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)

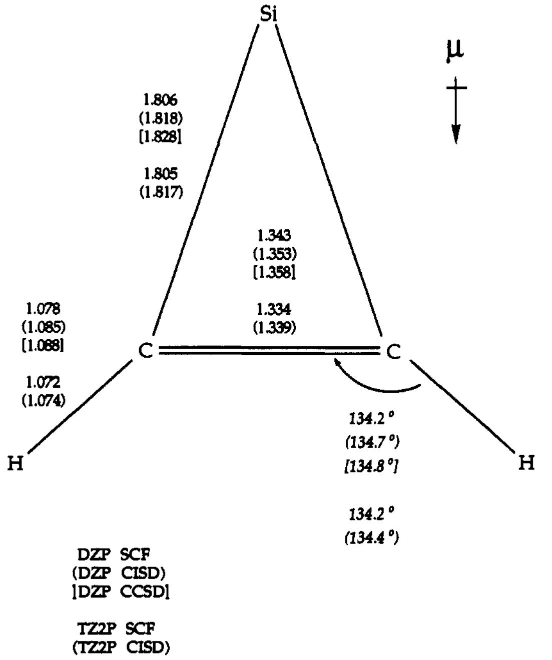

Figure 1. The optimized geometry of silacyclopropenylidene.

240 678 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}			dipole moment, D
	A	B	C	
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.

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

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The anisotropic magnetic susceptibility ($\Delta\chi$) 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 $\Delta\chi$ of cyclic bicalicene (**1**), a π-electron conjugated system isolated as stable

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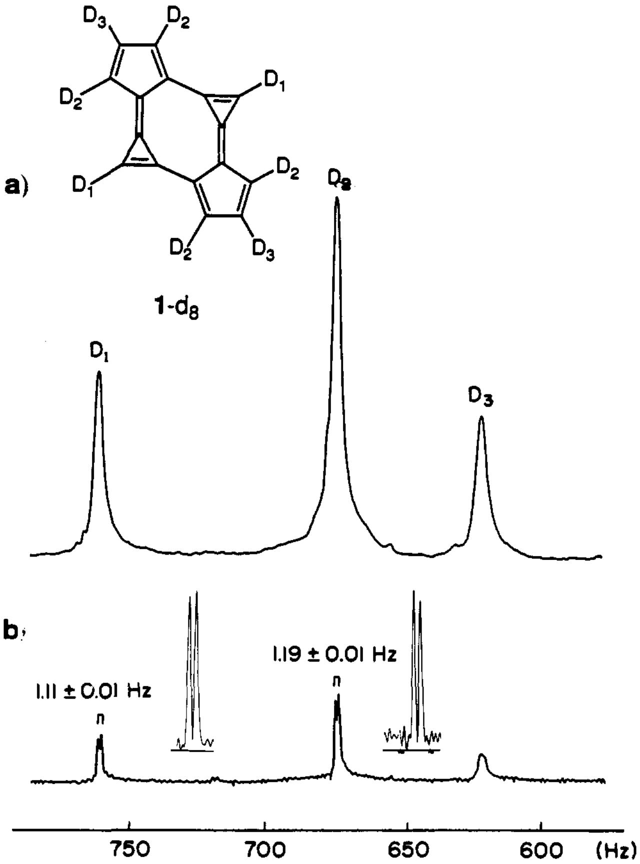

Figure 1. The ^{2}H NMR spectra of **1**-d_8 in CH_2Cl_2 (10 mM) at 23 °C at two magnetic fields: (a) 27.64 MHz, 4.2 T; (b) 95.2 MHz, 14.56 T. At higher magnetic field, the two signals are D_1 and D_2 were split into doublets with splitting constants of 1.11 ± 0.01 and 1.19 ± 0.01 Hz, respectively, while the D_3 signal was broadened.

crystals in spite of its antiaromatic peripheral 16π conjugation.[3]

