outside the peaks separated by 3596 Hz, isolated pairs of ^{13}C spins appear to predominate for our sample. This is consistent with estimates made assuming that atoms are randomly introduced into the molecules. In particular, for 6% enrichment, the probabilities for 2, 3, and 4 ^{13}C atom clusters are approximately in the ratio 100:10:1. We would also not expect the results to be affected significantly by C_{70} since (1) there is much less C_{70} present in the sample and (2) calculations indicate that it has seven different bond lengths.[21]

In conclusion, we have measured two carbon–carbon bond lengths in C_{60}: 1.45 ± 0.015 and 1.40 ± 0.015 Å. This result is consistent with the soccerball (truncated icosahedron) structure proposed for C_{60}. The observation of ^{13}C–^{13}C dipolar coupling in enriched C_{60} suggests that it may be possible to explore the mechanism of fullerene assembly with multiple quantum cluster counting.[22]

Acknowledgment. The authors enjoyed stimulating discussions with R. D. Johnson and H. C. Dorn. They are also grateful to R. D. Johnson for solution NMR measurements, M. S. DeVries for a mass spectrometric analysis, and R. D. Kendrick for skillful technical assistance. IBM France provided generous financial support for P.P.B. as an IBM Visiting Scientist.

---

(21) Rudzinski, J. M.; Slanina, Z. Togasi, M.; Osawa, E. *Therm. Acta* **1988**, *125*, 155.

(22) Baum, J.; Gleason, K. K.; Pines, A.; Garroway, A. N.; Reimer, J. A. *Phys. Rev. Lett.* **1986**, *56*, 1377.

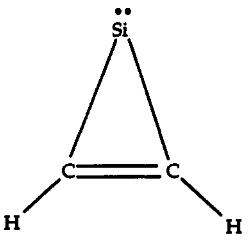
The Infrared Spectrum of Silacyclopropenylidene

George Vacek, Brenda Thies Colegrove,[†] and
Henry F. Schaefer, III*

Center for Computational Quantum Chemistry
University of Georgia, Athens, Georgia 30602

Received October 18, 1990

The laboratory synthesis and subsequent astronomical detection of cyclopropenylidene is a story that owes its success to the fruitful collaboration of experiment and theory. After two decades of theoretical[1-8] and experimental[9-14] investigation, Reisenauer, Maier, Riemann, and Hoffmann[15] identified cyclopropenylidene via matrix isolation. They were aided by the ab initio prediction of its vibrational frequencies and infrared intensities provided by Lee, Bunge, and Schaefer.[16] Shortly thereafter cyclopropenylidene was observed in various interstellar sources,[17,18] aided by the theoretically determined rotational constants. The silicon-substituted species, silacyclopropenylidene, is a likely candidate for investigation since in recent years there has been significant success in finding silicon analogues of organic molecules.[19]



One might expect the silicon molecule to be more stable than the hydrocarbon due to silicon's propensity for the divalent state.[20] On the other hand, three-membered rings containing a silicon atom are significantly more strained than the analogous hydrocarbon rings.[21] There have been two previous theoretical reports on the SiC_2H_2 molecular system. Frenking, Remington, and Schaefer[22] thoroughly surveyed the singlet potential energy surface, locating 15 different isomers. Of these, salicyclopropenylidene was the lowest energy structure. They reported the infrared spectrum at the DZP SCF level of theory. Su, Amos, and Handy[23] found 16 different triplet isomers of SiC_2H_2, but they concluded that the lowest triplet isomer lies 47 kcal/mol above singlet silacyclopropenylidene. Experimentally, both $Si^+(^2P)$ and $Si(^3P)$ have been observed to react with acetylene, yielding stable products.[24,25] Thus far, there is no evidence for a singlet species, although the data suggest that singlet silacyclopropenylidene would be the most stable neutral species. Because there has as yet been no observation of the SiC_2H_2 global minimum singlet silacyclopropenylidene despite these indications that it might be a synthesizable species, we have employed ab initio molecular orbital techniques[26] to predict its molecular properties at much higher levels of theory than have been previously reported.

