Theoretical Studies of Cyclic C2S12H4 Molecules

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Theoretical Studies of Cyclic C₂Si₂H₄ Molecules

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Received October 4, 1983

Thirteen cyclic C₂Si₂H₄ 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 silacyclopentenyliene 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 experimental1 and theoretical2 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 silicon is the next logical extension of this work.

The C₂Si₂H₄ 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 C₂Si₂H₄ 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:

\[ \text{Si} = \text{Si} \quad \text{Si} = \text{Si} \quad \text{Si} = \text{Si} \]

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 C₂Si₂H₄ 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 method5 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 Moller–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 CI11 and FORS MCSCF12 wave functions, containing the 12 1Ω configurations obtained by distributing the four π electrons among the four π orbitals in all pos-

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Symmetries are given in parentheses. In isomer 4: dihedral angle \(\omega_{(\text{CCSiSi})} = 23.9^\circ\); in isomer 10, \(\omega_{(\text{CCSiSi})} = -4.9^\circ\), \(\omega_{(\text{H}_{2}\text{SiSi})} = 86.0^\circ\), \(\omega_{(\text{H}_{2}\text{SiSi})} = 118.8^\circ\), \(\omega_{(\text{CCSiSi})} = -3.6^\circ\), and \(\omega_{(\text{CCSiSi})} = 1.1^\circ\).

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.

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

Figure 1. Calculated structures for C₅Si₃H₄ molecules. Bond lengths are given in angstroms and angles in degrees. The assumed symmetries are given in parentheses. In isomer 4: dihedral angle \(\omega_{(\text{CCSiSi})} = 23.9^\circ\); in isomer 10, \(\omega_{(\text{CCSiSi})} = -4.9^\circ\), \(\omega_{(\text{H}_{2}\text{SiSi})} = 86.0^\circ\), \(\omega_{(\text{H}_{2}\text{SiSi})} = 118.8^\circ\), \(\omega_{(\text{CCSiSi})} = -3.6^\circ\), and \(\omega_{(\text{CCSiSi})} = 1.1^\circ\).

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 de-

stabilization 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 addi-

tion 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 papers17 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 silylene 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.

<table>
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<th>Table I. Total and Relative Energies for C,Si,H Isomers</th>
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<sup>a</sup> Estimated on the basis of assumed additivity of correlation and polarization functions: see text.

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 unu-

usual since unsubstituted tetrahedrane<sup>b</sup> and singly sub-

stituted silatetrahedrane<sup>c</sup> 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 decays 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 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.<sup>15</sup>

The species to which 8 and 9 decay, isomer 10, possesses

an unusual geometry. This structure resembles an opened

disilylene, yet the most plausible symmetrized disilienes,

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 π orbital on the

adjacent silicon. Since the symmetry is C<sub>1</sub> 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-di-

disilacylobutadiene (13) is about 50 kcal/mol above the

<sup>19</sup>Jafri, J. A.; Newton, M. D. J. Am. Chem. Soc. 1978, 100, 5012.
<sup>21</sup>Borden, W. T.; Davidson, E. R.; Hart, P. J. Am. Chem. Soc. 1978,

100, 388.
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 diradical below by about 20.3 kcal/mol. Further improvement of the wave function using the UHF-NO CI procedure, in which a full σ 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 σ 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 C₂Si₂H₄ 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, disilatetrahedran, 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 Cᵥ 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.

Acknowledgment. This work was supported by donors of the Petroleum Research Fund, administered by the American Chemical Society. The computer time made available by the North Dakota State University Computer Center is gratefully acknowledged. We have benefited from several helpful discussions with Professor P. Boudjouk.

Intermolecular Forces and Hyperfine Interactions in Cyclic dibutyltin Compounds

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Received September 13, 1983

A number of cyclic dibutyltin distannoxanes have been examined by temperature-dependent ¹¹¹Sn 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 ≤ T ≤ 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.¹⁻⁴ 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 made⁵⁻⁷ concerning the configuration of the species.

References