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Cyclopolysilanes: Structure, Strain, and the Form of the Singly Occupied Molecular Orbital in Their Radical Anions

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Abstract: The cyclopolysilanes $(SiH_2)_n$, $n = 3$ to 5, have been investigated via ab initio quantum mechanical methods. Strain energies are determined through the use of homodesmotic reactions, and the strain of the three-, four-, and five-membered silicon rings relative to each other and to the corresponding hydrocarbon rings is reasonably explained by consideration of angle strain, torsional strain, and substituent effects. Arguments of σ-aromaticity, which ascribe the apparent unusual stability of three-membered rings (3MR's) to delocalization of six σ electrons, fail to account for the observed data, and their fundamental assumption that force constants at one geometry can be used to predict strain energies at a vastly different geometry is seriously called to question. Finally, a model for the singly occupied molecular orbital (SOMO) of cyclopolysilane anion radicals is suggested by our studies which is π-bonding between the ring atoms and silicon-substituent antibonding. For reasons of symmetry, this π^* model readily explains available evidence from ESR and UV spectroscopy, but cannot easily explain results from recent ^{29}Si ENDOR studies. On the other hand, a recently developed σ^* model, which appears to account for the ENDOR results, seems at odds with the ESR and UV intensity data.

Cyclic hydrocarbons, both saturated and unsaturated, have unique features that have intrigued chemists for the last century, and attempts to explain "anomalous behavior" in these systems have contributed much to the lore and love of chemistry as a whole. "Strain" and "aromaticity" are two primary concepts that have evolved to rationalize many of the anomalies: "strain" to explain the relative instability of geometrically constrained (usually saturated) hydrocarbons, and "aromaticity" to rationalize the unusual stability of certain unsaturated hydrocarbons.

Despite their general acceptance, specific applications of these ideas remain highly controversial. For example [5]paracyclophane, which consists of a benzene ring with a para bridging normal pentane group and hence is potentially both strained and aromatic, has been judged by various groups to be both aromatic[1] (based on UV and NMR data) and not aromatic (based on molecular mechanics[2] and MNDO methods[3]). Another currently debated topic is the explanation for the nearly identical strain energies of cyclobutane and cyclopropane. According to simple ideas of angle strain, one might expect the three-membered ring to be significantly more strained than the four-membered ring. By *assuming* that cyclobutane is "normally strained" and hence cyclopropane is "abnormally strained", various authors have attributed the unusual stability of cyclopropane to σ-aromaticity,[4,5] surface delocalization of electrons over the ring plane,[6] and AO relaxation.[7] Many standard textbooks, not attempting to be quantitative, attribute the similar strain energies to increased nonbonded repulsions in the four-membered ring.[8,9]

For concepts such as strain and aromaticity to be generally useful (i.e., of use to more than organic chemists), their application should not be simply restricted to compounds containing carbon. For example, any reasonable "definition" of aromaticity should allow us to decide whether cyclic P_6, N_6, or Si_6H_6 (all isovalent with benzene), or even [5]paracyclophane, is aromatic or not. Similarly, any reasonable definition of strain should be applicable to, for example, polysilanes and phosphanes as well as the hydrocarbons. In fact, the study of potentially strained and/or aromatic nonhydrocarbons is no doubt the key to understanding the essence of such phenomena. For instance, it is clear that electronic absorption in a particular region of the spectrum would be of absolutely no use in deciding whether cyclic P_6 was or was not aromatic. In fact, even within the hydrocarbon series it is inappropriate to decide whether a compound, e.g., [5]paracyclophane, is aromatic (a property of the ground state) based on the presence or absence of a particular UV absorption (a function of both the ground- *and* excited-state energies). The aromaticity of a given electronic state should not be based on any

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property which involves another electronic state.

In the above sense it is clear that an understanding of other, nonhydrocarbon, ring systems is desirable. Silicon, isovalent with carbon, appears to be ideal in this regard in that there exists an increasing body of experimental data to test our ideas. This is particularly so for the saturated cyclopolysilanes, multiply bonded silicon compounds being quite rare and unsaturated polysilacycles completely unknown.

One striking feature of polysilane chemistry is the observation that many of their properties, e.g., photoionization and UV spectra, can be interpreted by assuming that the Si–Si σ orbitals are competely delocalized.[10] In fact, many of their properties are reminiscent of unsaturated aromatic hydrocarbons. For example, they exhibit strong absorptions in the ultraviolet region, give charge-transfer complexes with π acceptors, and show large substituent effects on disubstitution.[10] In addition, the cyclopolysilanes form anion and cation radicals in which the unpaired electron is compeltely delocalized over the ring.[11] Of course, these similarities between saturated polysilanes and aromatic hydrocarbons do not imply that the cyclopolysilanes are themselves aromatic. Rather, the similar spectral properties are a result of the presence of high-lying Si–Si σ orbitals and low-lying unoccupied orbitals in the cyclopolysilanes, just like the π and π^* orbitals of aromatic compounds.

The nature of the singly occupied molecular orbital (SOMO) of the anion radicals is of particular interest. Evidence from ESR spectroscopy shows that the unpaired electron in the anion is fully delocalized and that there is no direct silicon 3s orbital contribution to the SOMO. To accomodate these data, West et al. originally proposed a π^* model in which the SOMO was mainly composed of silicon 4p and 3d orbitals. More recently, ENDOR studies by West's group yielded a small hyperfine anisotropy for ^{29}Si which was deemed inconsistent with the π^* model,[15] and a 3p–σ^* or 3d SOMO model was proposed instead.[14] As we will show below, however, the σ^* model is not without its faults.

With the goal of better understanding the unique aspects of cyclic silicon compounds in particular, and strain in general, we have undertaken an ab initio study of the cyclic silicon hydrides Si_3H_6 and Si_4H_8 and planar Si_5H_{10}. Optimized geometries, vibrational frequencies, and infrared intensities are obtained at the self-consistent-field (SCF) level of theory using moderate-sized basis sets.

Strain energies are determined via use of an appropriate homodesmotic reaction.[16] For this purpose, disilane (Si_2H_6) and trisilane (Si_3H_8) have also been included in the study. We will show that the strain energies of the cyclopolysilanes, and their values relative to the analogous hydrocarbons, can be reasonably explained by consideration, much in the traditional way,[8,9] of angle strain, torsional strain, and substituent effects. On the other hand, σ-aromaticity arguments[4–6] make predictions, both quantitative and qualitative, which are not borne out by this study. The assumption that force constants at one geometry, for one molecule, can be used to predict strain in a different molecule, with a vastly different geometry, appears to be bad.

This study also suggests a particular form of the SOMO in the radical anions which is of π^* type. We wish to emphasize here that our studies are not definitive in this regard as our results on the cyclic hydrides predict the radical anions to be unbound in the gas phase, whereas the experimental data correspond to substituted polysilanes in solution. We will show, however, that the proposed π^* model is consistent with most of the experimental data and is in many ways superior to the σ^* model of West and co-workers.

During the course of the present investigation, a number of other papers dealing with the bonding and strain in the cyclopolysilane rings have appeared.[17–19] Our numerical values for the strain in cyclotrisilane and cyclotetrasilane agree with those found by Sax using pseudopotential approximations, but the ordering relative to the hydrocarbon rings is at odds with Schoeller and Dabisch's results. This is undoubtedly because they used isodesmic reactions, instead of homodesmic, and the known failings of isodesmic reactions[16] are probably accentuated in polysilanes owing to the relatively poor description of Si–Si bonds at the SCF level of theory.

