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88780-46-5; **2** (R = PhN=N; R′ = CH_3), 88780-47-6; **2** (R = R′ = CH_3), 64588-23-4; **4**, 88780-49-8; **5**, 88780-50-1; **6**, 88780-51-2; **7**, 88780-52-3; **9**, 62346-57-0; **10**, 88780-53-4; $CH_3C(O)N$=NPh, 13443-97-5; PhCH=NCH_3, 622-29-7; benzaldehyde, 100-52-7; crotonaldehyde, 4170-30-3; pyridine-2-carboxaldehyde, 1121-60-4; thiophene-2-carboxaldehyde, 98-03-3; acetophenone, 98-86-2; benzophenone, 119-61-9; mesityl oxide, 141-79-7; 3-acetylpyridine, 350-03-8; 2-acetylfuran, 1192-62-7; 2-acetylthiophene, 88-15-3; 2,3-butanedione, 431-03-8; cyclopropyl methyl ketone, 765-43-5; acetylacetone, 123-54-6; 2,2-dimethylpropionaldehyde, 630-19-3; propanal, 123-38-6; acetone, 67-64-1; cyclohexanone, 108-94-1; *trans*-azobenzene, 17082-12-1.

Theoretical Studies of Cyclic $C_2Si_2H_4$ Molecules

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Thirteen cyclic $C_2Si_2H_4$ isomers, including disilatetrahedrane and the disilacyclobutadienes, have been studied by using ab initio quantum mechanics. At the MP3/6-31G*//3-21G level of computation, the silyl-substituted silacyclopropenylidene is found to be the most stable. Disilatetrahedrane is quite high on the energy surface, and the two possible planar 1,2-disilacyclobutadienes do not represent minima on this surface. Planar 1,3-disilacyclobutadiene is a stable structure and exhibits significant diradical character.

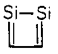
Introduction

Compounds containing highly strained carbon rings have been of interest to experimental[1] and theoretical[2] chemists for some time. In particular, much interest has centered around the elusive cyclobutadiene and tetrahedrane molecules.[3] Investigation of silicon-containing analogues to these small carbon rings, however, has hardly begun. For the case of four-membered rings, only single substitutions have been investigated to date.[4] In that paper, silatetrahedrane was found to be much less stable than silacyclobuta-1,3-diene but more stable than its dissociation products. The study of ring systems with two carbon atoms replaced by silicons is the next logical extension of this work.

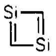
The $C_2Si_2H_4$ system is of particular interest because of the variety of bonding situations that may be hypothesized for silicon. These include single bonds to silicon, double bonds to silicon, and double bonds to carbon. Since these bonds occur within one system, a direct comparison of relative bond strengths may be made. The $C_2Si_2H_4$ system is also the simplest prototype for important structures in synthetic organosilicon chemistry. The basic ring structures of the normal valent compounds provide fundamental understanding useful in developing successful synthetic routes to these highly reactive species. The investigation of these prototypes was the primary motivation for the present work.

Since cyclobutadiene analogues are four π electron "antiaromatic" species, one can imagine three formal localized structures:

a



b



c

If these structures correspond to stable minima, they provide an interesting comparison of C=C vs. C=Si vs. Si=Si double bonds. In addition, **c** may exhibit significant diradical behavior. Beyond isomers **a**, **b**, and **c** and disilatetrahedrane, several other cyclic $C_2Si_2H_4$ species, especially those containing silylene functional groups, are of interest. The latter structures allow for the comparison of silicon-containing multiple bonds with silylenes. Characterized structures and corresponding energies are presented in the current work. Investigation of acyclic isomers will be presented in a future paper.

