

## Regular article

# Ab initio calculations find 2,2-disilylcyclopentane-1,3-diyl is a singlet diradical with a high barrier to ring closure\*

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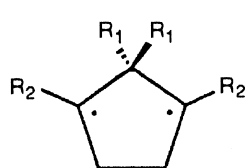
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**Abstract.** Ab initio calculations on the lowest singlet and triplet states of 2,2-disilylcyclopentane-1,3-diyl find that the singlet lies well below the triplet. The  $C_2$  singlet diradical is calculated to be a minimum on the potential energy surface with an enthalpic barrier to ring closure of  $\Delta H_{298}^\ddagger = 13.5$  kcal/mol at the CASPT2/6-31G\* level of theory. The energy of the 1,3-divinyl-substituted singlet diradical is calculated to be only 0.8 kcal/mol higher than that of 5,5-disilyl-1,3-divinylbicyclo[2.1.0]pentane at this level of theory, but the transition state for their equilibration is computed to be 12.8 kcal/mol above the diradical in energy.

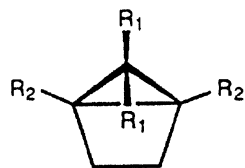
**Key words:** 1,3-Diradicals – Silyl substituents – CASSCF – CASPT2

## 1 Introduction

In 1975, Buchwalter and Closs [1] observed the triplet EPR spectrum of cyclopentane-1,3-diyl (**1**). In agreement with the results of this experiment, ab initio calculations by Conrad et al. [2] found the triplet to lie below the singlet by 0.9 kcal/mol. Subsequent CISD(Q) calculations by Sherrill et al. [3] obtained a value of 1.3 kcal/mol for the barrier to ring closure of singlet **1** to bicyclo[2.1.0]pentane (**5**). The calculated size of this barrier is in good agreement with the experimental estimate of Herman and Goodman [4].



- 1, R<sub>1</sub> = H, R<sub>2</sub> = H  
2, R<sub>1</sub> = F, R<sub>2</sub> = H  
3, R<sub>1</sub> = SiH<sub>3</sub>, R<sub>2</sub> = H  
4, R<sub>1</sub> = SiH<sub>3</sub>, R<sub>2</sub> = CH=CH<sub>2</sub>



- 5, R<sub>1</sub> = H, R<sub>2</sub> = H  
6, R<sub>1</sub> = F, R<sub>2</sub> = H  
7, R<sub>1</sub> = SiH<sub>3</sub>, R<sub>2</sub> = H  
8, R<sub>1</sub> = SiH<sub>3</sub>, R<sub>2</sub> = CH=CH<sub>2</sub>

A triplet ground state has also been predicted computationally for the (0,0) conformation of the trimethylene diradical (propane-1,3-diyl) [5], of which **1** is a derivative. However, substitution of geminal fluorines at C(2) of trimethylene and at C(2) of **1** has been predicted to result in a singlet ground state for both 2,2-difluoro-trimethylene [6] and 2,2-difluorocyclopentane-1,3-diyl (**2**) [7]. In both of these fluorinated diradicals the low-lying  $\sigma^*$  C-F orbitals at C(2) stabilize the in-phase combination of  $p$ - $\pi$  orbitals at C(1) and C(3), relative to the out-of-phase combination, which has a node at C(2). This selective stabilization of one of the non-bonding MOs is sufficiently large in **2** to result in the singlet being computed to fall below the triplet in energy by  $\Delta E_{S-T} = -10.0$  kcal/mol at the CASPT2 level of theory [7].

Because the in-phase combination of  $p$ - $\pi$  orbitals at C(1) and C(3) is selectively occupied in the lowest singlet state of **2**, this diradical is predicted to close to 5,5-difluorobicyclo[2.1.0]pentane (**6**) without a barrier; so **2** is the transition state for the ring inversion of **6**. The direct observation of **2** and, hence, experimental confirmation of the prediction of a singlet ground state for this diradical, is consequently, expected to be difficult. However, substitution of phenyl groups at C(1) and C(3) has been found to provide sufficient kinetic stabilization for a derivative of **2** to allow its observation [8]. The absence of an EPR signal, the kinetics of disappearance, and the failure to observe trapping by oxygen all point to a singlet ground state for this 1,3-diphenyl derivative of diradical **2**.

2,2-Disilyltrimethylene has also been predicted to be a ground-state singlet by recent ab initio calculations [9]. In this diradical the high-lying C-Si  $\sigma$  orbitals donate electron density into the in-phase combination of  $p$ - $\pi$  orbitals at C(1) and C(3), thus destabilizing this non-bonding orbital and leading to the selective occupancy of the out-of-phase combination of  $p$ - $\pi$  orbitals in the lowest singlet state. The same type of strong hyperconjugative electron donation from C-Si bonds should also be present in 2,2-disilylcyclopentane-1,3-diyl (**3**) and should make this diradical a ground-state singlet as well.

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We have undertaken *ab initio* calculations in order to verify that the singlet is computed to lie below the triplet in **3** and to predict the size of the singlet-triplet energy gap. Additionally, **3** is expected to have a barrier to ring closure, because, unlike the case in **2**, the out-of-phase combination of  $p$ - $\pi$  orbitals at C(1) and C(3) should be selectively occupied in the lowest singlet state of **3**. A sufficiently high barrier to ring closure to 5,5-disilylbicyclo[2.1.0]pentane (**7**) could render **3** kinetically stable at low temperatures, so calculating the height of this barrier was of considerable interest.

The dissociation energy of the C(1)–C(4) bond in **7** is expected to be unusually low. Strain relief makes the energy difference between cyclopentane-1,3-diyl (**1**) and bicyclo[2.1.0]pentane (**5**) less than 36 kcal/mol [3, 7, 10], and stabilization of diradical **3** by hyperconjugative electron donation from the C–Si bonds should make the energy difference between **3** and **7** significantly smaller.