Theoretical Methods

All of the molecules investigated here have been optimized at the self-consistent-field (SCF) level of theory. The basis set used was the standard Huzinaga–Dunning[20,21] double-ζ (DZ) basis set of contracted Gaussians technically designated Si(11s 7p/6s 4p), H(4s/2s). In addition, we have optimized all the structures using a DZ+d basis set which includes a single set of Cartesian d-like functions on silicon. Selected molecules have been reoptimized using a fully polarized basis set, labeled DZP, which also appends a set of p functions to hydrogen. The polarization function exponents were $\alpha_d(\mathrm{Si}) = 0.5$ and $\alpha_p(\mathrm{H}) = 0.75$.

Analytic SCF gradient techniques[22,23] were used to determine the geometrical structure of all the molecules studied. The optimization of the three-, four-, and five-membered cyclic structures was initially carried out within the confines of D_{nh} symmetry. The nature of these symmetry constrained structures was then tested via the determination, using analytic SCF second-derivative techniques,[24] of all quadratic force constants and the resulting harmonic vibrational frequencies. Only the three-membered ring (3MR) was found to be a true minimum in high symmetry, with the planar four-membered ring (4MR) being a transition state between equivalent D_{2d} symmetry minima, and the five-membered ring (5MR) having a degenerate pair of imaginary vibrational frequencies. Disilane and trisilane were optimized in D_{3d} and C_{2v} symmetry, respectively, and were determined to be minima. In addition to the vibrational frequencies, we have obtained the associated infrared intensities analytically.[25]

The effects of electron correlation on the barrier to planarity of the 4MR have been included by the method of configuration interaction (CI).[26] Only the valence electrons have been included in the CI; i.e., all core-like (Si 1s, 2s, 2p) orbitals and their virtual orbital counterparts have been omitted from the CI. Otherwise, all singly and doubly excited configurations relative to the SCF reference function have been included (CISD). The largest CI included 65 343 configuration state functions when carried out in D_2 symmetry. The effects of unlinked quadruple excitations are included in an approximate manner using Davidson's formula (CISD-Q).[27]

The electron configuration of the rings are as follows:

$$4a_1'^2\ 5e'^4\ 2a_2''^2\ 5a_1'^2 2e''^4 6e'^4 \qquad (\mathrm{Si_3H_6},\ D_{3h})$$

$$4a_{1g}^2\ 5e_u^4\ 4b_{1g}^2\ 2a_{2u}^2\ 5a_{1g}^2\ 2e_g^4\ 2b_{2u}^2\ 6e_u^4\ 2b_{2g}^2 \qquad (\mathrm{Si_4H_8},\ D_{4h})$$

$$5a_1^2\ 6e^4\ 5b_2^2\ 6b_2^2\ 6a_1^2\ 7e^4\ 7a_1^2\ 8e^4\ 2b_1^2 \qquad (\mathrm{Si_4H_8},\ D_{2d})$$

$$4a_1'^2\ 5e_1'^4\ 5e_2'^4\ 2a_2''^2\ 2e_1''^4\ 5a_1'^2\ 2e_2''^4\ 6e_1'^4\ 6e_2'^4 \qquad (\mathrm{Si_5H_{10}},\ D_{5h})$$

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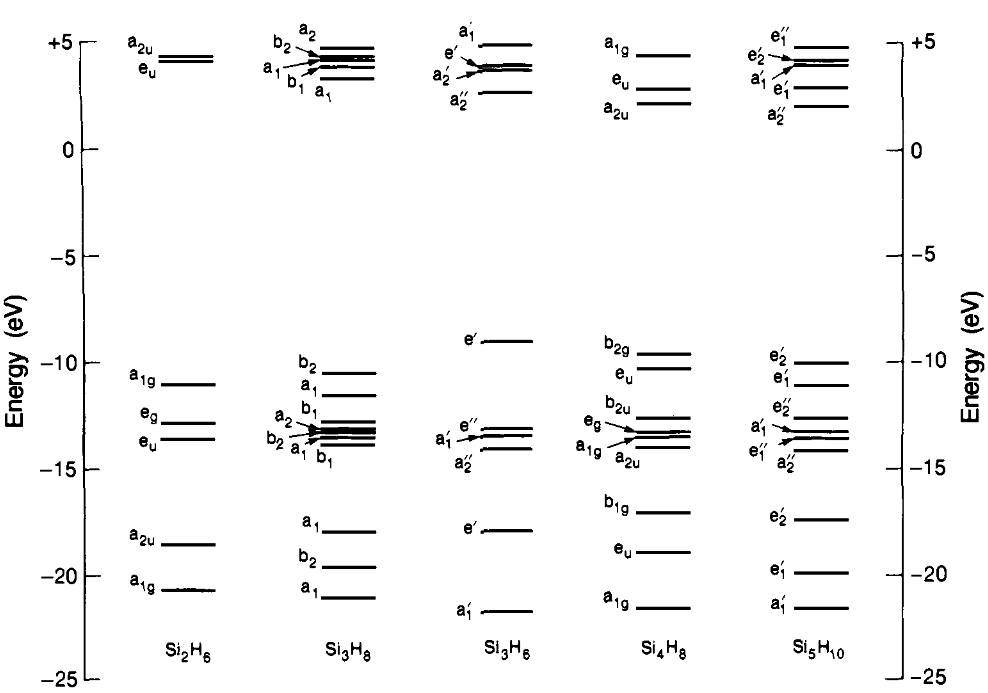

Figure 1. Orbital energies (in eV) and symmetry designation of the valence occupied and lowest lying unoccupied orbitals of disilane, trisilane, cyclotrisilane, and planar cyclotetrasilane and cyclopentasilane. These results were obtained using the DZ+d basis.

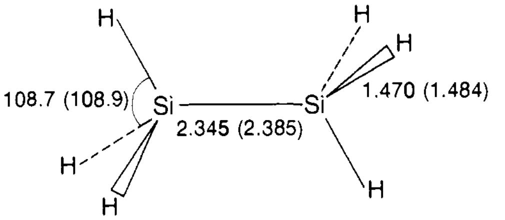

Figure 2. Optimized geometry of disilane (D_{3d} symmetry) using DZ (in parentheses) and DZ+d basis sets. Bond distances are in angstroms.

Qualitatively, this is similar to those in cycloalkanes, but the ring bonding orbitals, except for the totally symmetric one, are much higher in energy than the Si–H bonding orbitals.[17] This can be seen in Figure 1, where the orbital energies of the valence occupied and lowest lying unoccupied orbitals are shown, along with their symmetry designations.

Structural Predictions

1. Disilane and Trisilane. The optimized geometries obtained in this study are shown in Figures 2–6 for both the DZ (in parentheses) and DZ+d basis sets. Of all the structures investigated here, extensive experimental data are available only for disilane.[28-30] Cyclopentasilane is known to be nonplanar[31] but has been investigated here only in its planar D_{5h} configuration. The parent three- and four-membered rings are unknown but various substituted rings are known.[32-37] Although, no experimental structure for trisilane has been reported, the permethylated derivative, octamethyltrisilane, is known.[38]

Table I. Disilane (Si_2H_6) Vibrational Frequencies (in cm^{-1}) and (in Parentheses) Absolute Infrared Intensities (in km/mol)

symmetry	DZ	DZ+d	DZP	expt	description
a_{1g}	2295	2397	2344	2163	SiH_3 stretch
	975	1040	1035	920	SiH_3 deformation
	407	466	466	432	Si–Si stretch
a_{1u}	119	128	132		SiH_3 torsion
a_{2u}	2279	2380 (184)	2330 (156)	2154 (vs)	SiH_3 stretch
	903	957 (753)	952 (715)	844 (vs)	SiH_3 deformation
e_u	2290	2384 (594)	2336 (499)	2179 (vs)	SiH_3 stretch
	1028	1055 (313)	1048 (292)	940 (s)	SiH_3 deformation
	417	420 (75)	417 (71)	379 (s)	SiH_3 rock
e_g	2282	2377	2328	2155	SiH_3 stretch
	1015	1038	1032	941	SiH_3 deformation
	676	703	699	628	SiH_3 rock