For the high-field ^{2}H NMR measurement, an octadeuterio-substituted derivative of **1** (**1**-d_8) was necessary. The synthesis was achieved as follows: When 3,11-bis(tri-*n*-butylstannyl) cyclic bicalicene (**3**), obtained by desulfurative stannylation of **2**, was treated with a catalytic amount of 20% $DCl-D_2O$ in CH_3OD-benzene (1:1 v/v) at room temperature for 6 h, **1**-d_8 was isolated[4] as orange crystals (mp 107° C dec) in 45% yield after separation by column chromatography and recrystallization from $CHCl_3$. The ^{2}H NMR spectra were measured in CH_2Cl_2 at 23 °C at two magnetic fields (Figure 1). At the lower field (27.64 MHz, 4.2 T) three singlet signals due to D_1, D_2, and D_3 were observed at δ 7.99, 7.09, and 6.53 (benzene-d_6 (7.27) as a standard) in an area ratio of 1:2:1, respectively. At the higher field (95.2 MHz, 14.56 T) the D_1 and D_2 signals were split into doublets[5] with splittings ($\Delta\nu$) of 1.11 ± 0.01 Hz and 1.19 ± 0.01 Hz, respectively. The splitting of the upfield D_3 doublet could not be resolved by conventional resolution enhancement, but was estimated as 1.22 ± 0.02 Hz by the cosine division technique.[6] The equation relating $\Delta\nu$ and the principal susceptibilities, χ_{ii}, is

$$\Delta\nu = \frac{H_0^2}{10kT}\left(\frac{e^2qQ}{h}\right)\sum_i \chi_{ii}\left(\frac{3}{2}\cos^2\theta_i - \frac{1}{2}\right) \qquad i = x, y, z \qquad (1)$$

where (e^2qQ/h) is the deuteron quadrupole coupling constant in hertz[7], H_0 is the magnetic field strength, and θ_i is the angle between the C–D bond axis and the ith principal susceptibility axis. From eq 1, we find[8]

$$\Delta\chi = \chi_{zz} - \frac{1}{2}(\chi_{xx} + \chi_{yy}) = \frac{-10kT}{H_0^2}\left(\frac{h}{e^2qQ}\right)(\Delta\nu_{D1} + \Delta\nu_{D3}) = -2.53 \times 10^{-28}\ \mathrm{cm^3/molecule} \qquad (2)$$

and

$$\delta\chi = (\chi_{xx} - \chi_{yy}) = \frac{10kT}{H_0^2}\left(\frac{h}{e^2qQ}\right)(\Delta\nu_{D3} - \Delta\nu_{D1}) = -0.11 \times 10^{-28}\mathrm{cm^3/molecule} \qquad (3)$$

The splitting predicted for D_2 with these parameters is 1.12 Hz.

The value for $\Delta\chi$ is surprisingly high, comparable to that of pyrene. Planar aromatic systems in general appear to have an anisotropy which is the sum of a ring-current term and a term for local (trigonal carbon) anisotropies. The latter can be estimated as ~-0.07×10^{-28} cm^3/trigonal carbon. Thus pyrene, with a total measured anisotropy of a -3.7×10^{-28} cm^3/molecule,[1b] will have a local contribution of ~-1.12×10^{-28} cm^3/molecule and a ring-current contribution of ~-2.6×10^{-28} cm^3/molecule. For **1** the local term is identical, yielding a ring-current contribution of ~-1.3×10^{-28} cm^3/molecule. This is an unexpectedly large diamagnetic ring current in a 16-peripheral-π electron system. Graph theoretical and Hückel extended MO calculations yield a ring current smaller by an order of magnitude.