Benzylic stabilization of both radical centers in **1** lowers the barrier to ring inversion of 1,4-diphenylbicyclo[2.1.0]pentane to only 12 kcal/mol [11]; and a sufficiently high degree of hyperconjugative stabilization of singlet **3** might render its 1,3-diphenyl derivative lower in energy than the corresponding ring-closed product. Since the allylic stabilization energy is known to be only 1–2 kcal/mol larger than the benzylic stabilization energy [12 (and refs. therein), 13], rather than performing calculations on the diphenyl derivatives of **3** and **7** we chose, instead, to carry out calculations on the divinyl derivatives, **4** and **8**.

Herein we report the results of our *ab initio* calculations on the singlet-triplet energy differences in diradicals **3** and **4**, the heights of their barriers to ring closure, and the energies of these diradicals relative to the corresponding bicyclopentanes, **7** and **8**, respectively.

## 2 Computational methodology

Calculations were performed with the 6-31G\* basis set [14]. The geometry of triplet **3** was optimized using an ROHF wave function. TCSCF wave functions were used to optimize the geometries of singlet **3** and **7**. The geometries of the divinyl derivatives **4** and **8** were optimized using (6/6)CASSCF wavefunctions. All of the geometry optimizations<sup>1</sup> and the subsequent vibrational analyses were performed with Gaussian 94 [15].

The effects of including dynamic electron correlation (review: [16]) were investigated by performing CASPT2 calculations [17], for which the ROHF, TCSCF, and (6/6)CASSCF wave functions were used as the references. The CASPT2 calculations were carried out with the MOLCAS suite of *ab initio* programs [18].

## 3 Results and Discussion

Vibrational analyses found the optimized  $C_{2v}$  geometries of the singlet and the triplet states of **3** each to have two

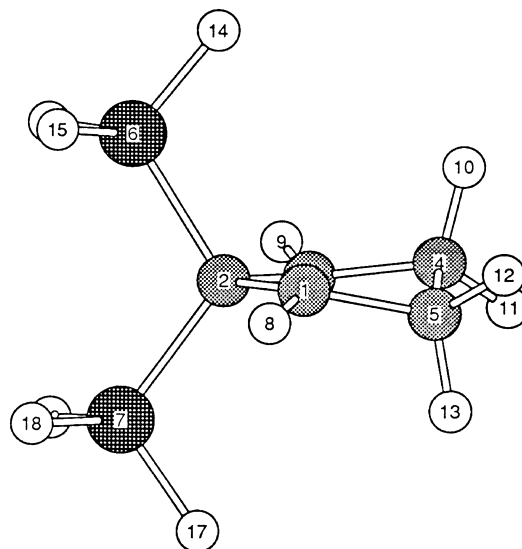
imaginary frequencies. For each state, one of the modes with an imaginary frequency preserves  $C_2$  symmetry, and the other preserves  $C_s$  symmetry. The  $C_2$  and  $C_s$  geometries were both optimized for each state, and vibrational analyses showed that the  $C_2$  structures are minima and the  $C_s$  structures are transition states, connecting mirror-image  $C_2$  minima. One of the  $C_2$  minima is shown in Fig. 1.

The geometry for **7** was optimized with  $C_s$  symmetry, but a vibrational analysis found this geometry to have one imaginary frequency, corresponding to rotation of the *endo* silyl group. Following this mode led to an optimized  $C_1$  structure, which a vibrational analysis confirmed was an energy minimum.

The TCSCF, ROHF, and CASPT2 energies of the stationary points on the singlet and triplet potential surfaces for **3** are given in Table 1. The  $C_2$  structures have an advantage over the  $C_s$  and  $C_{2v}$  structures for both the singlet and triplet because, as shown in Fig. 1, in the  $C_2$  structures the C–H bonds at C(4) and C(5) can be staggered, whereas in the  $C_s$  and  $C_{2v}$  structures these C–H bonds must be pairwise eclipsed.

In addition, *anti* pyramidalization of C(1) and C(3) minimizes the interaction between the nonbonding AOs at these two carbons. This interaction is slightly antibonding in the triplet, where the nonbonding MOs are each occupied by one electron, but much more so in the singlet, where the nonbonding MO in which these two AOs are out-of-phase has more than double the occupation number of the MO in which these two AOs are in-phase (1.37 versus 0.63 in the TCSCF wavefunction for  $^1A_1$ ).

Both the greater antibonding interaction between the  $p$ - $\pi$  AOs at C(1) and C(3) and the larger electron density in these AOs in the singlet than in the triplet probably contribute to the singlet having the larger pyramidalization angle at these carbons by 6.1°. As in 2,2-disilylpropane-1,3-diyl [9], the larger C(1)–C(2)–C(3) bond



**Fig. 1.** The optimized  $C_2$  geometry for  $^1A$  2,2-disilylcyclopentane-1,3-diyl (**3**)

<sup>1</sup> Optimized geometries are available as supplementary material

**Table 1.** Calculated TCSCF,<sup>a</sup> ROHF,<sup>b</sup> (6/6)CASSCF,<sup>c</sup> CASPT2/6-31G\*, and Zero-Point Relative Energies (kcal/mol) for the Stationary Points on the Singlet and Triplet Potential Surfaces for 2,2-Disilylcyclopentane-1,3-diyl (**3**) and for 2,2-Disilyl-1,3-divinylcyclopentane-1,3-diyl (**4**).