Methodology

All isomers characterized were optimized by using the Schlegel method[5] and the GAUSSIAN80 program package,[6] with the 3-21G basis set.[7] Single point energy calculations were carried out at the 3-21G optimal geometries using the extended 6-31G* basis set.[8] Correlation was accounted for with use of third-order Møller–Plesset perturbation theory (MP3).[9] Because of the size of the molecules studied, correlation corrections and basis set corrections, i.e., polarization functions, are assumed to be additive in order to obtain MP3/6-31G* relative stabilities. This assumption offers a considerable savings in computer time, especially in large systems, while giving results to within 4–5 kcal/mol of an actual calculation.[10]

Diradical behavior was investigated by using π space UHF-NO CI[11] and FORS MCSCF[12] wave functions, containing the 12 $^1A_1$ configurations obtained by distributing the four π electrons among the four π orbitals in all pos-

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[1] (a) Lin, C. Y.; Krantz, A. J. *J. Chem. Soc., Chem. Commun.* **1972**, 1111. (b) Chapman, O. L.; McIntosh, C. L.; Pacansky, J. *J. Am. Chem. Soc.*, **1973**, *95*, 615. (c) Maier, G.; Pfreim, S.; Schafer, U.; Matusch, R. *Angew. Chem.* **1978**, *90*, 552.

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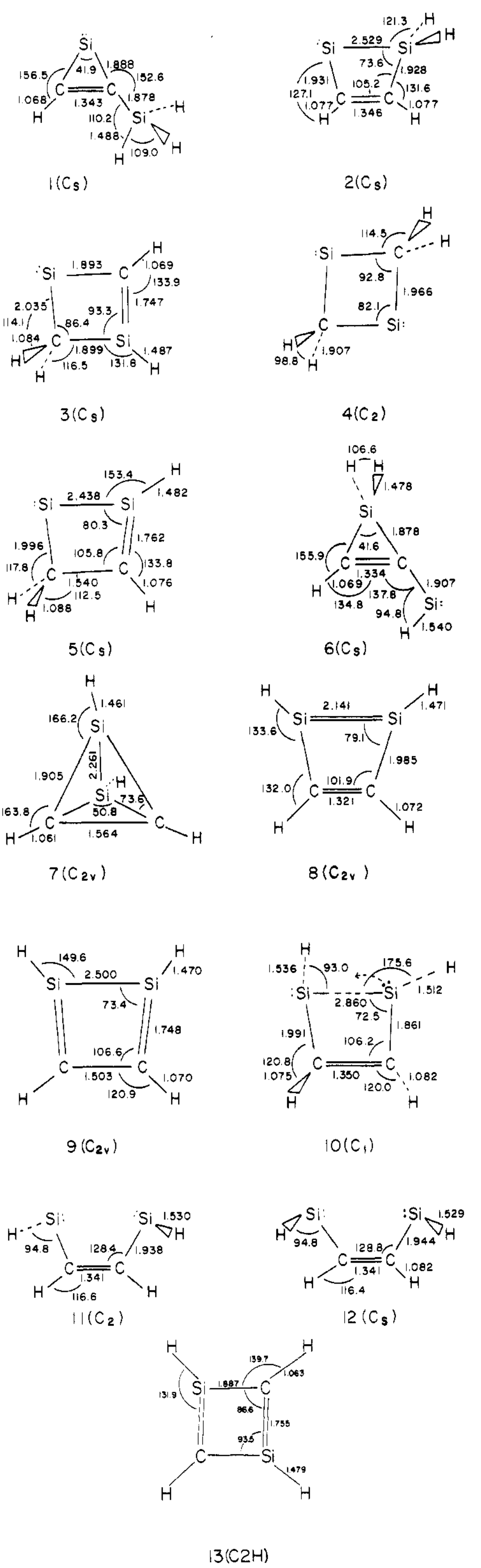

Figure 1. Calculated structures for $C_2Si_2H_4$ molecules. Bond lengths are given in angstroms and angles in degrees. The assumed symmetries are given in parentheses. In isomer 4: dihedral angle ω(SiCSiC) = 23.9°; in isomer 10, ω(CCSiSi) = −4.9°, $\omega(H_ASiSiC)$ = 98.0°, $\omega(H_BSiSiC)$ = 118.8°, $\omega(H_C$ CCSi) = −3.6°, and $\omega(H_D$ CCSi) = 1.1°.

sible ways. Atomic charges were determined by using Mulliken population analyses,[13] and localized orbitals were obtained by using the Boys localization procedure[14] contained in the GAMESS program package.[15]