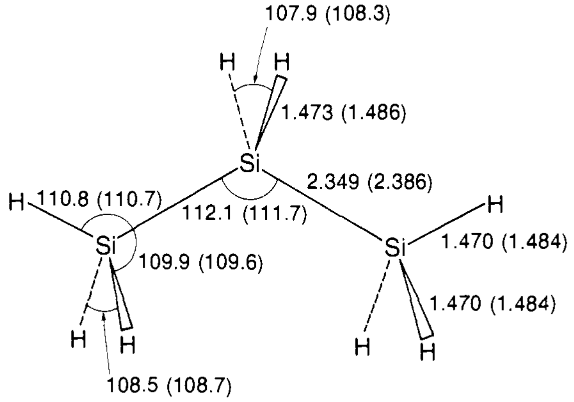

Figure 3. Optimized geometry of trisilane (C_{2v} symmetry) using DZ (in parentheses) and DZ+d basis sets. Bond distances are in angstroms.

Disilane (Figure 2) was found to be a minimum in D_{3d} symmetry with an Si–Si bond distance of 2.385 Å using the DZ basis

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Table II. Trisilane (Si_3H_8) Vibrational Frequencies (in cm^{-1}) and Absolute Infrared Intensities (in km/mol)

symmetry	DZ	DZ+d	description
a_1	2291	2393 (8.5)	SiH_3 stretch
	2286	2382 (244)	SiH_3 stretch
	2268	2361 (103)	SiH_2 stretch
	1028	1055 (112)	SiH_3 deformation + SiH_2 scissors
	994	1034 (44)	SiH_3 deformation + SiH_2 scissors
	947	997 (267)	SiH_3 deformation + SiH_2 scissors
	609	631 (14)	SiH_3 deformation
	367	415 (0.8)	Si–Si stretch
	111	112 (2.2)	Si–Si–Si bend + SiH_2 scissors
a_2	2283	2378	SiH_3 stretch
	1017	1043	SiH_3 deformation
	768	785	SiH_2 twist + SiH_3 deformation
	472	471	SiH_3 deformation + SiH_2 twist
	72	77	SiH_3 torsion
b_1	2288	2383 (354)	SiH_3 stretch
	2273	2361 (43)	SiH_2 stretch
	1022	1046 (139)	SiH_3 deformation
	635	661 (15)	SiH_3 deformation + SiH_2 rock
	341	350 (35)	SiH_2 rock + SiH_3 deformation
	89	97 (0.0)	SiH_3 torsion
b_2	2284	2385 (218)	SiH_3 stretch
	2283	2380 (44)	SiH_3 stretch
	1022	1045 (46)	SiH_3 deformation
	930	991 (478)	SiH_3 deformation
	765	812 (385)	SiH_2 wag + SiH_3 deformation
	493	507 (27)	SiH_3 deformation + Si–Si stretch and SiH_2 wag
	437	486 (12)	Si–Si stretch + SiH_3 deformation

set. This is a full 0.054 Å longer than the experimental value of 2.331 Å,[29] and represents the major failure of the DZ basis set in the study of polysilanes. The DZ+d basis set does much better in this regard, predicting r(Si–Si) = 2.345 Å, or only 0.014 Å longer than experiment. While the Si–Si bond distances are longer than the experimental values, the Si–H bond distances are uniformly shorter than the experimentally determined value r(Si–H) = 1.492 Å, more so with the DZ+d basis set (0.022 Å error) than with DZ (0.008 Å). The bond angles are, in all cases, within the range of experimental errors.

The vibrational frequencies and absolute infrared intensities of disilane are shown in Table I, along with the experimental values.[28,30] To test the sensitivity of the results to the inclusion of p functions on hydrogen, we have included results for disilane optimized using the fully polarized DZP basis set as well. The DZP geometry obtained was r(Si–Si) = 2.346 Å, r(Si–H) = 1.477 Å, and θ(H–Si–H) = 108.8°, differing from the DZ+d results mainly in that the Si–H bond length has increased by 0.007 Å. The effect on the frequencies is to lower all the Si–H stretches by ~50 cm^{-1}, with all other modes remaining largely unchanged. The absolute intensities change as well, but are qualitatively similar to the DZ+d results. Compared to experiment the polarized basis sets uniformly overestimate the actual frequencies, with an average error of 11.0% for DZ+d, reduced to 9.8% with the DZP basis set.

The normal trisilane optimized geometry and vibrational frequencies are shown in Figure 3 and Table II, respectively. The geometry is unremarkable, with Si–Si bond distances only slightly longer than that in Si_2H_6 (~0.004 Å DZ+d) and an Si–Si–Si bond angle ~2.5° larger than tetrahedral. The SiH_3 groups are essentially the same as those in disilane, with approximate C_{3v} local symmetry, and the central SiH_2 group has a slightly compressed H–Si–H angle and correspondingly longer Si–H bond distances.

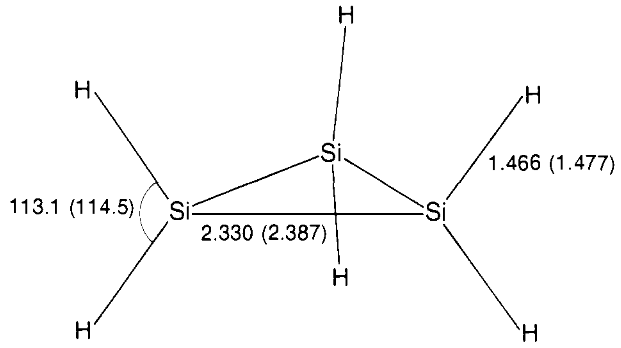

Figure 4. Optimized geometry of cyclotrisilane (D_{3h} symmetry) using DZ (in parentheses) and DZ+d basis sets. Bond distances are in angstroms.

Table III. Cyclotrisilane (Si_3H_6) Vibrational Frequencies (in cm^{-1}) and Absolute Infrared Intensities (in km/mol)

symmetry	DZ	DZ+d	DZP	description
a_1'	2308	2401	2351	Si–H stretch
	928	992	988	SiH_2 scissors
	474	548	548	Si–Si stretch
a_2'	444	521	519	SiH_2 wag
e'	2301	2392	2345 (310)	Si–H stretch
	923	981	978 (501)	SiH_2 scissors
	708	747	743 (278)	SiH_2 wag
	366	410	410 (8.8)	Si–Si stretch
a_1''	722	736	732	SiH_2 twist
a_2''	2333	2416	2368 (225)	Si–H stretch
	342	384	384 (103)	SiH_2 rock
e''	2326	2407	2360	Si–H stretch
	630	662	658	SiH_2 twist + rock
	273	272	272	SiH_2 rock + twist

2. The Cyclopolysilanes. Cyclotrisilane's optimized structure and vibrational frequencies are shown in Figure 4 and Table III, respectively. The DZ basis predicts a longer Si–Si bond length than in either di- or trisilane, but this prediction is reversed with the DZ+d basis set where we find it to be 2.330 Å, or 0.015 Å shorter than in disilane. The Si–H bonds are also shorter than in Si_2H_6 and the H–Si–H angle is correspondingly larger. We have also optimized Si_3H_6 using the DZP basis set and, as in Si_2H_6, its major effect is to lengthen the Si–H bond distance (by 0.006 Å to 1.472 Å). Our results for the geometry of Si_3H_6 are similar to earlier theoretical predictions.[17,19] Crystal structures of a few heavily substituted cyclotrisilanes are known, and all have significantly longer bond distances than those found here for the hydride. For example hexa-2,6-dimethylphenylcyclotrisilane,[32] which has approximate C_{2v} symmetry, has a unique Si–Si bond length of 2.375 Å and roughly equivalent bonds with r(Si–Si) = 2.422 and 2.425 Å, and hexa-*tert*-butylcyclotrisilane,[33] which possesses complete D_{3h} symmetry, has a remarkably long Si–Si bond distance of 2.511 Å. Cis–cis and cis–trans 1,2,3-tri-*tert*-butyl-1,2,3-trimesitylcyclotrisilane are also known[34] and have bond distances ranging from 2.39 to 2.43 Å. Although electronic effects may be responsible for some of these observations, steric crowding undoubtedly plays a major role.