Species	symmetry	CASSCF <sup>a-c</sup>	CASPT2	ZPE
<b>3</b> ( <sup>1</sup> A)	C <sub>2</sub>	0 <sup>d</sup>	0 <sup>e</sup>	0 <sup>f</sup>
<b>3</b> ( <sup>1</sup> A <sub>1</sub> )	C <sub>2v</sub>	2.2	1.1	-2.0
<b>3</b> ( <sup>1</sup> A')	C <sub>s</sub>	2.1	1.7	-1.3
<b>3</b> ( <sup>3</sup> B)	C <sub>2</sub>	2.9	5.8	-0.7
<b>3</b> ( <sup>3</sup> B <sub>2</sub> )	C <sub>2v</sub>	3.9	5.8	-2.1
<b>3</b> ( <sup>3</sup> A'')	C <sub>s</sub>	3.6	6.5	-1.1
<b>7</b> ( <sup>1</sup> A)	C <sub>1</sub>	-20.8	-24.5	2.2
TS ( <b>3</b> → <b>7</b> )	C <sub>1</sub>	9.5	14.5	-0.6
<b>4</b> ( <sup>1</sup> A)	C <sub>2</sub>	0 <sup>g</sup>	0 <sup>h</sup>	0 <sup>i,j</sup>
<b>4</b> ( <sup>3</sup> B)	C <sub>2</sub>	0.8	2.1	-
<b>8</b> ( <sup>1</sup> A)	C <sub>1</sub>	-0.1	-0.8 <sup>k</sup>	-0.2 <sup>j</sup>
TS ( <b>4</b> → <b>8</b> )	C <sub>1</sub>	14.4	12.8 <sup>k</sup>	-2.3 <sup>j</sup>

<sup>a</sup>TCSCF for singlets **3**, **7**, and the transition state for closure of **3** to **7**

<sup>b</sup>ROHF for triplet **3**

<sup>c</sup>(6/6)CASSCF for singlet and triplet **4**, **8**, and the transition state for closure of **4** to **8**

<sup>d</sup> $E(\text{TCSCF}/6\text{-}31\text{G}^*) = -774.062267$  hartrees

<sup>e</sup> $E(\text{CASPT2}/6\text{-}31\text{G}^*) = -774.898575$  hartrees

<sup>f</sup>ZPE = 96.5 kcal/mol

<sup>g</sup> $E((6/6)\text{CASSCF}/6\text{-}31\text{G}^*) = -927.910468$  hartrees

<sup>h</sup> $E(\text{CASPT2}/6\text{-}31\text{G}^*) = -929.233530$  hartrees

<sup>i</sup>ZPE = 139.7 kcal/mol

<sup>j</sup>Although all the gradients in the vibrational analyses were close to zero, some of the displacements, corresponding to rotation of the *endo* silyl group, were larger than the default limits for convergence

<sup>k</sup>CASPT2 energy estimated from the CASPT2 energy in C<sub>s</sub> symmetry and the (6,6)CASSCF energy difference between these two geometries

angle in the C<sub>2v</sub> singlet (105.2°) than in the C<sub>2v</sub> triplet (102.1°) also reflects the differing degree to which the interaction between the *p*- $\pi$  AOs on these two carbons is antibonding in these two states.

At the CASPT2 level, the advantage of pyramidalization at C(1) and C(3) is compensated for, partially in the singlet and fully in the triplet, by the fact that the planar C<sub>2v</sub> geometry allows more hyperconjugative electron delocalization from the C—Si  $\sigma$  bonds at C(2) into the in-phase combination of the *p*- $\pi$  AOs at C(1) and C(3). Delocalization is generally favored by increasing the amount of dynamic electron correlation in a calculation [16].

The C<sub>2</sub> singlet is 2.9 kcal/mol below the C<sub>2</sub> triplet at the TCSCF-ROHF level and 5.8 kcal/mol below it at the CASPT2 level. As discussed in the introduction, the singlet lies below the triplet because hyperconjugative electron donation from the silyl groups destabilizes the in-phase combination of *p*- $\pi$  orbitals sufficiently that selective occupancy of the lower-lying, out-of-phase combination in the singlet overcomes the lower electron repulsion energy in the triplet. The increase in the size of the singlet-triplet energy difference upon inclusion of dynamic electron correlation is consistent with greater delocalization of the electrons in the C—Si  $\sigma$  bonds in the singlet state than in the triplet [16].

The selective stabilization of the singlet, relative to the triplet, by hyperconjugation is evident in comparison of the C<sub>2v</sub> geometries of the two states. In the singlet the

bond length of 1.491 Å between C(1) and C(2) is 0.020 Å shorter than in the triplet, and, as already noted, the 3.1° larger C(1)—C(2)—C(3) bond angle in the singlet also reflects the larger amount of electron delocalization from the C—Si  $\sigma$  bonds in the singlet than in the triplet state.

The presence of the five-membered ring in **3** constrains the C(1)—C(2)—C(3) bond angle to be fully 15.2° smaller in <sup>1</sup>A<sub>1</sub> than the corresponding bond angle in the (0,0) conformation of singlet 2,2-disilyltrimethylene [9]. The smaller distance between C(1) and C(3) in **3** results in a stronger antibonding interaction between these two carbons in the lowest singlet state of the cyclic, than of the acyclic, diradical.

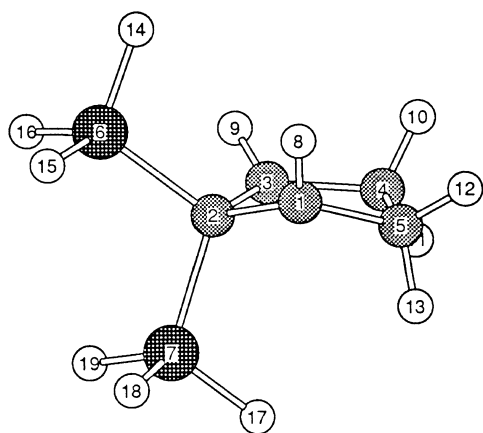
In order to assess the extent to which this antibonding interaction contributes to the calculated reduction in the singlet-triplet gap in the cyclic diradical, we constrained the C(1)—C(2)—C(3) angle in the <sup>1</sup>A<sub>1</sub> and <sup>3</sup>B<sub>2</sub> states of 2,2-disilyltrimethylene to be the same as in the corresponding states of **3**. The resulting decrease in this angle of 15.2° in the singlet is 6.1° larger than in the triplet, so it is not at all surprising that the computed singlet-triplet splittings of -3.6 kcal/mol at the TCSCF/ROHF level and -6.1 kcal/mol at the CASPT2 level for constrained 2,2-disilyltrimethylene are much smaller in magnitude than at the unconstrained geometries. The latter values are -6.2 and -11.9 kcal/mol, respectively [9].