The large diamagnetic $\Delta\chi$ observed suggests the possibility of other structures contributing to the ground state of **1** in addition to covalent and polar structures. The most likely structures are the (3,11) or (6/8, 14/16) diradicals, which have comparatively low energy owing to the aromatic 14π or 10π conjugation, in the remaining moiety. The diradical contribution can decrease the paramagnetic ring current and increase the diamagnetic ring current due to 10π- or 14π-electron conjugation, leading to a significant increase of overall diamagnetic $\Delta\chi$ in **1**. Indeed, such a participation has now been evidenced by ESR measurements on **2**. Figure 2 shows ESR spectra of the single microcrystalline solids freshly obtained by recrystallization. One weak and sharp signal was observed at g = 2.003 30 at 299 K. On the other hand, at 99 K the signal intensity markedly decreased. On both wings of the central signal, a pair of weak signals due to the triplet fine structure were visible, separated by 12.6 G.[11] The signal intensity increased on raising the temperature. The temperature dependence of the central signal intensity from 30 to 299 K is also shown in Figure 2. On lowering the temperature, the intensity gradually decreased, but below 60–70 K, it increased. These observations are characteristic of a thermally excited triplet species contam-

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(4) A satisfactory elemental analysis was obtained.

(5) The D_3 signal was not split into a doublet, but only broadened. This suggests slower rotation of the **1**-d_8 molecule around the D_1–D_1 axis as compared with that around the long D_3–D_3 axis.

(6) (a) Bothner-By, A. A.; Dadok, J. *J. Magn. Reson.* **1987**, *72*, 540. (b) Lisicki, M.; Bothner-By, A. A.; Dadok, J., unpublished.

(7) The value is usually 186 ± 5 kHz for aromatic compounds.

(8) The sign of $\Delta\chi$ could not be straightforwardly determined from the high-field ^{2}H NMR method. However, the negative assignment is reasonable, since the D_1, D_2, and D_3 signals appear in the chemical shift region characteristic of aromatic molecules.

(9) Lonsdale, K.; Krishnan, K. S. *Proc. R. Soc. London* **1963**, *A153*, 597.

(10) The magnetic susceptibility was calculated by the $\beta\omega'\omega''$ method, the ω technique considering bond alternation: (a) Aihara, J. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2689. (b) Aihara, J. *J. Am. Chem. Soc.* **1985**, *107*, 298. The calculated value was $0.045\chi_0$ (χ_0 = magnetic susceptibility of benzene = -0.99×10^{-28} cm^3/molecule).

(11) The value corresponds to $2|D|$, where $|D|$ is one of the fine structure constants. Accordingly, the $|D|$ is 6.3 G while the $|E|$, the other fine structure constant, cannot be determined, since the remaining fine structure signals are not observed because of their overlap with the strong monoradical signal. The other characteristic of a triplet, the half-field resonance signal, was not detected in the temperature range of 299–30 K at all.

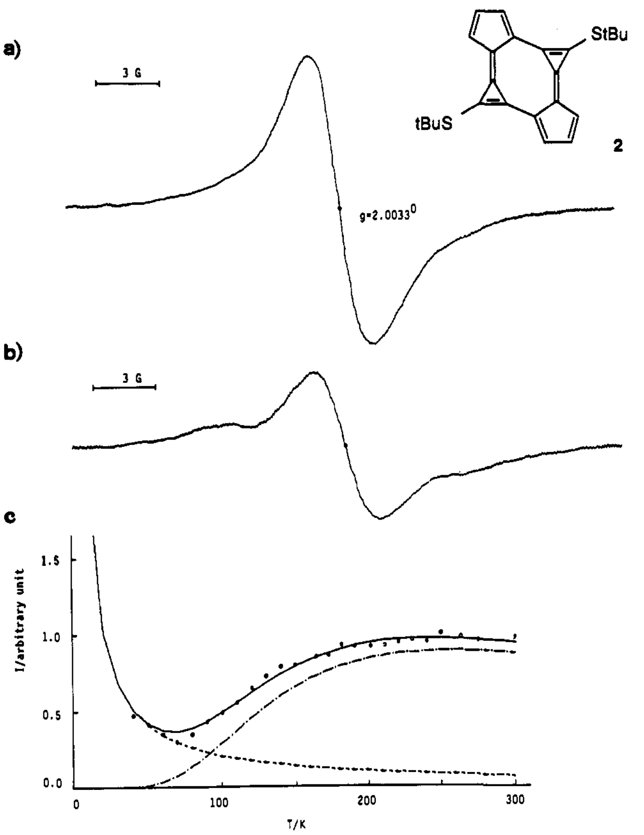

Figure 2. The ESR spectra of the microcrystalline solids of **2** measured at (a) 299 K and (b) 99 K, respectively. (c) Plot of experimental intensity (O) versus temperature and decomposition into triplet (-··-) and impurity signal (---) signals. Sum of calculated intensities (—).