The optimized geometry of cyclotetrasilane is shown in Figure 5. The planar structure is found to be a transition state with an imaginary b_{1u} mode of 59i cm^{-1} (60i cm^{-1}) at the DZ (DZ+d) SCF level of theory (Table IV), leading to a minimum energy structure of D_{2d} symmetry just as in cyclobutane (Table V). The barrier to planarity is 0.54 kcal/mol with the DZ basis set, increasing to 0.74 kcal/mol with DZ+d. This result is similar to that of Sax who found a barrier of 0.53 kcal/mol.[18] CISD energies at the SCF optimized structure, however, increase this to 1.48 (DZ) and 1.54 kcal/mol (DZ+d), and the Davidson corrected results yield 1.64 (DZ) and 1.75 kcal/mol (DZ+d). On the other hand, zero-point vibrational energy effects lower the DZ and DZ+d barrier by 0.36 and 0.25 kcal/mol, respectively. The tilt of the SiH_2 groups, defined as the angle between the H–Si–H angle bisector and the Si–Si–Si bisector, is 6.7° with both basis sets. The Si–Si bond distance is 0.008 Å shorter in D_{2d} than in D_{4h} symmetry, and the value found here, 2.368 Å, falls in the range of values found experimentally,[35,37,38] 2.359–2.409 Å.

While the folded nature of Si_4H_8 might seem obvious to an organic chemist, it is of interest in that the symmetrically substituted cyclotetrasilanes that are known experimentally take on a variety of configurations. For example, octamethylcycotetrasilane,[35] $[Me_2Si]_4$, and octakis(trimethylsilyl)cyclotetrasilane,[36] $[(Me_3Si)_2Si]_4$, are reported to be planar, while others such as

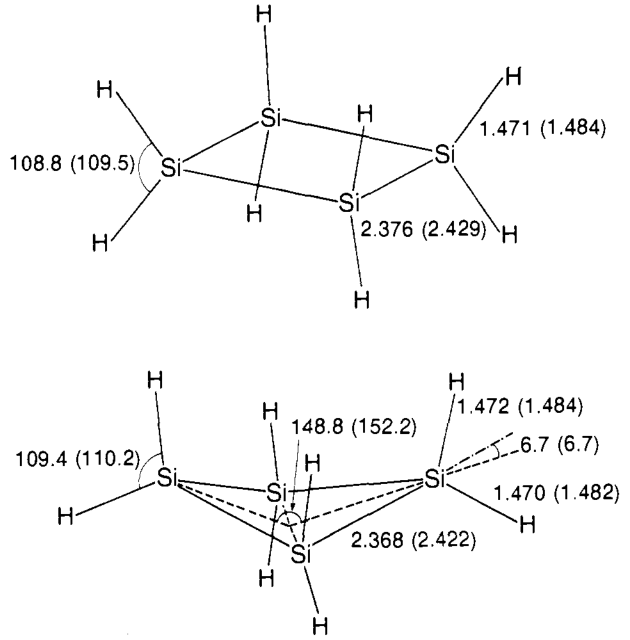

Figure 5. Optimized geometry of cyclotetrasilane in its planar (D_{4h} symmetry) and minimum energy (D_{2d}) configurations using DZ (in parentheses) and DZ+d basis sets. Bond distances are in angstroms.

Table IV. Si_4H_8 (D_{4h} symmetry) ${}^1A_{1g}$ Vibrational Frequencies (in cm^{-1})

symmetry	DZ	DZ+d	description
a_{1g}	2286	2382	Si-H stretch
	984	1032	SiH_2 scissors
	401	454	Si-Si stretch
a_{2g}	579	651	SiH_2 wag
b_{1g}	732	770	SiH_2 wag
	388	440	Si-Si stretch
b_{2g}	2269	2362	Si-H stretch
	962	1004	SiH_2 scissors
	284	282	ring deformation
e_g	2285	2372	Si-H stretch
	698	723	SiH_2 twist
	279	307	SiH_2 rock + twist
a_{1u}	753	775	SiH_2 twist
a_{2u}	2294	2380	Si-H stretch
	318	340	SiH_2 rock
b_{1u}	2279	2365	Si-H stretch
	470	536	SiH_2 rock
	59i	60i	SiH_2 rock + ring pucker
b_{2u}	506	513	SiH_2 twist
e_u	2272	2366	Si-H stretch
	957	1003	SiH_2 scissors
	768	824	SiH_2 wag
	377	437	Si-Si stretch

octaneopentylcyclotetrasilane,[37] $[(^t\mathrm{BuCH_2})_2\mathrm{Si}]_4$, and octakis(isopropyl)cyclotetrasilane,[39] $[i\text{-}\mathrm{Pr_2Si}]_4$, are highly folded with out-of-plane angles of 38.8 and 37.1°, respectively. Cyclotetrasilane appears, at least at this level of theory, to be between these extremes, with an out-of-plane angle of 31.2° (DZ+d), slightly larger than the value found by Sax[18] (28.7°). The reasons why such different experimental structures are obtained are not clear.[40] Table IV lists the vibrational frequencies of Si_4H_8 at its D_{2d} minimum.

Cyclopentasilane's structure is known experimentally,[31a] and it has been studied by IR and Raman spectroscopy.[31b] Its geometry is similar to that of cyclopentane; i.e., it is puckered, and models of the C_2 and C_s symmetry give good agreement with experimental data. Here we have optimized only the planar structure, shown in Figure 6. The Si-Si bond distance is intermediate between those found for Si_3H_6 and planar Si_4H_8. If we assume that the bond distances will shorten by the same amount as those of Si_4H_8 upon geometrical relaxation, then we would predict a bond distance in nonplanar Si_5H_{10} of 2.359 Å, or 0.017 Å longer than the experimentally determined value of 2.342 Å,[31] similar to the errors in disilane. A frequency deter-

Table V. Si_4H_8 (D_{2d} Symmetry) Vibrational Frequencies and Absolute Infrared Intensities (in km/mol)

symmetry	DZ	DZ+d	description
a_1	2294	2389	Si-H stretch
	2280	2367	Si-H stretch
	986	1036	SiH_2 scissors
	535	579	SiH_2 rock
	408	463	Si-Si stretch
	68	77	ring pucker + SiH_2 rock
a_2	578	644	SiH_2 wag
	508	506	SiH_2 twist
b_1	793	821	SiH_2 wag + twist
	685	704	SiH_2 wag + twist
	383	430	Si-Si stretch
b_2	2296	2384 (296)	Si-H stretch
	2272	2365 (138)	Si-H stretch
	964	1007 (62)	SiH_2 scissors
	388	415 (30)	SiH_2 rock + ring deformation
	221	219 (11)	ring deformation + SiH_2 rock
e	2291	2381 (394)	Si-H stretch
	2274	2364 (217)	Si-H stretch
	958	1004 (482)	SiH_2 scissors
	767	816 (549)	SiH_2 wag
	701	723 (2.0)	SiH_2 twist
	385	444 (2.9)	Si-Si stretch
	308	327 (10)	SiH_2 rock + SiH_2 twist