The singlet-triplet splittings, computed at the geometries of 2,2-disilyltrimethylene that are constrained to have the same C(1)—C(2)—C(3) bond angles as the <sup>1</sup>A<sub>1</sub> and <sup>3</sup>B<sub>2</sub> states of **3**, are slightly larger in magnitude than the corresponding values of -1.7 and -4.7 kcal/mol at the optimized C<sub>2v</sub> geometries of both states of **3** (Table 1). Hyperconjugative electron donation from the C—H bonds of the ethano bridge in the cyclic diradical competes with donation from the C—Si bonds and destabilizes the singlet relative to the triplet, thus reducing the magnitude of the singlet-triplet gap by 1.9 kcal/mol at the TCSCF-ROHF level and by 1.4 kcal/mol at the CASPT2 level. Alkyl substituents at C(1) and C(3) have also been found to destabilize the <sup>1</sup>A<sub>1</sub> state of unsubstituted trimethylene [6].

Unlike both **1** [3, 4] and **2** [7], **3** should have a large barrier to ring closure. In **3** the nonbonding MO in which the AOs at C(1) and C(3) are out-of-phase has a much higher occupation number than in **1** or **2**. This should result in closure to the corresponding bicyclo[2.1.0]pentane, which is geometrically constrained to be disrotatory, being much more highly forbidden by orbital symmetry in **3** than in **1** or **2**.

In order to find a transition state for the closure of **3** to **7**, the C(1)—C(3) distance in **3** was iteratively shortened from the distance of 2.39 Å in the diradical to the optimized bond length of 1.53 Å in **7**, and at each point the geometry was optimized with this distance fixed. Starting from the structure of highest energy that was found by this scan, the actual transition state was located. Vibrational analysis confirmed that it was a transition state, and following of the intrinsic reaction coordinate showed it to be the transition state for the closure of **3** to **7**.

The geometry of the transition state is shown in Fig. 2. It has only C<sub>1</sub> symmetry, so the pathway from



**Fig. 2.** The  $C_1$  transition state for the ring closure of 2,2-disilylcyclopentane-1,3-diyl (**3**) to 5,5-disilylbicyclo[2.1.0]pentane (**7**)

**3** to it cannot be purely disrotatory. Indeed, since the equilibrium geometry of **3** has  $C_2$ , rather than  $C_s$ , symmetry, the reaction path for disrotatory ring closure must in its early stages have only  $C_1$  symmetry. Since, as expected from Hammond's postulate, the transition state resembles the geometry of **3** more than **7**, it is perhaps not surprising that it deviates significantly from  $C_s$  symmetry.

The energy barrier for ring closure of **3** to **7** is predicted to be 9.5 kcal/mol at the TCSCF level of theory and 14.5 kcal/mol at the CASPT2 level. After correction for differences in zero-point energies and heat capacities, the latter value yields  $\Delta H_{298}^\ddagger = 13.5$  kcal/mol. This large barrier should result in **3** being persistent enough to be studied at low temperatures by a variety of methods [8], possibly including  $^{13}\text{C}$  cross polarization magic angle spinning NMR in the solid state. This technique has been elegantly applied by Zilm and coworkers [19] to confirm that some EPR-silent diradicals really do have singlet ground states, and it might also be used to provide experimental evidence that **3** also has a singlet ground state.

The energy difference between **3** and **7** is only 24.5 kcal/mol at the CASPT2 level. Since vinyl groups at C(1) and C(3) might provide nearly this amount of allylic stabilization for the diradical [12], we undertook calculations to test computationally whether vinyl substituents at these two carbons would actually make the 1,3-divinyl derivative of **4** stable toward ring closure to **8**.

The lowest singlet and triplet states of diradical **4** were optimized with  $C_{2v}$  and  $C_2$  symmetries. As with **3**, the  $C_2$  structures were found to be the lower in energy. The singlet-triplet gap in **4** is  $-0.8$  kcal/mol at the (6/6)CASSCF level and  $-2.1$  kcal/mol at CASPT2.

The much smaller magnitude of the singlet-triplet gap in **4** than in **3** is obviously due to conjugation of the radical centers with the vinyl groups in **4**. Allylic delocalization reduces the magnitude of the coefficients of the in-phase combination of  $p$ - $\pi$  orbitals at C(1) and C(3) and thus decreases the destabilization of the nonbonding MO that results from interaction of this combination with the C—Si bonds. The resulting reduction in the energy difference between this nonbonding MO

and the nonbonding MO that involves the out-of-phase combination of  $p$ - $\pi$  orbitals at C(1) and C(3) selectively stabilizes the triplet relative to the singlet.

As shown in Table 1, the energy difference between **4** and **8** is nearly zero at the (6/6)CASSCF level. Unfortunately, performing CASPT2 calculations on **8** in  $C_1$  symmetry required disk storage in excess of that available to us. However, we were able to perform CASPT2 calculations on **8** in  $C_s$  symmetry. Since our calculations found that the CASPT2 energy difference of 0.16 kcal/mol between the  $C_s$  and  $C_1$  geometries of **7** is almost exactly the same as the TCSCF energy difference, we assume that the CASPT2 and (6/6)CASSCF energy differences between these two geometries of **8** are also the same. Adding this energy difference of 0.4 kcal/mol between the  $C_s$  and  $C_1$  geometries of **8** to the CASPT2 energy difference of 0.4 kcal/mol between **4** and the  $C_s$  geometry of **8** gives an estimate of 0.8 kcal/mol for the difference between the CASPT2 energies of the equilibrium geometries of **4** and **8**.

