	−15.7	94.3	126.4	107.2	+19.2	50.6
9	0	94.5	−94.5	0	77.6	165.1	−87.5	0
10	89.7	−4.2	93.9	188.4	0	2.1	−2.1	85.4

[a] This work. [b] Data from refs 7 and 11. [c] Key: A, relative energy (*ab initio*); B, strain energy (+) or resonance energy (−), $A - B$, bond additivity level (unstrained, nonresonance stabilized); $A - B + C$, bond additivity level (renormalized).

resonance energies of **4′**, −13.4/−19.3 kcal/mol (RHF/MP2) are smaller than the resonance energy of D_{6h} benzene (CH)$_6$, −24.7 kcal/mol, obtained at the RHF/6-31G** level.

The puckered square **3** is another special case. All four Si−Si bonds in **3** are equivalent, as they are in **4** and **4′**. We have chosen to calculate the strain energy of **3** with a reaction similar to eq 4 involving the potentially delocalized tetrasilabutadiene product. In fact, these results, reported in Table 8, differ by only 3 or 4 kcal/mol from those obtained with an analog of eq 3.

We can interpret the strain energies of the polyhedral silanes **1**−**10** using the rule of approximate additivity of ring strain energies. This rule, often applied in organic chemistry, says that the strain energy of a polycyclic molecule is approximately the sum of strain energies of the individual rings which make up the polycyclic system.[12,49−51] In the following comparisons, we use MP2 results from Tables 5 ($s = +2$), 8, and 9.

Tetrahedrane (**1**), for example, is composed of four cyclopropane rings. For (SiH)$_4$, the estimated strain energy $= 4 \times 38.3 = 153.2$ kcal/mol, compared to the value 139.0 kcal/mol calculated directly—an error of 10% and typical of the rule. For (CH)$_4$, the estimated strain energy is $4 \times 30.8 = 123.2$ kcal/mol—a result near the low end of the estimates in Table 8. Nagase and co-workers report (CH)$_4$ strain energies of 140.9 and 141.4 kcal/mol using homodesmotic reactions and SCF energies calculated with the 6-31G* basis set. The largest errors involve the bicyclobutane structure. From the additivity rule, the strain energy of **14** should be $2 \times 38.3 = 76.6$ kcal/mol, but the directly calculated value is 54.0 kcal/mol. The strain energy of the benzvalene structure **5** can be estimated in two ways: as two cyclopropanes plus two cyclopentenes, $2 \times (38.3 + 2.1) = 80.8$ kcal/mol, or as bicyclobutane plus two cyclopentanes, $54.0 + 2 \times 2.1 = 58.2$ kcal/mol—values that widely bracket the direct value of 68.7 kcal/mol.

Examples of ring strain additivity estimates are collected in Table 10. The ring strain additivity rule provides a convenient qualitative rationalization of the relative energies of polyhedral silanes and alkanes. Strain energies of (CH$_2$)$_3$ and (CH$_2$)$_4$ rings are both large, with that of (CH$_2$)$_4$ only slightly smaller than the (CH$_2$)$_3$ strain energy. In contrast, (SiH$_2$)$_3$ is much more strained than (CH$_2$)$_3$ while (SiH$_2$)$_4$ is much less strained than (CH$_2$)$_4$. The strain energy of tetrasilatetrahedrane (**1**) is large, perhaps even larger than that of (CH)$_4$, because of the large strain energy of trisilacyclopropane. Although (SiH)$_4$ tetrahedrane is not a minimum on the MP2 energy surface, it is conceivable that appropriate substituents might be found that could make it a minimum. If (CH)$_4$ tetrahedrane has been elusive, then the (SiH)$_4$ analog, with at best a problematic minimum, larger strain, and weak Si−Si bonds, is an even more challenging synthetic goal. Those polyhedral silanes containing four-membered and larger rings have lower strain energies than their hydrocarbon analogs because those silicon rings have low strain energies. For the cubane structure **9**, with six cyclobutane rings, the strain energy of (SiH)$_8$ is low (95 kcal/mol) compared to that of (CH)$_8$ (150 kcal/mol).