inated with some monoradial impurities.[12] By using the equation

$$I = (N_m \mu_B{}^2 g^2)[\tfrac{1}{2}(\tfrac{1}{2} + 1)/T] + (N_\alpha \mu_B{}^2 g^2)[1(1 + 1)]/[T\{1 + \tfrac{1}{3}\exp(\Delta E/kT)\}] \quad (4)$$

where I is the signal intensity calibrated with a reference TANOL, N_m and N_α are the respective amounts of monoradical and diradical, and ΔE is the energy gap between the singlet and the thermally excited triplet, N_m, N_α, and ΔE were determined: $N_m = 2.0 \times 10^{17}$ molecules/mol, $N_\alpha = 2.3 \times 10^{18}$ molecules/mol, and $\Delta E = 0.81$ kcal/mol. The excited diradical contribution to the ground state of **1** is remarkably small (10^{-4}–10^{-3}%).

The present finding provides a first instance of excited diradical contribution to the ground state of a closed-shell nonalternant hydrocarbon system, although this has already been known for quinodimethane and the quinone derivatives, Chichibabin's hydrocarbon,[13] and 2,5-bis(3,5-di-*tert*-butyl-4-oxocyclohexadienylidene)thieno[3,2-*b*]thiophene.[14] Such a contribution should increase in the excited state; some useful applications of this unique physical property may be expected in the near future.

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(12) The amount of monoradical was much less for **2** freshly obtained by recrystallization. However, on exposing the sample to air, the monoradical concentration gradually increased. For **1** even the recrystallized sample contained a large amount of monoradical impurity because of its oxidation susceptibility. Accordingly, the temperature change of the ESR signal intensity was not investigated in detail.

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Theoretical and Experimental Analysis of the Absolute Stereochemistry of *cis*-β-Methylstyrene Epoxidation by Cytochrome P450$_{cam}$

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Members of the cytochrome P450 family of enzymes can generally be divided into two classes based on the stringency of their substrate specificity: one for enzymes evolutionarily optimized to oxidize specific physiological substrates (e.g., aromatase, lanosterol 14-demethylase) and a second for enzymes that primarily oxidize xenobiotics (e.g., most hepatic cytochrome P450 enzymes). Understanding the binding of substrates to both classes of cytochrome P450 enzymes, but particularly to the low-specificity forms, is a challenging task because substrate binding is frequently determined in these enzymes by relatively nonspecific lipophilic interactions. Despite the difficulties, clarification of this problem is important for efforts to predict the roles of individual isozymes in drug and xenobiotic metabolism, to develop therapeutically useful, isozyme-specific inhibitors, and to tailor the substrate specificity of cytochrome P450 enzymes for biotechnological purposes.

Cytochrome P450$_{cam}$, a cytosolic enzyme expressed by *Pseudomonas putida*, catalyzes the first step in the degradation of camphor under conditions where camphor is the sole carbon source for the organism.[1] As the only cytochrome P450 enzyme for which a crystal structure is available,[2] it has become the template for all efforts to model the active sites of the membrane-bound enzymes. The crystal structure of cytochrome P450$_{cam}$ suggests the existence of three relatively specific interactions between the substrate and the enzyme: hydrogen bonding of the camphor oxygen to Tyr 96 and interaction of the substrate methyl groups with Val 295 and Val 247.[2,3] Experimental support for these interactions is provided by the fact that site-specific replacement of the tyrosine by a phenylalanine or the valines by isoleucines decreases the regio- and stereospecificity of the oxidation reaction.[4,5] Cytochrome P450$_{cam}$ is generally considered to be a camphor-specific enzyme, but it has been shown to oxidize cam-

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