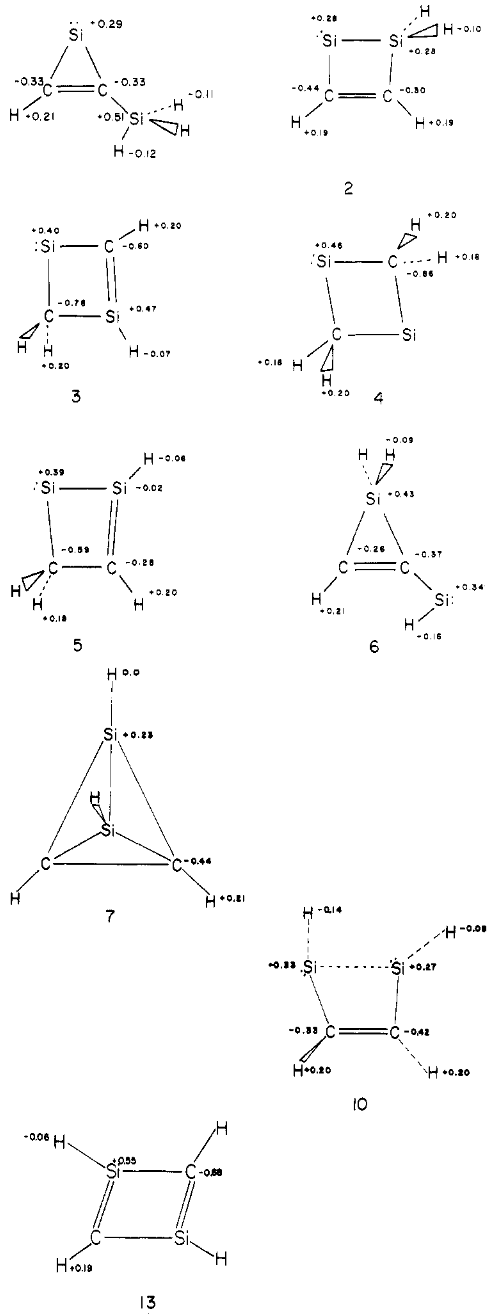

Figure 2. Mulliken 6-31G* population analyses.

Results and Discussion

The structures of all isomers are shown in Figure 1. The first seven isomers represent local minima on the energy surface and are presented in the order of their relative stability, at the MP3/6-31G* level of calculation. Absolute and relative energies are given in Table I, while atomic charges of selected isomers are displayed in Figure 2. Note that the addition of correlation corrections only modifies the relative energies in a quantitative manner, leaving the order of the isomers unchanged. The addition of polarization functions, on the other hand, has a substantial qualitative effect.

Isomer 1 may seem an unlikely choice as the most stable isomer of those reported, since the three-membered ring undoubtedly possesses greater strain than do the four-membered rings. Additional stability in 1 may be obtained from the silyl group and some delocalization stabilization,

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Table I. Total and Relative Energies for $C_2Si_2H_4$ Isomers

	3-21G		6-31G*//3-21G		MP3//6-31G*[a]
isomer	energy, au	ΔE, kcal/mol	energy, au	ΔE, kcal/mol	ΔE, kcal/mol
1	−652.352 506	0.0	−655.811 887	0.0	0.0
2	−652.351 383	0.7	−655.800 251	7.3	9.3
3	−652.357 530	−3.2	−655.794 794	10.7	11.6
4	−652.366 606	−9.9	−655.780 302	19.8	28.6
5	−652.317 036	22.3	−655.755 316	35.5	31.6
6	−652.294 131	36.6	−655.754 169	36.2	38.3
7	−652.219 55	83.4	−655.667 780	90.4	87.4
8	−652.279 364	45.9			
9	−652.241 951	69.3			
10	−652.315 334	23.3	−655.753 211	36.8	42.7
11	−652.306 784	28.7			
12	−652.306 596	28.8			
13	−652.268 768	52.6	−655.732 723	49.7	49.7

[a] Estimated on the basis of assumed additivity of correlation and polarization functions: see text.

which is suggested by the shorter C–Si: and C–Si bond distances in **1** relative to **2**. Formally, isomer **2** contains nearly the same bonds as isomer **1**. The main difference is that an Si–H σ bond in **1** has been replaced by an Si–Si σ bond in **2**. Apparently, the relative stability of the former plus the delocalization noted above more than make up for the ring strain increase in the three-membered ring relative to the four-membered ring.