Table VI. Si_5H_{10} Vibrational Frequencies (in cm^{-1})[a]

symmetry	DZ	exp	description
a_1'	2285	2135	Si-H stretch
	999	926	SiH_2 scissors
	348	382	Si-Si stretch
a_2'	630		SiH_2 wag
e_1'	2272	2141	Si-H stretch
	974	901	SiH_2 scissors
	786	715	SiH_2 wag
	381	406	Si-Si stretch
e_2'	2264	2135	Si-H stretch
	967	893	SiH_2 scissors
	736	700	SiH_2 wag
	452	464	Si-Si stretch
	235	172	ring deformation
a_1''	799		SiH_2 twist
a_2''	2287	2141	Si-H stretch
	317	591	SiH_2 rock
e_1''	2281	2135	Si-H stretch
	755	637	SiH_2 twist
	331	591	SiH_2 rock + twist
e_2''	628		SiH_2 twist + rock
	447		SiH_2 rock + twist
	45i		ring deformation + SiH_2 rock

[a] Experimental values from ref 31b.

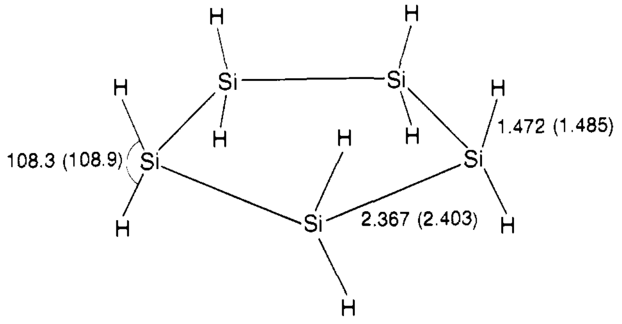

Figure 6. Optimized geometry of planar cyclopentasilane (D_{5h} symmetry) using DZ (in parentheses) and DZ+d basis sets. Bond distances are in angstroms.

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(39) Watanabe, H.; Kato, M.; Okawa, T.; Kougo, K.; Nagai, Y.; Goto, M. referred to in ref 37.

Table VII. Total SCF Energies (in hartrees), Zero-Point Vibrational Energies (ZPVE, in kcal/mol), and Zero-Point Corrected Strain Energies (in kcal/mol) of the Molecules Investigated

molecule	symmetry	DZ energy	DZ+d energy	DZ–ZPVE	DZ+d–ZPVE	DZ strain	DZ+d strain
Si_3H_6	D_{3h}	−870.067 26	−870.180 86	32.3	33.9	38.0	36.7
Si_4H_8	D_{4h}	−1160.145 84	−1160.294 00	44.0[a]	46.2[a]		
Si_4H_8	D_{2d}	−1160.146 71	−1160.295 17	44.4	46.5	16.1	16.2
Si_5H_{10}	D_{5h}	−1450.210 47	−1450.393 44	56.1[a]		4.8[b]	6.2[b]
Si_3H_8	C_{2v}	−871.265 12	−871.385 92	43.4	45.2		
Si_2H_6	D_{3d}	−581.221 50	−581.305 25	32.0	33.3		

[a] Neglecting imaginary frequencies. [b] Not zero-point corrected. See text.

mination using the DZ basis set shows it to have a degenerate e″ imaginary frequency of 45i cm^{-1}. The vibrational frequencies are shown in Table VI, along with the experimental values.[31b] We generally agree with Hengges results[31b] except for the a_2'' and e_1'' rocking modes which were assigned to a very weak transition at 591 cm^{-1}. We find these modes to be near 300 cm^{-1}, and a logical explanation would be that the observed mode was a combination or overtone band.

Finally, we note that the bond distances in the parent cyclosilanes have been found to increase in the order 3MR < 5MR < 4MR, whereas in experimentally known substituted compounds it is usually 5MR < 4MR < 3MR. It seems clear that the reason for this is the steric repulsion between the bulky substituents required on the smaller rings to protect them from attack.[40]

Strain

The ring strain in the cyclopolysilanes has been determined via use of the homodesmotic reactions[16]

$$(SiH_2)_n + nSi_2H_6 \rightarrow nSi_3H_8$$

which are known, in the case of hydrocarbons, to yield values of strain which are in excellent agreement with the more traditional group increment method.[41] The total SCF energies and zero-point vibrational energies determined are found in Table VII. The strain energies derived from them (i.e., the exothermicity of the above reaction) are also shown in Table VII and agree well with the results of Sax using a local pseudopotential SCF procedure for the three- and four-membered rings.[18,19] Given the large changes in Si–Si bond distances that occur upon addition of polarization functions to the silicon DZ basis set, it is somewhat surprising how little the strain energies vary from one basis set to the other. The non-zero-point corrected values are 1–2 kcal/mol higher for the three- and four-membered rings. As mentioned earlier, the five-membered planar ring is not a minimum and thus does not have the required number of real vibrational frequencies to determine the zero-point vibrational energy correction. The values given without zero-point correction are reasonable, however, in that the difference in energy between the actual Si_5H_{10} minimum and the planar ring is probably 1–2 kcal/mol[31a] and would thus approximately cancel the expected zero-point correction. Our final values for the strain are 36, 16, and 6 kcal/mol for the three-, four-, and five-membered unsubstituted silicon rings, respectively. When we compare these values with the ones for the corresponding alkanes, cyclopropane (27), cyclobutane (26), and cyclopentane (6), we see that the cyclopolysilane 3MR is ~10 kcal/mol more strained, and the 4MR is ~10 kcal/mol less strained than the analogous hydrocarbon rings.

As we noted in the Introduction, one of the goals of this research is a comparison of various models of strain and aromaticity as they apply to other, nonhydrocarbon, molecules, the purpose being to see which models apply only to hydrocarbons and which appear to be more general in nature. Since the debate about strain in hydrocarbon rings has centered on an explanation for the nearly identical strain energies in the 3MR and 4MR, we will apply the various models and explanations to our polysilane 3MR and 4MR to see what they would predict, and compare these model results with the ab initio predictions reported here.

The first model is the traditional one found in many standard textbooks on organic chemistry and is only qualitative in nature.[8,9] Essentially it notes that, while cyclopropane has three 60° bond angles, and six eclipsed hydrogens, cyclobutane has four 90° bond angles and eight eclipsed hydrogens. Furthermore, the eclipsing hydrogens are closer to each other in planar cyclobutane than in cyclopropane. In addition, reduction of the torsional strain due to the eclipsed hydrogens is generally cited as the reason why cyclobutane adopts a folded configuration with CH_2 groups tilted out of the local C–C–C plane. The size of these eclipsing interactions can be estimated from the known 3-kcal/mol rotational barrier of ethane which, with three sets of eclipsed hydrogens, yields an interaction ~1 kcal/mol per eclipsed pair. The corresponding value in disilane is 1.2 kcal/mol,[30] giving a value of ~0.4 kcal/mol per eclipsing interaction. Thus, this model would predict that the difference in the polysilane 3MR and 4MR strain energies should be increased and that, by itself, torsional strain (as opposed to angle or total strain) should be ~8 (1.0 – 0.4) = 4.8 kcal/mol less in Si_4H_8 than C_4H_8 and around 6 (1.0 – 0.4) = 3.6 kcal/mol less in Si_3H_6 than in C_3H_6. As it stands, this model does not make any predictions about the actual difference in the strain of the 3MRs and 4MRs, and the fact that the actual difference is ~20 kcal/mol could certainly not have been predicted based on torsional considerations alone. On the other hand, it is well known that di- and tricoordinate heavier main group elements routinely form bond angles close to 90°, and in general have much smaller angles than the corresponding first-row species.[42] This would explain why cyclotetrasilane is at least twice as stable relative to cyclobutane as we would have expected based on torsional considerations alone. By itself, however, it suggests that cyclotrisilane, too, should have less strain than cyclopropane, which it does not.