CASPT2 is known to overestimate the resonance stabilization energy of the allyl radical by 1–2 kcal/mol [12], so our CASPT2 calculations suggest that, although the C(1)—C(4) bond in **8** is weak, it does have a positive dissociation energy. Since phenyl substituents would each be expected to provide 1–2 kcal/mol less resonance stabilization than the vinyl substituents provide for **4** [12], it seems highly likely that the C(1)—C(4) bond in the 1,4-diphenyl derivative of **7** also has a positive bond dissociation energy.

Even though **4** is not predicted to be thermodynamically stable with respect to closure to **8**, ring closure of **4**, like that of **3**, should encounter a sizable kinetic barrier. Unfortunately, the  $C_1$  geometry of the transition state for ring closure of **4** prevented us from performing CASPT2 calculations on it. However, the CASSCF energy of the  $C_s$  constrained transition state is only 0.03 kcal/mol higher than that of the  $C_1$  transition state, so we expect their CASPT2 energies also to be essentially the same. Therefore, 12.8 kcal/mol should provide a very good estimate of the CASPT2 energy difference between **4** and the  $C_1$  transition state for its closure to **8**.

## 4 Conclusions

The high barriers to ring closure predicted for diradical **4** and, by inference [12], its diphenyl analog, make these derivatives of **3** of considerable interest for experimental study. Additionally, the allylic and benzylic chromophores that are present in these derivatives should facilitate the detection of these diradicals and allow the rates of ring closure and reaction to be conveniently monitored by UV spectroscopy [8].

On the other hand, the singlet-triplet splitting of only  $-2.1$  kcal/mol that is predicted for **4** at the CASPT2 level is uncomfortably small. Since in benzylic radicals the unpaired electrons are slightly more localized than in allylic radicals [12], the 1,3-diphenyl derivative of diradical **3** would be expected to have a singlet-triplet energy splitting that is larger than that in the divinyl

derivative **4**, although certainly not as large as the CASPT2 value of  $-5.8$  kcal/mol in **3** itself.

The angle constraints that are present in the five-membered ring of **3** are computed to make the singlet-triplet splitting in this diradical considerably smaller than in the acyclic 2,2-disilyltrimethylene diradical. Nevertheless, the singlet is predicted to be the ground state by a sufficiently large margin in **3** that this diradical and hopefully also its 1,3 diphenyl analog could be used to test the prediction [9] that silyl groups at C(2) of 1,3-diradicals should confer upon them singlet ground states.

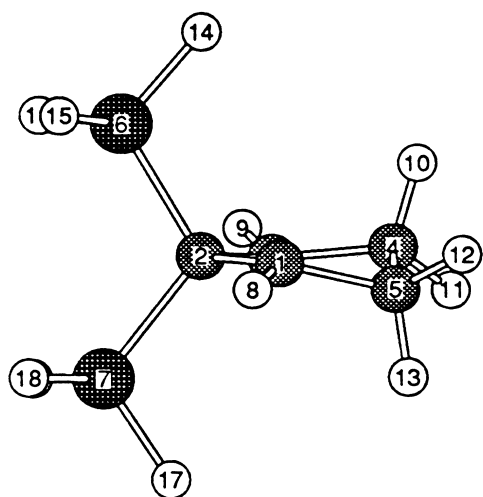
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## Supporting information

Optimized geometries, energies, frequencies and thermodynamic quantities for the species in Table 1 and the  $C_s$  structures of 8 and of the transition state from 4 to 8. (16 pages).



2,2-Disilylcyclopentane-1,3-diyl (**3**)  
 $^1A (2/2)$  CASSCF/6-31G\*  $C_2$  Geometry

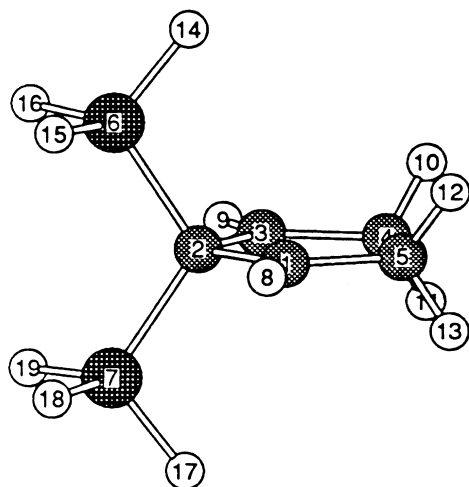
(2/2) CASSCF/6-31G*	-774.062267
$E_{\text{nuc}}$	440.294698
ZPE (kcal/mol)	96.54
$C_v^{298}$ (cal/mol-K)	34.34
$S^{298}$ (cal/mol-K)	90.60
CASPT2/6-31G*	-774.898574

Bond Lengths (Å) and Angles (°)