Isomer **3** is the most stable species that contains a multiply bonded silicon atom. The silicon–carbon double bond is generally thought to be considerably less stable than the unsubstituted carbon analogue.[16] It is interesting, therefore, that there is a relatively favorable isomer that contains such a bond. It is likely that this is related to the replacement of Si–Si and Si–H bonds in **2** by Si–C and C–H bonds in **3** and to delocalization stabilization of the Si–C bonds relative to **2** and **4**.

Isomer **4** contains no multiply bonded silicon atoms, yet is less stable than a structure with a Si=C double bond (**3**). A 1,2-hydrogen migration in isomer **3** will yield isomer **4** and will cost 17 kcal/mol in energy. Isomer **4** contains a more stable C–H bond than the Si–H bond of isomer **3**. The additional silylene group may contribute to the destabilization of **4**, and, as noted above, the Si–C bonds are longer than those in **2** and **3**. This is consistent with the increased stability of **2** and **3** relative to **4** upon the addition of polarization functions and correlation corrections (see Table I). Isomer **5** contains a Si=C double bond and is slightly less stable than **4**. The former structure contains a very long Si–Si single bond and a C–C single bond. The energy of these two bonds is apparently less than that of two Si–C single bonds, since isomer **5** differs only by those bonds from isomer **3** and is 20 kcal less stable. The longer Si=C double bond in isomer 5 suggests a weaker π bond without the usual delocalization stabilization into adjacent bonds. Finally, it has been noted in earlier papers[17] that a negative Mulliken charge tends to destabilize silicon, and **5** is the only isomer that demonstrates such a negative charge (see Figure 2).

Isomer **6** contains a three-membered ring but has no particularly stable group to counteract the ring strain as in the case of isomer **1**. The structure is considerably more stable than any normal valent ring structures. This isomer is interesting since it contains two highly active functional groups: the silirene itself is very reactive as is the silylene group attached to the ring.

Isomer **7** is the only saturated normal valent compound (i.e., non-silylene) that represents an actual local minimum. Force field calculations on isomer **7** indicate a positive definite force constant matrix, thereby assuring the validity of the local minimum. The disilatetrahedrane is very far above the previous six isomers, however. This is not unusual since unsubstituted tetrahedrane[3] and singly substituted silatetrahedrane[4] are both very high on their respective surfaces.

Isomers **8** and **9** do not represent minima on the energy hypersurface, since both have force constant matrices with two negative eigenvalues. The structures shown decay to isomer **10** when all symmetry restrictions are relaxed. The ability to determine distinct planar structures is important since these isomers allow one to compare the stability of several types of silicon-containing multiple bonds. At the 3-21G level of calculation, isomer **8** is 23.5 kcal/mol more stable than is isomer **9**. Since the only difference between **8** and **9** is the position of the π bonds, one can see that the stability of the C=C double bond relative to the C=Si double bond more than compensates for the energy loss of the Si=Si double bond relative to C=Si. Still, these results must be viewed in the light that the compounds are not actually minima. In the case of isomer **8**, this is consistent with the nonplanarity of disilene.[18]

The species to which **8** and **9** decay, isomer **10**, possesses an unusual geometry. This structure resembles an opened disilylene, yet the most plausible symmeterized disilylenes, isomers **11** and **12**, to which the structure might revert are both 5 kcal/mol higher in energy at the 3-21G level of calculation. Boys localized orbitals suggest that the added stability of isomer **10** results from the donation of electrons from the silicon lone pair into an empty p orbital on the adjacent silicon. Since the symmetry is C_1 the structure is apparently a minimum on the 3-21G surface. Isomers **11** and **12** have been shown to demonstrate they are not decay products. Further calculations on these and other acyclic isomers will be presented in a later paper.

Isomer **13** does represent a minimum on the RHF energy surface, and it may be stabilized relative to **8** and **9** by the electronegativity difference between carbon and silicon. This isomer resembles isomers of cyclobutadiene that have been shown to possess diradical behavior;[19–21] thus the RHF description of this isomer is subject to doubt. For this reason UHF-NO CI and FORS MCSCF calculations were carried out on this structure.