In this study, we have used two different basis sets (DZP and TZ2P) and several theoretical methods: self-consistent field (SCF), single and double excitation configuration interaction (CISD) and singles and doubles coupled cluster (CCSD). (Studies at the TZ2P CCSD level, however, were slightly beyond our current facilities.) The DZP basis set consisted of a standard Huzinaga–Dunning–Hay[27-29] contracted double-ζ basis set supplemented with a set of polarization functions on each atom, i.e., Si(11s7p1d/6s4p1d), C(9s5p1d/4s2p1d), and H(4s1p/2s1p). The polarization function orbital exponents were $\alpha_d(Si) = 0.50$, $\alpha_d(C) = 0.75$, and $\alpha_p(H) = 0.75$. For the TZ2P basis set on silicon we used McLean and Chandler's[30] 6s5p contraction of Huzinaga's 12s9p primitive Gaussian set augmented by two sets of six Cartesian d-like functions with orbital exponents $\alpha_d(Si) = 1.0$, 0.25. For carbon and hydrogen we used a standard Huzinaga–Dunning–Hay triple-ζ basis set and two sets of polarization functions, each with $\alpha_d(C) = 1.50$ and 0.375 and $\alpha_p(H) = 1.50$ and 0.375, i.e., C(10s6p2d/5s3p2d) and H(4s2p/3s2p). The TZ2P CISD wave functions included 120 787 configuration state functions (CSFs) for the C_{2v} equilibrium geometry, and up to

---

[†] Present address: Dow Chemical USA, Texas Division, Freeport, TX 77541.

(1) Gleiter, R.; Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 5457.

(2) Lathan, W. H.; Radom, L.; Hariharan, P. c.; Hehre, W. J.; Pople, J. A. In *Topics in Current Chemistry*; Springer-Verlag: New York, 1973; Vol. 40.

(3) Hehre, W. J.; Pople, J. A.; Lathan, W. A.; Radom, L.; Wasserman, E.; Wasserman, Z. R. *J. Am. Chem. Soc.* **1976**, *98*, 4378.

(4) Lee, C. K.; Li, W. K. *J. Mol. Struct.* **1977**, *38*, 253.

(5) Kollmar, H. *J. Am. Chem. Soc.* **1978**, *100*, 2660.

(6) Baird, N. C.; Taylor, K. F. *J. Am. Chem. Soc.* **1978**, *100*, 1333.

(7) Shepard, R.; Banerjee, A.; Simons, J. *J. Am. Chem. Soc.* **1979**, *101*, 6174.

(8) Schoeller, W. W. *Tetrahedron Lett.* **1980**, *21*, 1509.

(9) Jones, W. M.; Stowe, M. E. *Tetrahedron Lett.* **1964**, 3459.

(10) Jones, W. M.; Denham, J. M. *J. Am. Chem. Soc.* **1964**, *86*, 944.

(11) Breslow, R.; Altman, L. J. *J. Am. Chem. Soc.* **1966**, *88*, 504.

(12) McGregor, S. D.; Jones, W. M. *J. Am. Chem. Soc.* **1968**, *90*, 123.

(13) Jones, M. W.; Stowe, M. E.; Wells, E. E.; Lester, E. W. *J. Am. Chem. Soc.* **1968**, *90*, 1849.

(14) Yoshida, Z. *Pure Appl. Chem.* **1982**, *54*, 1059.

(15) Reisenauer, H. P.; Maier, G.; Riemann, A.; Hoffmann, R. W. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 641.

(16) Lee, T. J.; Bunge, A.; Schaefer, H. F. *J. Am. Chem. Soc.* **1985**, *107*, 137.

(17) Matthews, H. E.; Irvine, W. M. *Astrophys. J.* **1985**, *298*, L61.

(18) Thaddeus, P.; Vrtilek, J. M.; Gottlieb, C. A. *Astrophys. J.* **1985**, *299*, L63.

(19) Apeloig, Y. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons Ltd.: New York, 1989; Part 1, p 57 ff.