(1-2)	1.498	(1-5)	1.510	(1-8)	1.076
(2-6)	1.901	(4-5)	1.541	(4-10)	1.092
(4-11)	1.085	(6-14)	1.475	(6-15)	1.476
(6-16)	1.478	(2-1-5)	109.0	(2-1-8)	121.7
(5-1-8)	121.6	(1-2-3)	105.5	(1-2-6)	108.9
(1-2-7)	110.1	(6-2-7)	113.0	(3-4-5)	103.9
(3-4-10)	109.5	(3-4-11)	113.4	(5-4-10)	109.9
(5-4-11)	113.1	(10-4-11)	107.1	(2-6-14)	109.6
(2-6-15)	110.7	(2-6-16)	110.3	(14-6-15)	109.2
(14-6-16)	108.6	(15-6-16)	108.3	(5-1-2-3)	-9.7
(5-1-2-6)	-127.9	(5-1-2-7)	107.7	(8-1-2-3)	-159.5
(8-1-2-6)	82.3	(8-1-2-7)	-42.1	(2-1-5-4)	24.6
(2-1-5-12)	147.8	(2-1-5-13)	-92.7	(8-1-5-4)	174.5
(8-1-5-12)	-62.4	(8-1-5-13)	57.1	(1-2-6-14)	62.0
(1-2-6-15)	-58.5	(1-2-6-16)	-178.4	(3-2-6-14)	-53.2
(3-2-6-15)	-173.8	(3-2-6-16)	66.4	(7-2-6-14)	-175.2
(7-2-6-15)	64.2	(7-2-6-16)	-55.7	(3-4-5-1)	-29.4
(3-4-5-12)	-152.7	(3-4-5-13)	87.7	(10-4-5-12)	-35.7
(10-4-5-13)	-155.2	(11-4-5-12)	83.9		

Frequencies ( $\text{cm}^{-1}$ )

97.3	146.2	159.5	169.9	206.8	225.5	286.6	357.7	400.5
588.1	593.6	639.5	693.8	708.4	727.1	732.9	871.1	896.3
938.4	974.3	1013.2	1016.5	1021.0	1035.3	1040.0	1046.1	1052.6
1059.2	1100.0	1116.9	1229.8	1248.1	1331.8	1403.8	1432.9	1468.4
1494.0	1620.2	1636.9	2359.5	2362.2	2377.1	2378.1	2378.3	2384.4
3152.2	3160.0	3249.5	3251.6	3347.7	3350.1			



2,2-Disilylcyclopentane-1, 3-diyl (3)  
 $^1A_1$  (2/2) CASSCF/6-31G\*  $C_{2v}$  Geometry

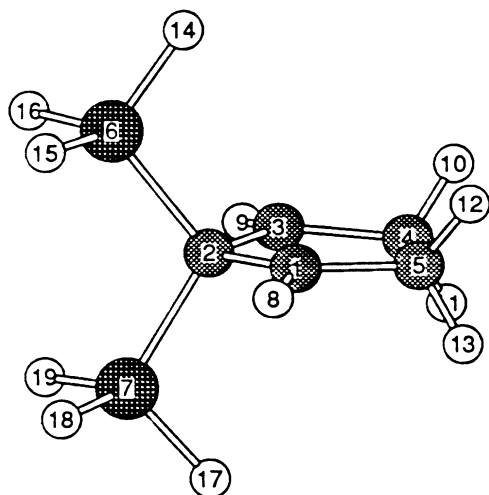
(2/2) CASSCF/6-31G*	-774.058786
$E_{\text{nuc}}$	438.807640
ZPE (kcal/mol)	94.59
$C_v^{298}$ (cal/mol-K)	32.53
$S^{298}$ (cal/mol-K)	96.03
CASPT2/6-31G*	-774.896786

Bond Lengths (Å) and Angles (°)

(1-2)	1.490	(1-5)	1.510	(1-8)	1.073
(2-6)	1.901	(4-5)	1.556	(4-10)	1.087
(4-11)	1.087	(6-14)	1.476	(6-15)	1.478
(6-16)	1.478	(2-1-5)	111.8	(2-1-8)	124.1
(5-1-8)	124.1	(1-2-3)	105.2	(1-2-6)	109.3
(6-2-7)	114.0	(3-4-5)	105.6	(3-4-10)	111.2
(3-4-11)	111.2	(5-4-10)	111.4	(5-4-11)	111.4
(10-4-11)	106.2	(2-6-14)	109.5	(2-6-15)	110.6
(2-6-16)	110.6	(14-6-15)	108.9	(14-6-16)	108.9
(15-6-16)	108.2	(5-1-2-3)	0.0	(5-1-2-6)	-117.3
(8-1-2-3)	180.0	(8-1-2-6)	62.7	(2-1-5-4)	0.0
(2-1-5-12)	120.9	(2-1-5-13)	-120.9	(8-1-5-4)	180.0
(8-1-5-12)	-59.1	(8-1-5-13)	59.1	(1-2-6-14)	57.3
(1-2-6-15)	-62.7	(1-2-6-16)	177.4	(3-2-6-15)	-177.4
(3-2-6-16)	62.7	(7-2-6-14)	180.0	(7-2-6-15)	59.9
(7-2-6-16)	-59.9	(3-4-5-1)	0.0	(3-4-5-12)	-120.9
(3-4-5-13)	120.9	(10-4-5-12)	0.0	(10-4-5-13)	-118.3
(11-4-5-12)	118.3				

Frequencies ( $\text{cm}^{-1}$ )

-353.4	-131.9	5.6	134.6	155.6	158.4	212.1	221.7	241.1
364.1	396.0	636.9	692.8	698.6	724.2	763.5	834.9	869.7
912.2	962.4	1012.3	1013.1	1019.8	1033.2	1039.6	1045.1	1052.5
1057.9	1060.1	1125.5	1222.7	1247.2	1368.3	1391.8	1414.3	1470.6
1500.6	1625.8	1650.8	2357.3	2363.6	2368.0	2373.1	2376.0	2381.9
3184.7	3201.1	3201.2	3227.3	3398.3	3401.1			



2,2-Disilylcyclopentane-1,3-diyl (3)  
 $^1A'$  (2/2) CASSCF/6-31G\*  $C_s$  Geometry

(2/2) CASSCF/6-31G*	-774.058895
$E_{\text{nuc}}$	438.811961
ZPE (kcal/mol)	95.21
$C_v^{298}$ (cal/mol-K)	34.05
$S^{298}$ (cal/mol-K)	93.14
CASPT2/6-31G*	-774.895866