One other factor that has to be considered is the effect of the substitutents, in this case the hydrogens, on the value of the strain energy. It has been shown that electronegative substituents increase the value of the strain energy and electropositive substituents decrease the strain in hydrocarbon 3MR's.[43] Since hydrogen is more electronegative than silicon, but less electronegative than carbon, it would be expected to increase the strain of cyclotrisilane relative to cyclopropane. To our knowledge, no systematic studies of a similar nature have been done on substituted cyclobutanes, but one might guess that substituent effects will become smaller as the ring expands and the bonding between ring atoms becomes more localized in nature. In fact, if this is true, it may help explain the similar strain energies of C_3H_6 and C_4H_8, insofar as the relatively electropositive hydrogen would stabilize C_3H_6 relative to C_4H_8. In support of this notion, we note that the strain energy of hexafluorocyclopropane (75–80 kcal/mol) has been found to be significantly larger than that of octafluorocyclobutane (45–50 kcal/mol).[44] A systematic study along these lines could definitely clear up this issue.

In short, it seems that the traditional model of strain in ring systems gives a reasonable explanation, not only for the relative stabilities of cyclic hydrocarbons, but also for the strain energies

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[40] Watanabe, H.; Nagai, Y. In *Organosilicon and Bio-organosilicon Chemistry*; Sakurai, H., Ed.; Ellis Horwood: Chichester, West Sussex, England, 1985; Chapter 9, pp 107–114.

[41] Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; Wiley: New York, 1976.

[42] Cherry, W.; Epiotis, N.; Borden, W. T. *Acc. Chem. Res.* **1977**, *10*, 167.

[43] Dill, J. D.; Greenberg, A.; Liebman, J. F. *J. Am. Chem. Soc.* **1979**, *101*, 6814.

[44] Greenberg, A.; Liebman, J. F.; Dolbier, W. R.; Medinger, K. S.; Skancke, A. *Tetrahedron* **1983**, *39*, 1533.

in cyclopolysilanes and their relationship relative to the hydrocarbons. Due consideration of angle strain, torsional (eclipsing) strain, and substituent effects appear to account in a qualitative way for a vast array of data, and for these reasons we consider it to be a success.

The second model is due to Dewar,[4,5] and is a combination of traditional ideas of angle strain along with an analogy between unsaturated cyclic aromatic species and saturated ring systems. Essentially Dewar notes that if we consider the 4- and 5MR's to be somehow "normally strained", then the fact that the 3MR has essentially the same strain as the 4MR implies that it has some special stability not predictable by bond angle strain considerations. He attributes this unusual stability to "σ-aromaticity", i.e., to delocalization of six σ ($6 = 4n + 2$ for $n = 1$) electrons around the ring. The original argument went as follows: first, for reasons that can be found in the original articles,[4,5] Dewar assumed that cyclobutane would have essentially no antiaromatic destabilization and that its conventional strain energy (CSE) would be equal to the sum of its angle strain, R, and eclipsing strain, taken to be 12 kcal/mol (we assume he was including 1,3 eclipsing interactions). Thus

$$\mathrm{CSE}(C_4H_8) = R + 12 = 27.4\ \mathrm{kcal/mol}$$

yielding a value of 15.4 kcal/mol for the angle strain in C_4H_8. Then, since the angle strain per CH_2 group in C_3H_6 should be $(49.5/19.5)^2 = 6.44$ times that of C_4H_8, the total angle strain in C_3H_6 should be $(3/4)(6.44) = 4.83$ times that in C_4H_8. The CSE of C_3H_6 should then be

$$\mathrm{CSE}(C_3H_6) = 4.83R + 9 - A$$

where A is the aromatic stabilization energy. Inserting 28.3 kcal/mol for CSE(C_3H_6), Dewar obtained a value for the σ-aromatic stabilization energy of 55 kcal/mol for cyclopropane. Our analogous calculation on the silicon rings yields a similar stabilization, but smaller, only 22 kcal/mol. Given that measures of aromatic stabilization in planar Si_6H_6, the all-silicon analogue of benzene, are about one-half those in benzene itself, this seems reasonable. The fundamental assumption here is that the force constants obtained for the 4MR, in the way described above, are applicable to the analysis of strain in 3MR's. In fact, if one attempts to predict the strain of cyclobutane from cyclopentane in the same way, one would have to conclude that cyclobutane, too, was aromatic. It seems that smaller rings are always more stable than can be predicted by parameters derived from larger rings, and while it might be tempting to attribute this to some sort of delocalization phenomena, it appears instead to be a basic defect of the fundamental assumption.

Somewhat surprisingly, since he uses a different method, Cremer has also concluded that cyclopropane is a σ-aromatic molecule with an aromatic delocalization energy of 48 kcal/mol.[6] His arguments are based on a Bader-type analysis of the electron density of cyclopropane determined from ab initio SCF wave functions. Cremer neglects eclipsing hydrogen repulsions and determines the ring strain by using a normal aliphatic hydrocarbon C–C–C bending force constant[45] of 1.07 mdyn·Å/rad^2, with the calculated interbond path angles at the carbon atoms. This angle, determined to be 78.8°, in conjunction with the above force constant, yields a value of 75 kcal/mol which, when compared with the CSE of 27 kcal/mol, yields the 48-kcal/mol value for the delocalization energy. We are not aware of a similar analysis of cyclobutane, but the following observations are in order. First, the degree of bond angle bending in cyclobutane is undoubtedly less than that in cyclopropane (78.8 - 60 = 18.8°). For example, valence electron density plots of Si_3H_6 by Sax give a difference of 24° between the internuclear angle and the angle determined by the maximum in the electron density plots, while the same value for Si_4H_8 is only 5.4° (these angles are not formally identical with those used by Cremer but serve our purposes here). On this basis we might guess that the actual value of the angle for C_4H_8 is near 95°. Thus we would obtain a value for the angle strain of C_4H_8 of 20 kcal/mol, and, if we include eclipsing interactions or argue that C_4H_8 is antiaromatic, we would be in the right area for the actual CSE of C_4H_8. Since the actual angle is unknown, we can consider this a qualified success.

Applying Cremer's analysis to the cyclopolysilanes creates some immediate difficulties. Using an experimentally determined force constant[46] of 0.274 mdyn·Å/rad^2 in conjunction with the *internuclear* angles of 60 and 90°, we obtain angle strain values of 44 and 9 kcal/mol for Si_3H_6 and Si_4H_8, respectively. Neglecting torsional strain, we would conclude that Si_3H_6 has a σ-aromatic stabilization energy of only 8 kcal/mol, an unrealistically low estimate compared to that in C_3H_6. If instead we used the interpath bond angle of 84° obtained by Sax,[19] we would obtain a value of 12 kcal/mol for the ring strain, a full 24 kcal/mol *below* that obtained in our study, and hence we would have to conclude that Si_3H_6 was considerably *antiaromatic*, not aromatic as it should be according to the model. We cannot imagine any way to rehabilitate this result, which is *at least* 30 kcal/mol below that expected and casts serious doubt on the model's general validity.