According to the results summarized in Table I, 1,3-disilacyclobutadiene (**13**) is about 50 kcal/mol above the

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most stable isomer at both RHF and MP3 levels of approximation. This is misleading, however, since the expected diradical character for this structure may lead to instability of the RHF wave function. To test this possibility an unrestricted Hartree–Fock calculation was carried out by using the 3-21G basis set at the RHF/3-21G geometry. This lowered the energy of the singlet disilacyclobutadiene by about 20.3 kcal/mol. Further refinement of the wave function using the UHF-NO CI procedure, in which a full π space CI is used and a correct spin eigenfunction is obtained, results in an additional 10.5 kcal/mol lowering. Since the CI corrects for more than just the diradical instability, the actual correction is likely to be in the range of 20.3–30.8 kcal/mol. This will still leave the 1,3-butadiene well above the most stable isomers.

The FORS MCSCF results for the 1,3-disilacyclobutadiene are very similar to the UHF-NO CI results. The 12 configuration π space MCSCF energy is some 31.8 kcal/mol below the RHF energy given in Table I and 1 kcal/mol below the UHF-NO CI result. The SCF configuration represents just 82.3% of this MCSCF wave function, so that one might speculate on the accuracy of the RHF geometry. Nonetheless, the amount of correlation recovered still places isomer **13** at the upper end of the stability order.

Conclusions

We have carried out ab initio calculations on strained ring compounds of the $C_2Si_2H_4$ energy surface. The most stable isomers contain silylene groups and only singly bonded silicon atoms. Of these isomers the most stable is 1-silyl-3-sila-1-cyclopropen-3-ylidene (1). Saturated non-silylene can be found on the SCF surface, disilatetrahedrane, and it is very high in energy relative to those isomers containing silylene groups.

3,4-Disilacyclobuta-1,3-diene and 3,4-disilacyclobuta-2,4-diene are not local minima on the surface. They may be differentiated when they are constrained to C_{2V} symmetry, but they decay to the same nonplanar isomer upon relaxation of those symmetry constraints. 2,4-Disilacyclobuta-1,3-diene was found to possess significant diradical character and cannot be adequately described at the RHF level of calculation. While UHF-NO CI or FORS MCSCF calculations give some energy improvement by accounting for the diradical behavior, they do not indicate it will be the favored isomer on the surface.

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Registry No. 1, 88303-66-6; 2, 88303-67-7; 3, 88303-68-8; 4, 88303-69-9; 5, 88303-70-2; 6, 88303-71-3; 7, 88303-72-4; 8, 88303-73-5; 11, 88303-74-6; 13, 88303-75-7.

Intermolecular Forces and Hyperfine Interactions in Cyclic Dibutyltin Compounds

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A number of cyclic dibutyltin distannoxes have been examined by temperature-dependent ^{119}Sn Mössbauer-effect spectroscopy, both as neat solids and as frozen solutions in *n*-butylbenzene, in order to elucidate the structural similarity and lattice dynamical properties of chiral conformers and their racemic mixtures. The systematics of the isomer shift and quadrupole splitting parameters show that the ring-substituted compounds are all isostructural and suggest—together with the systematics of the temperature dependence of the recoil-free fraction as well as solution molecular weight and NMR data reported earlier—that they consist of dimeric species with pentacoordinated metal centers. No difference (within experimental error) could be observed in the lattice dynamical properties of the neat solid pure chiral conformers and their respective racemic mixtures, suggesting that the differences in the intermolecular packing forces are negligible in their effect on the motional behavior of the Mössbauer-active probe atom. The intensity asymmetry of the two components of the quadrupole doublet resonance was observed to be temperature independent in the range $78 \le T \le 170$ K, and there is no evidence of motional anisotropy of the metal atom in these solids in this temperature range.

Cyclic butyltin stannoxanes and distannoxanes have found considerable use in the synthesis of stereospecific macrocycles and serve as useful templates in the construction of ring compounds of varying complexity.[1-6] In this context, it is interesting to note that the structure of these organometallic reagents in solution is still a subject of some controversy and that a number of suggestions have been made[7-9] concerning the configuration of the species

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