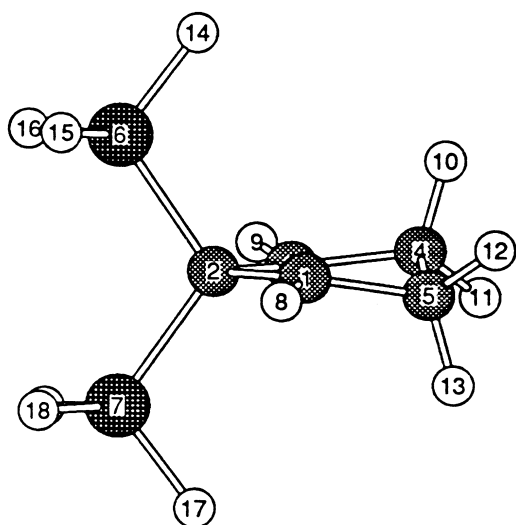
Bond Lengths (Å) and Angles ( $^\circ$ )

(1-2)	1.493	(1-5)	1.511	(1-8)	1.074
(2-6)	1.902	(2-7)	1.900	(4-5)	1.556
(4-10)	1.087	(4-11)	1.088	(6-14)	1.475
(6-15)	1.478	(6-16)	1.478	(7-17)	1.476
(2-1-5)	111.5	(2-1-8)	123.4	(5-1-8)	123.3
(1-2-3)	105.2	(1-2-6)	109.2	(1-2-7)	109.5
(6-2-7)	113.8	(3-4-5)	105.7	(3-4-10)	111.1
(3-4-11)	111.2	(5-4-10)	111.4	(5-4-11)	111.4
(10-4-11)	106.2	(1-5-12)	111.1	(1-5-13)	111.3
(2-6-14)	109.5	(2-6-15)	110.6	(2-6-16)	110.6
(14-6-15)	109.0	(14-6-16)	109.0	(15-6-16)	108.1
(2-7-17)	109.4	(2-7-18)	110.7	(2-7-19)	110.7
(17-7-18)	108.9	(17-7-19)	108.9	(18-7-19)	108.3
(5-1-2-3)	-6.8	(5-1-2-6)	-123.9	(5-1-2-7)	110.9
(8-1-2-3)	-171.6	(8-1-2-6)	71.3	(8-1-2-7)	-53.9
(2-1-5-4)	4.3	(2-1-5-12)	125.2	(2-1-5-13)	-116.7
(8-1-5-4)	169.1	(8-1-5-12)	-70.0	(8-1-5-13)	48.1
(1-2-6-14)	57.3	(1-2-6-15)	-62.9	(1-2-6-16)	177.4
(3-2-6-15)	-177.4	(3-2-6-16)	62.9	(7-2-6-14)	180.0
(7-2-6-15)	59.8	(7-2-6-16)	-59.8	(1-2-7-17)	-57.5
(1-2-7-18)	62.5	(3-2-7-19)	-62.5	(6-2-7-18)	-60.0
(6-2-7-19)	60.0	(2-3-4-10)	-125.2	(2-3-4-11)	116.7
(9-3-4-10)	70.0	(9-3-4-11)	-48.1	(3-4-5-1)	0.0
(3-4-5-12)	-120.7	(3-4-5-13)	120.9	(10-4-5-1)	120.7
(10-4-5-12)	0.0	(10-4-5-13)	-118.3	(11-4-5-1)	-120.9
(11-4-5-12)	118.3				

Frequencies ( $\text{cm}^{-1}$ )

-164.2	74.1	146.8	156.6	179.6	208.4	221.7	242.5	302.8
394.2	401.4	636.5	692.3	699.0	723.5	766.3	834.0	869.1
916.1	962.8	1012.2	1013.0	1019.3	1033.8	1039.9	1044.6	1052.4
1059.5	1062.7	1126.8	1225.8	1247.0	1368.6	1392.3	1410.5	1470.7
1499.2	1625.3	1650.3	2357.9	2364.1	2368.8	2371.4	2375.9	2383.6
3185.4	3202.3	3204.8	3230.3	3384.4	3387.3			





2,2-Disilylcyclopentane-1,3-diyl (3)  
<sup>3</sup>B ROHF/6-31G\* C<sub>2</sub> Geometry

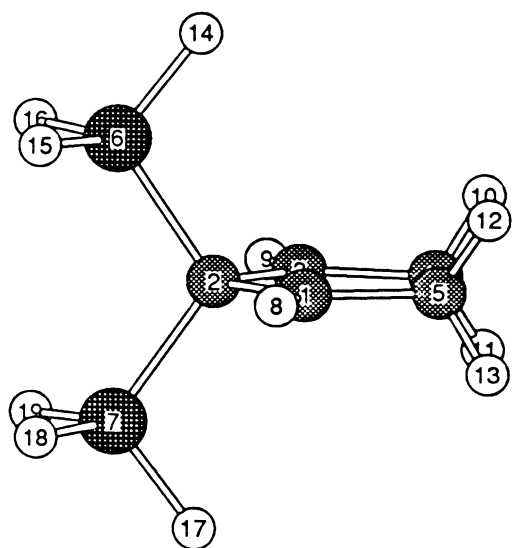
ROHF/6-31G*	-774.057688
E <sub>nuc</sub>	437.411192
ZPE (kcal/mol)	95.81
C <sub>v</sub> <sup>298</sup> (cal/mol-K)	32.25
S <sup>298</sup> (cal/mol-K)	95.16
CASPT2/6-31G*	-774.889318

Bond Lengths (Å) and Angles (°)