(20) Colegrove, B. T.; Schaefer, H. F. *J. Phys. Chem.* **1990**, *94*, 5593.

(21) (a) Boatz, J. A.; Gordon, M. S. *J. Phys. Chem.* **1989**, *93*, 3025. (b) Grev, R. S.; Schaefer, H. F. *J. Am. Chem. Soc.* **1987**, *109*, 6569.

(22) Frenking, G.; Remington, R. B.; Schaefer, H. F. *J. Am. Chem. Soc.* **1986**, *108*, 2169.

(23) Su, M.-D.; Amos, R. D.; Handy, N. C. *J. Am. Chem. Soc.* **1990**, *112*, 1499.

(24) Bohme, D. K.; Wlodek, S.; Fox, A. In *Rate Coefficients in Astrochemistry*; Mollar, T. J., Williams, D. A., Eds.; Astrophysics Space Science Library; Kluwer Academic Publishers: Boston, 1988.

(25) Basu, S. C.; Husain, D. *J. Photochem. Photobiol.* **1988**, *A42*, 1.

(26) All investigations were performed by using the PSI suite of computer programs, distributed by PSITECH, Inc., Watskinsville, GA.

(27) Huzinaga, S. *J. Chem. Phys.* **1965**, *42*, 1293.

(28) Dunning, T. H. *J. Chem. Phys.* **1970**, *53*, 2823.

(29) Dunning, T. H.; Hay, P. H. In *Modern Theoretical Chemistry*; Schaefer, H. F., Ed.; Plenum Press: New York, 1977; Vol. 3, p 1 ff.

(30) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639.

0002-7863/91/1513-3192$02.50/0

Table I. Silacyclopropenylidene Harmonic Vibrational Frequencies (cm^{-1}) and Infrared Intensities (kcal mol^{-1})

DZP					TZ2P				
SCF		CISD		CCSD	SCF		CISD		
ω	*I*	ω	*I*	ω	ω	*I*	ω	*I*	assignment
3378	4	3310	4	3258	3371	2	3315	2	sym CH stretch (a_1)
3356	4	3285	4	3234	3349	4	3393	3	asym CH stretch (b_2)
1569	<1	1524	1	1494	1562	<1	1520	1	CC stretch (a_1)
1233	49	1167	39	1138	1249	53	1194	45	asym CH rock (b_2)
1061	0	984	0	948	1111	0	1048	0	trans CH wag (a_2)
976	15	930	13	909	988	7	957	5	sym CH rock (a_1)
849	59	818	42	796	839	63	809	51	sym SiC stretch (a_1)
749	95	681	81	650	778	74	740	67	cis CH wag (b_1)
729	45	705	46	685	728	50	707	51	asym ring def (b_2)

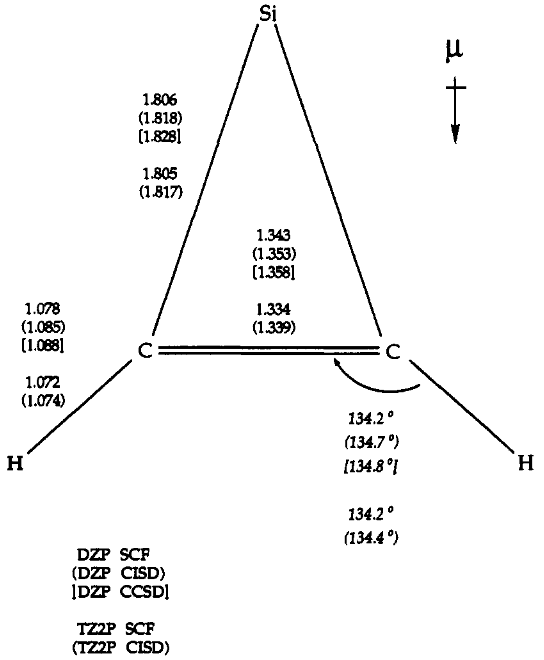


Figure 1. The optimized geometry of silacyclopropenylidene.