The methods of Dewar[4,5] and Cremer[6] have one thing in common, namely, that they assume that force constants obtained from other species can be accurately used to predict the strain of the 3MR's. Dewar uses force constants appropriate for a hypothetical cyclobutane molecule which, given certain assumptions about eclipsing interactions in C_4H_8, is required to give the exact conventional strain energy of C_4H_8. The resulting difference between the predicted strain and actual strain of C_3H_6 using the internuclear angles is then attributed to σ-aromaticity. Cremer, on the other hand, uses actual force constants for aliphatic straight-chain paraffins, neglects torsional strain, and uses the bond path angles at the atoms to determine the strain, once again attributing the difference to σ-aromaticity. That the two methods obtain very similar results for cyclopropane seems nothing short of magical. That they obtain quite different results for cyclotrisilane is hardly surprising and attests to the arbitrary nature of using any set of force constants at one geometry to determine the strain at a vastly different geometry.

Finally, we would like to analyze the qualitative arguments given by Dewar to rationalize the existence of such a large proposed σ-aromatic stabilization energy in C_3H_6. His argument is based on perturbation molecular orbital (PMO) theory and makes essential use of the fact that the resonance integral between orthogonal hybrid AOs on a given atom in a saturated molecule does not vanish and, indeed, is even larger than that between adjacent 2p orbitals in conjugated hydrocarbons. To zeroth order in the PMO model we have electrons in a set of localized bond orbitals. First-order perturbations are large but do not change the total energy of the system, only the individual orbital energies. Second-order perturbations allow the bonding and antibonding orbitals to mix, producing an overall stabilization of the molecule. The familiar result from perturbation theory, found in any standard quantum mechanics book, is that the magnitude of this interaction is inversely proportional to the difference of the orbital energies.

The importance of this statement is as follows. It is well known that the cyclopolysilanes have very high orbital energies relative to those of the cycloalkanes and in fact absorb light in the same regions of the UV spectra as the hydrocarbon polyenes. Thus, on this basis alone, one would expect the nonadditive stabilizing second-order interactions to be much *larger* in cyclopolysilanes than in cycloalkanes. This, however, is in no way the case. Even using the hypothetical force constants for the appropriate 4MR, as done by Dewar,[4] predicts a stabilization energy of only 20 kcal/mol for cyclotrisilane compared to ~50 kcal/mol for cyclopropane. This objection seems to be most fundamental and in addition to the earlier mentioned ambiguities leads us to conclude that σ-aromaticity has no role in any discussion of strain in ring systems.

To summarize, the traditional model of strain,[8,9] albeit a qualitative one, seems to work quite well, but may need more

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(45) Snyder, R. G.; Zerbi, G. *Spectrochim. Acta, Part A* **1967**, *23*, 391.

(46) Smith, Z.; Almenningen, A.; Hengge, E.; Kovar, D. *J. Am. Chem. Soc.* **1982**, *104*, 4362.

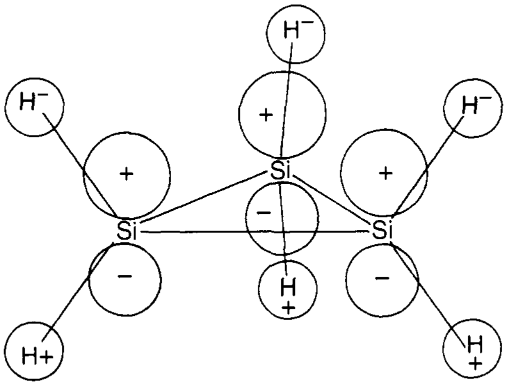

Figure 7. A minimum basis representation of the LUMo (a_2'' symmetry) in cyclotrisilane. LUMO's analogous to this were also found for planar Si_4H_8 (a_{2u} symmetry) and Si_5H_{10} (a_2'' symmetry).

investigation particularly on the relative role of substituent effects on 3MR and 4MR strain energies. The σ-aromaticity model[4-6] seems to be sorely lacking and fraught with arbitrary assumptions about the applicability of force constants at one geometry for use at another. In addition, even the qualitative aspects embodied in PMO theory make predictions about the relative strain of cycloalkanes and cyclopolysilanes which are incompatible with the available evidence.

Cyclopolysilane Anion Radicals

The substituted four-, five-, and six-membered silicon rings are known experimentally[11-14] to form stable radical anions in solution, just like aromatic hydrocarbons, and dodecamethylcyclohexasilane, $[(CH_3)_2Si]_6$, radical anion has even been observed in the gas phase.[47] The form of the singly occupied molecular orbital (SOMO) in these radical anions has been of great interest, and here we will propose that a particular form of the SOMO, π^* in character, can readily explain much, if not all, of the available experimental data. West originally proposed a π^*-type model[11-13] but more recently has changed this to one which involves Si–Si in-plane σ^* orbitals and Si–C σ^* orbitals[14] (to avoid confusion we must note that the vast majority of experimental data refer to alkyl-substituted cyclopolysilanes; the analogous model for the silicon hydrides studied here would involve Si–Si σ^* and Si–H σ^* orbitals).

The model we propose here was motivated by the observation that, for each of the planar neutral rings studied here, and for all previously described basis sets, one particular orbital was found to be the ab initio SCF LUMO. Specifically, it was an orbital that is completely π-bonding between all the silicons, but antibonding to the hydrogens. A representative LUMO for cyclotrisilane is shown in Figure 7 and is of a_2'' symmetry. The LUMO's of cyclotetrasilane and cyclopentasilane are of the exact same form and are of a_{2u} and a_2'' symmetry, respectively (see Figure 1). We attempted to study these anion-radical states but found that the energies were invariably above those of the neutral ground state, even using extended basis sets and incorporating electron correlation via CI. We thus conclude that the anion radicals of the silicon hydrides may be unstable in the gas phase, at least with the methods used here. Ab initio single configuration SCF studies of such species are meaningless because, if we were to extend our basis sets to include more and more diffuse functions, the electron would occupy the most diffuse orbitals available and eventually we would recover the energy and optimized geometry of the neutral molecule. This is generally true for any molecular system with a negative electron affinity, such as typical aromatics like benzene. From a theoretical standpoint, such systems can only be described by scattering theory, with proper inclusion of continuum functions. Thus the π^* model we propose here is not proven by our methods; it is only suggested by them, and the validity of the model rests in its ability to successfully account for the available experimental data, as it must in the end to be deemed successful.

It is possible that the form of the LUMO in the neutral cyclic silicon hydrides obtained here could be substantially different from that found experimentally in alkyl-substituted cyclopolysilanes. Indeed, it is experimentally known that some of the odd electron density in the radical anions resides on the alkyl groups. To test this we determined the LUMO of hexamethylcyclotrisilane using a DZ basis set consisting of 150 basis functions. The geometry of this molecule was not optimized. Rather, we determined the SCF wave function at an assumed geometry, with an Si–Si bond distance identical with that found in Si_3H_6 with the same DZ basis set. The methyl groups were placed in a tetrahedral geometry with r(Si–C) = 1.920 Å, r(C–H) = 1.090 Å, and θ(C–SI–C) = 113°, in such a way as to give a molecule with C_{2v} symmetry. The resulting LUMO was once again of the same form, i.e., π-bonding between the silicon atoms, and Si–C antibonding. Thus the form of the LUMO does not appear to be an artifact of using hydrogen atoms instead of alkyl groups as substituents.