Average Bond Energies

Strain energies and resonance energies produce major changes in the relative energies of (SiH)$_{2n}$ valence isomers **1**−**10** estimated from average bond energies. To discover what those average bond energy relative stabilities are, we took *ab initio* relative energies and subtracted from each the calculated strain energy, or—in the case of the hexagonal rings **4** and **4′**—added back the calculated resonance stabilization energy. This is shown in Table 11, the left half of which is devoted to structures **1**−**10** for (SiH)$_{2n}$ and the right based on quantities for the (CH)$_{2n}$ isomers **4**−**10** as reported by others.[7,11,36−38] A in Table 11 sets out the relative isomer energies at the *ab initio* level from Table 3 (MP2 results). B recalls the corresponding strain or resonance energies from Table 8. The third column, $A - B$, is the difference between A and B, or the relative isomer energies but without strain or resonance. In the fourth column, $A - B + C$, these relative energies have been normalized by subtracting

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from $A - B$ in each isomer set the energy of the most stable isomer in that set at the bond additivity level.

Defer consideration of **3**, **4**, and **4′** for a moment and focus on **1**, **2**, and **5**−**10**. The relative energies of isomers in each set are given by $m\Delta$, where m is the number of double bonds in the isomer, and $\Delta = 2D(\text{X—X}) - D(\text{X=X})$—the energy difference between two X—X single bonds and one X=X double bond. Inspection of the $A - B + C$ lines of Table 11 reveals that $\Delta = 47$ kcal/mol for silicon and $\Delta = 25$ kcal/mol for carbon. Assuming standard values for average CC bond energies ($D(\text{C—C}) = 83$ kcal/mol; $D(\text{C=C}) = 146$ kcal/mol)[52] yields $\Delta = 20$ kcal/mol for carbon, giving at least an impression of the size of error involved in estimating bond energy differences from the results in Table 11 or, for that matter, the errors implicit in the concept of average bond energies.

The consistency of the value of Δ among isomers within a given set, as well as among different isomer sets, is not an accident.[53] For **1**, **2**, **5**−**10**, the energy difference between isomers $m\Delta$ is, in the case of silicon, m times the energy change for the reaction

$$2\text{HSi—(SiH}_3)_3 \rightarrow 2\text{H}_3\text{Si—SiH}_3 + \text{H}_3\text{Si—HSi=SiH—SiH}_3 \quad (5)$$

the effect of which, in bond additivity terms, is to convert two Si—Si single bonds into one Si=Si double bond. Reactions such as eq 5 are said to be *isogyric* in that they conserve numbers of electron pairs. Failure of eq 5 to conserve bond types and atomic valence environments means chances of cancellation of basis set and electron correlation errors between reactant and product total energies are less favorable than for homodesmotic reactions such as eqs 1−4. Still, as the results above for Δ for carbon suggest, *ab initio* calculations of energy changes for isogyric reactions have met with some success.[21]

For **4** (or **4′**) the bond additivity relative energy in Table 11 is three times the energy change for another isogyric reaction

$$2\text{HSi—(SiH}_3)_3 + \text{H}_2\text{Si=SiH}_2 \rightarrow 3\text{H}_3\text{Si—SiH}_3 + \text{H}_2\text{Si=HSi—SiH=SiH}_2 \quad (6)$$

which, for bond additivity considerations, converts two Si—Si single bonds into one Si=Si double bond. From the value for **4** and **4′** for silicon in Table 11, $3\Delta = 137.0$ or $\Delta = 45.7$ kcal/mol—essentially the same as the result for eq 5. For the puckered square **3**, $2\Delta = 85.8$ kcal/mol is the energy change for yet another isogyric reaction, with $\Delta = 42.9$—still rather close to the values from eqs 5 and 6. Assuming for silicon $\Delta = 47$ kcal/mol and rearranging the relationship above for Δ gives eq 7.