240678 CSFs were required for the finite displacement vibrational frequency determination.

Our predictions for the optimized molecular structure of silacyclopropenylidene are shown in Figure 1. Table I summarizes the predicted harmonic vibrational frequencies and infrared intensities, and Table II contains the dipole moment and rotational constants determined at the various levels of theory. Although silacyclopropenylidene ($\mu \approx 1$ D) does not have as large a dipole moment as cyclopropenylidene (3.3 D^{31}), it is still a polar molecule and should have an observable rotational spectrum. In comparing the two basis sets, the TZ2P vibrational frequencies change only slightly except for the CH wags and CH rocks, which increase by 5–9% and 1–3%, respectively, with respect to the DZP basis set. There are only slight changes in the optimized molecular structures, while the dipole moment increases by about 20% with the large basis set. However, inclusion of electron correlation has the opposite effect on the dipole moment with a similar magnitude, so our best prediction of the dipole moment is about the same as that reported by Frenking et al. at the DZP SCF level. The CISD frequencies are, on the average, 3–4% lower than the SCF frequencies. The coupled cluster method (CCSD) lowers the frequencies another 2–5% with the DZP basis set.

The infrared intensities indicate that several bands should be observable. The most intense band is the b_1 cis CH wag (650 cm^{-1} at the DZP CCSD level). Other bands with large intensities include the CH antisymmetric rock (1138 cm^{-1}, DZP CCSD) and the SiC symmetric (796 cm^{-1}, DZP CCSD) and antisymmetric (685 cm^{-1}, DZP CCSD) stretches.

Table II. Silacyclopropenylidene Rotational Constants and Dipole Moment at Various Levels of Theory

level of theory	rotational constants, cm^{-1} *A*	*B*	*C*	dipole moment, D
DZP SCF	1.132	0.404	0.298	0.95
DZP CISD	1.112	0.399	0.294	0.78
DZP CCSD	1.103	0.395	0.300	0.69
TZ2P SCF	1.146	0.404	0.298	1.15
TZ2P CISD	1.137	0.398	0.295	0.95

The ring bonding is best described as a combination of the Dewar–Chatt–Duncanson model[32,33] plus some delocalization of the out-of-plane C–C π electrons into the empty silicon p orbital. If one considers the separated silicon atom plus acetylene system, these effects weaken the C–C triple bond by withdrawing π_{C-C} electron density and adding π^*_{C-C} character. Our evaluation of the C–C bond length (1.339 Å at the TZ2P CISD level) indicates a slightly weakened double bond, since double bonds in cyclic molecules tend to be shorter than in acyclic molecules.

Acknowledgment. This research was supported by the U.S. National Science Foundation, Grant CHE-8718469. We thank Dr. Roger S. Grev for helpful discussions.

---

(31) Swade, D. A. *Astrophys. J.* **1989**, *345*, 828.

(32) Dewar, M. J. S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C71.

(33) Chatt, J.; Duncanson, L. A. *J. Chem. Soc.* **1953**, 2939.

Unexpected Participation of an Excited Diradical Structure in the Ground State of Cyclic Bicalicene

Toyonari Sugimoto,*,† Masashi Sakaguchi,† Hiroshi Ando,† Yoshihisa Arai,† Tomohiro Tanaka,† Zen-ichi Yoshida,*,† Jun Yamauchi,*,† Aksel A. Bothner-By,*,‡ and Mark Lisicki‡

Department of Synthetic Chemistry and
Liberal Arts and Science, Kyoto University
Yoshida, Kyoto 606, Japan
Department of Chemistry, Carnegie Mellon University
Pittsburgh, Pennsylvania

Received September 17, 1990

The anisotropic magnetic susceptibility (Δχ) gives a measure of electron delocalization in π-electron conjugated systems.[1] A convenient measurement method has recently been developed, which can be performed by using high-field ^2H NMR spectroscopy.[2] We have used this method to measure the Δχ of cyclic bicalicene (**1**), a π-electron conjugated system isolated as stable

---

† Kyoto University.

‡ Carnegie Mellon University.