The most direct evidence regarding the electron distributions in the SOMO of the anion radicals is from ESR spectroscopy. Generally speaking, the symmetrically substituted rings $[R_2Si]_n$, $n = 4$ to 6, form radical anions which show only single values for the α-^{13}C and α^1H hyperfine splitting constants (hfsc), suggesting that these species are either planar or rapidly pseudorotating on the ESR time scale. (Recently, however, two bent cyclotetrasilane anion radicals have been observed, reminiscent of the dichotomy that exists for the neutral 4MR geometries.[48]) Furthermore, the ^{29}Si hfsc are apparently accountable by spin polarization effects, indicating no direct silicon 3s orbital contribution to the SOMO. The π^* model readily accounts for this observation, as s-orbital participation is excluded by symmetry in the π^* model. This is not the case for the σ^* model. In fact, all the unoccupied orbitals with orbital energies within 0.1 hartree (~60 kcal/mol) of the π^* orbital for cyclotetrasilane and cyclopentasilane appear to have substantial silicon 3s orbital participation.

Another observation that is readily explained with the π^* orbital, but not with the σ^* model, is that the long-wavelength transition of the cyclopolysilanes has a rapidly decreasing extinction coefficient with smaller ring size. In the more nearly planar small rings, one can achieve near σ–π separation, and the electronic HOMO–LUMO excitation is more strictly forbidden. Indeed, for the planar rings the HOMO–LUMO excitations are not allowed by symmetry in the π^* model. For the σ^* model, however, this is not the case. In fact, for each of the silicon hydride rings studied here, the HOMO–2nd LUMO (always in-plane σ^*) excitations are allowed by symmetry.

One observation which we cannot easily explain, and seems incompatible with a p–π^* model (but not necessarily a d–π^* model), is the recent ^{29}Si ENDOR results, for substituted cyclopolysilanes, of Kirste, West, and Kurreck.[15] They found only a small hyperfine anisotropy for ^{29}Si in their ENDOR studies, and concluded that the majority of the spin population was in p- or d-type orbitals, symmetrically distributed about the silicon nuclei. This was no doubt responsible for West's rejection of the original π^* model for the more recent σ^* model and cleary represents the most serious objection to the π^* model available to us.

We are thus left in the unusual situation that neither the π^* nor the σ^* model can simply account for the available experimental data. The π^* model suggested by our studies, for reasons of symmetry, can readily account for the ESR and electronic excitation intensity data, whereas the σ^* cannot. The σ^* model explains the small ^{29}Si hyperfine anisotropy in the ENDOR studies, which the π^* cannot. There are only σ^* and π^* orbitals available in planar cyclic molecules like the cyclopolysilane anion radicals. Has the MO model itself broken down? We hope that future experiments will clear up the issue of the form of the SOMO in these radical anions.

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To date we are not aware of any unsaturated aromatic polysilacyles, but the cyclic anion radicals appear to resemble traditional aromats in certain respects. Whether the SOMO is of the π^* or σ^* type, the electron is found to be completely delocalized around the ring and both are quite stable. Indeed, they can be formed readily from straight-chain silicon polymers through addition of naphthalide radical anion[49] and thus appear to be "unusually stable" with respect to straight-chain anion radicals. Unfortunately, no experimental or theoretical thermochemical data are available that would allow us to assess any measure of this stability.

Conclusion

While the cyclopolysilanes are structural analogues of cycloalkanes, the strain energy of cyclotrisilane is 10 kcal/mol more than that of cyclopropane, and cyclotetrasilane is 10 kcal/mol less strained than cyclobutane. The strain energies can be rationalized by consideration of angle and torsional strain components, and substituent effects. We suggest that substituent effects (i.e., the peculiar role of hydrogen) may also be partially responsible for the nearly identical strain energies in C_3H_6 and C_4H_8. That is, if we replace the hydrogens with other substituent the strain energies may be, and in the case of fluorine it is, quite different for the three- and four-membered rings. The arguments which conclude that cyclopropane has unusual stability, i.e., is σ aromatic, may be based on a questionable assumption about the ability of force constants at one geometry to predict strain in a different molecule at a vastly different geometry.

For each of the neutral planar silicon hydride rings investigated here, the LUMO was of the same type, totally π-bonding between the silicon ring atoms and silicon-substituent antibonding. If we assume the SOMO of the substituted rings is of the same type, as our results for hexamethylcyclotrisilane suggest, then the available ESR and long-wavelength UV intensity data may be explained by reasons of symmetry alone. Alternative explanations for recent ^{29}Si ENDOR data, which seems inconsistent with this π^* model, are not apparent at this time. On the other hand, the σ^* model, which accounts for the small hyperfine anisotropy for ^{29}Si in the ENDOR studies by assuming equal participation of p_x, p_y, and p_z orbitals in the SOMO of the radical anions, does not rigorously exclude s-orbital participation in the SOMO as ESR studies suggest. In addition, the small extinction coefficients observed for the longest wavelength transitions of cyclopolysilanes are not easily explained by the σ^* model. While the π^* model seems to rest on firmer ground, we are not in a position to decide which, if either, of these models is correct.

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Registry No. Si_3H_6, 18548-76-0; Si_4H_8, 287-69-4; Si_5H_{10}, 289-22-5; $Si_3H_6^-$, 110174-36-2; $Si_4H_8^-$, 110174-37-3; $Si_5H_{10}^-$, 110174-38-4.

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Hetero-Substituted Cyclopolysilanes: Unusual Structures and a New Model of Bonding in 1,3-Disubstituted Four-Membered Rings

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Abstract: The monosubstituted cyclopolysilanes $(SiH_2)_nX$ (X = CH_2, NH, O, PH, and S; n = 2 and 3) are investigated with ab initio quantum mechanical techniques. The monosubstituted four-membered rings do not exhibit any remarkable structural features, while all the monosubstituted three-membered rings have unusually short Si–Si bond distances and nearly planar Si–Si–H_2 units, which can be explained via Dewar's model of metal–olefin bonding. A simple extension of this model to the case of 1,3-disubstituted four-membered rings readily explains the unusual geometries found in many of these systems. This model is quite general and focuses on the ring orbitals themselves, unlike previous models which often invoked large lone pair–lone pair interactions to explain observed deviations from ideal square-planar geometries. Thus, it is applicable to both three- and four-membered substituted and unsubstituted rings alike. The bonding in cyclodisiloxane is described as that of a "dibridged π-complex", and the bond between the silicons, if it exists, is most likely that of an "unsupported π-bond".

Saturated silicon ring systems $(SiR_2)_n$ are structural analogues of cycloalkanes yet they exhibit many unusual features not observed in saturated cyclic hydrocarbons. Unsubstituted cyclopolysilanes, for example, show strong absorptions in the ultraviolet, give charge-transfer complexes with π acceptors, and form cation and anion radicals in which the unpaired electron is completely delocalized around the ring. In addition, their photoionization and UV spectra can be interpreted by assuming that the Si–Si σ electrons are completely delocalized. Thus, despite their structural similarity to cycloalkanes, the cyclopolysilanes behave in many ways like typical unsaturated aromatic hydrocarbons.[1]

In contrast substituted cyclopolysilanes, in which one or more SiR_2 units are replaced by isovalent units such as O, S, CH_2, etc., exhibit unusual *structural* features. For example, the S- and CH_2-substituted three-membered rings (3MRs) 1,1,2,2-tetramesityl-1,2-disilathiirane[2] and 1,1,2,2-tetrakis(2,6-dimethylphenyl)-1,2-disilacyclopropane[3a] have Si–Si bond distances at least 0.1 Å shorter than trisilacyclopropane rings with similar functional groups attached to silicon.[4–6] These molecules are also unusual

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