$$D(\text{Si=Si}) = 2D(\text{Si—Si}) - 47 \text{ kcal/mol} \quad (7)$$

Compounds containing Si=Si double bonds have been prepared, but direct thermochemical measurements of the bond energy have not been reported. Using an established value for the average energy of the Si—Si single bond, we can estimate the energy of the Si=Si double bond. In his highly regarded review of chemical bonding in the main group elements, Kutzelnigg[54] proposed $D(\text{Si—Si}) = 46$ kcal/mol with a π-bond increment of 28 kcal/mol or $D(\text{Si=Si}) = 74$ kcal/mol. Using $D(\text{Si—Si}) = 46$ kcal/mol in eq 7 gives $D(\text{Si=Si}) = 45$ kcal/mol; the double bond is weaker than the single bond. Although this result seems absurd, see the discussion of Schaefer *et al.* for another viewpoint.[55] Walsh, in a review of bond dissociation energies in silicon-containing compounds, mentions 54 kcal/mol for $D(\text{Si—Si})$ in crystalline silicon.[56] Indeed, this value is commonly included as $D(\text{Si—Si})$ in tables of average bond energies in general chemistry textbooks.[52] The 54 kcal/mol single bond energy gives $D(\text{Si=Si}) = 61$ kcal/mol—a more reasonable result. But the Walsh review also cites experimental Si—Si bond dissociation energies from several silanes $\text{Si}_n\text{H}_{2n+2}$ with values ranging from 68 to 80 kcal/mol.[56] The average, or 74 kcal/mol, also happens to be the result for $D(\text{H}_3\text{Si—SiH}_3)$. Using $D(\text{Si—Si}) = 74$ kcal/ mol in eq 7 gives $D(\text{Si=Si}) = 101$ kcal/mol—the value we recommend. This result implies a π bond energy increment of $101 - 74 = 27$ kcal/mol, which is very close to π increments proposed on other grounds by Kutzelnigg,[54] Gordon,[57] and Schaefer.[31,55]

Average bond energies and ring strain energies allow convenient rationalizations of the relative stabilities of isomers and their differences for carbon and silicon analogs. As an example, compare the cubane (**9**) and cyclooctatetraene (**10**) structures. Thermochemical heats of formation for $(\text{CH})_8$ give **10** as more stable than **9** by 77.6 kcal/mol. *Ab initio* calculations show that the order is reversed for $(\text{SiH})_8$; **9** is more stable than **10** by 89.7 kcal/mol. From the bond additivity model we would expect the cubane forms **9** of both $(\text{CH})_8$ and $(\text{SiH})_8$ to have lower energies than their corresponding cyclooctatetraenes **10** because the cubanes contain single bonds only. With four C=C double bonds $(\text{CH})_8$ **10** should be $4\Delta = 100$ kcal/mol higher in energy than **9**. For silicon, Δ is almost twice as large as that for carbon, so the bond additivity value predicts $(\text{SiH})_8$ **10** to be $4\Delta = 188$ kcal/mol above **9**. The strain energies of **10** are negligible for both carbon and silicon. But both cubane structures have large strain energies. The 165 kcal/mol strain energy of $(\text{CH})_8$ **9** lifts the molecular energy of **9** far above that of $(\text{CH})_8$ **10**, or **9** is much less stable than **10**, as observed. The strain energy of $(\text{SiH})_8$ cubane, 94.5 kcal/mol, raises the molecular energy of this structure but, because of the large value of $4\Delta = 188$, **9** still lies far below **10**. The differences in relative stabilities of cubane and cyclooctatetraene structures of carbon and silicon systems are mainly the result of differences in single and double bond energies among carbon and silicon bonds.

Figure 5 summarizes the comparisons of relative energies of $(\text{CH})_6$ and $(\text{SiH})_6$ valence isomers **4**−**8** based on calculated *ab initio* energies and as inferred from average bond energies. At the bond additivity level (center of the diagram), relative energies of structures increase with the number of double bonds each contains.

The bond energy difference Δ for silicon is almost twice that of carbon, and the bond additivity relative energies of $(\text{SiH})_6$ are spread out compared to those for carbon, but the two sets have the same stability order. Both orders are changed significantly when resonance stabilization and strain destabilization are introduced. For the carbon isomers, resonance energy provides a modest stabilization for benzene (**4**), while larger strain energies for **5**−**8** lift the energies of these structures far above that of benzene (**4**). Figure 4 shows that benzene is the most stable $(\text{CH})_6$ isomer by default; even without resonance stabilization, but with no strain, benzene would be the most stable of the $(\text{CH})_6$ isomers. Among the silicon isomers, the hexagons **4** and **4′** have the highest energies at the bond additivity level, with isomers **5**−**8** far below because of the large difference between single and double bond energies. Resonance

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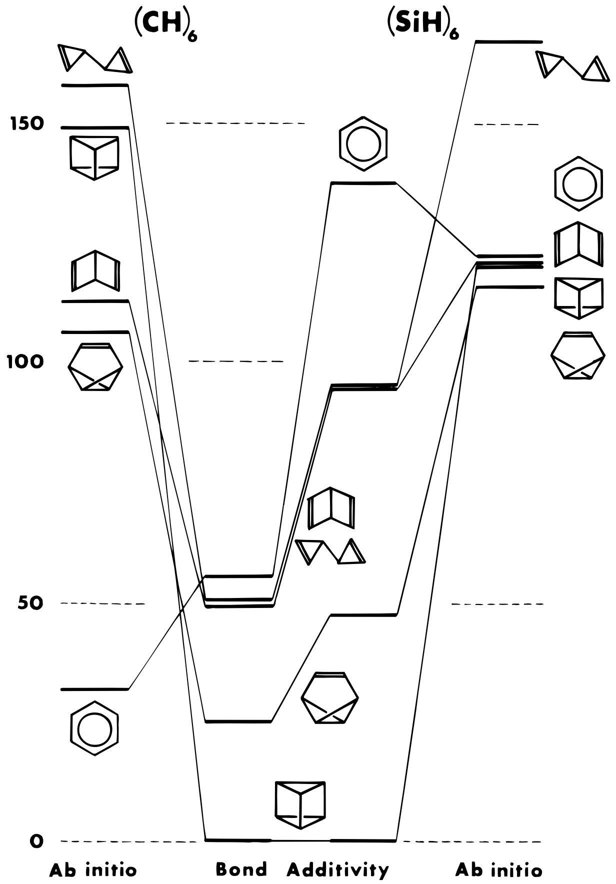

Figure 5. Relative energies of valence isomers $(XH)_6$ based on the bond additivity model (center) and, as stabilized by resonance or destabilized by strain, *ab initio* total energies (edges).

gives modest stabilization of **4** and **4′**, and strain energies push up from below the relative energies of **5**−**8** with the result that the energies of **4**−**7** are squeezed closely together. With two double bonds and two highly strained cyclopropene rings, the energy of **8** gets pushed far above those of the other isomers.

Conclusions

The three-membered cyclosilane ring has a larger strain energy than the comparable cycloalkane, but the four- and five-membered cyclosilanes are much less strained than the hydrocarbon analogs. For rings containing one double bond, the cyclosilenes are uniformly less strained than the comparable cycloalkenes. The strain energies of polyhedral clusters can be rationalized following the ring strain additivity rule. Strain energies of $(CH)_4$ and $(SiH)_4$ tetrahedrane are comparable and large. Carbon and silicon analogs of cyclooctatetraene both have negligible strain energies. All the other polyhedral silanes considered here have strain energies that are smaller than those of the analogous hydrocarbons because the individual component silicon rings have smaller strain energies. Hexagonal (planar and not quite planar) $(SiH)_6$ and $(CH)_6$ structures are both resonance stabilized, the hydrocarbon more so than silicon, but these resonance energies are quite modest compared to the strain energies of other clusters.

The relative energies of the polydedral silane analogs of $(CH)_{2n}$ valence isomers can be interpreted as resulting from differences in numbers of single and double bonds, the average energies associated with those bonds, and resonance energies and strain energies. Such considerations permit an estimate of the average energy of the SiSi double bond: $D(Si{=}Si) = 101$ kcal/mol.

The approximate additivity of average bond energies has been an extremely useful rule in rationalizing the signs and magnitudes of energy changes in chemical reactions. Substantial deviations from the additivity rule can be accounted for by introducing the concepts of strain and resonance. Structural clues warn us when these deviations might be significant and, at least for a number of examples from organic chemistry, we already have in hand rather well established values of strain and resonance energies to apply as corrections to the additivity model. Results in this paper provide estimates of strain and resonance energy parameters to the rings and clusters of silicon.

IC9512439