(1-2)	1.517	(1-5)	1.506	(1-8)	1.076
(2-6)	1.907	(4-5)	1.540	(4-10)	1.090
(4-11)	1.086	(6-14)	1.477	(6-15)	1.478
(6-16)	1.479	(2-1-5)	111.5	(2-1-8)	122.1
(5-1-8)	122.1	(1-2-3)	102.2	(1-2-6)	109.6
(1-2-7)	111.5	(6-2-7)	112.0	(3-4-5)	104.0
(3-4-10)	110.7	(3-4-11)	112.4	(5-4-10)	110.3
(5-4-11)	112.8	(10-4-11)	106.8	(2-6-14)	109.8
(2-6-15)	110.5	(2-6-16)	110.6	(14-6-15)	108.9
(14-6-16)	108.5	(15-6-16)	108.5	(5-1-2-3)	-8.8
(5-1-2-6)	-127.1	(5-1-2-7)	108.2	(8-1-2-3)	-166.0
(8-1-2-6)	75.7	(8-1-2-7)	-49.0	(2-1-5-4)	22.2
(2-1-5-12)	144.4	(2-1-5-13)	-96.2	(8-1-5-4)	179.4
(8-1-5-12)	-58.4	(8-1-5-13)	61.0	(1-2-6-14)	62.1
(1-2-6-15)	-58.0	(1-2-6-16)	-178.1	(3-2-6-14)	-50.3
(3-2-6-15)	-170.4	(3-2-6-16)	69.5	(7-2-6-14)	-173.6
(7-2-6-15)	66.3	(7-2-6-16)	-53.8	(3-4-5-1)	-25.9
(3-4-5-12)	-147.9	(3-4-5-13)	92.8	(10-4-5-12)	-29.2
(10-4-5-13)	-148.5	(11-4-5-12)	90.1		

Frequencies (cm<sup>-1</sup>)

79.9	119.8	148.4	168.1	169.1	223.4	260.0	300.8	403.2
460.3	504.7	619.5	684.3	705.3	710.0	726.2	844.4	896.9
928.7	978.2	1010.7	1020.6	1030.2	1036.0	1038.7	1044.4	1047.5
1052.9	1085.7	1133.0	1200.6	1231.8	1338.7	1403.2	1434.1	1470.4
1503.0	1625.5	1645.0	2354.1	2356.7	2368.5	2369.2	2369.2	2377.2
3170.8	3174.5	3237.0	3241.7	3357.1	3359.3			



2,2-Disilylcyclopentane-1,3-diyl (**3**)  
 $3B_2$  ROHF/6-31G\*  $C_{2v}$  Geometry

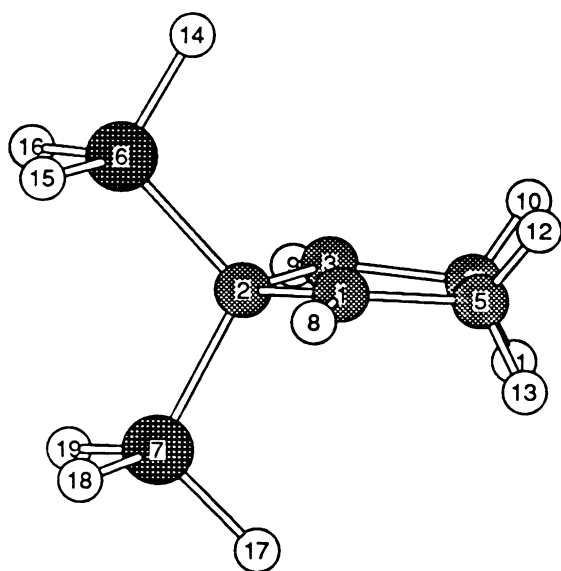
ROHF/6-31G*	-774.056069
$E_{\text{nuc}}$	436.447434
ZPE (kcal/mol)	94.40
$C_v^{298}$ (cal/mol-K)	32.78
$S^{298}$ (cal/mol-K)	93.58
CASPT2/6-31G*	-774.889280

Bond Lengths (Å) and Angles (°)

(1-2)	1.511	(1-5)	1.504	(1-8)	1.074
(2-6)	1.908	(4-5)	1.548	(4-10)	1.088
(4-11)	1.088	(6-14)	1.477	(6-15)	1.479
(6-16)	1.479	(2-1-5)	113.5	(2-1-8)	123.4
(5-1-8)	123.2	(1-2-3)	102.1	(1-2-6)	110.5
(6-2-7)	112.4	(3-4-5)	105.5	(3-4-10)	111.3
(3-4-11)	111.3	(5-4-10)	111.4	(5-4-11)	111.4
(10-4-11)	106.2	(2-6-14)	109.7	(2-6-15)	110.6
(2-6-16)	110.6	(14-6-15)	108.7	(14-6-16)	108.7
(15-6-16)	108.4	(5-1-2-3)	0.0	(5-1-2-6)	-117.5
(8-1-2-3)	180.0	(8-1-2-6)	62.5	(2-1-5-4)	0.0
(2-1-5-12)	120.9	(2-1-5-13)	-120.9	(8-1-5-4)	180.0
(8-1-5-12)	-59.1	(8-1-5-13)	59.1	(1-2-6-14)	56.1
(1-2-6-15)	-63.8	(1-2-6-16)	176.1	(3-2-6-15)	-176.1
(3-2-6-16)	63.8	(7-2-6-14)	180.0	(7-2-6-15)	60.1
(7-2-6-16)	-60.1	(3-4-5-1)	0.0	(3-4-5-12)	-120.9
(3-4-5-13)	120.9	(10-4-5-12)	0.0	(10-4-5-13)	-118.3
(11-4-5-12)	118.3				

Frequencies ( $\text{cm}^{-1}$ )

-205.5	-182.2	108.6	113.8	152.0	166.1	173.3	218.9	221.6
289.7	408.1	615.7	681.0	708.3	709.1	770.0	847.6	848.6
900.2	972.8	1010.2	1021.8	1033.0	1036.2	1037.7	1043.4	1047.5
1052.0	1052.2	1153.3	1213.7	1222.2	1355.1	1413.6	1414.0	1472.7
1515.7	1627.2	1653.1	2352.8	2357.6	2364.1	2367.3	2369.1	2376.5
3182.5	3197.6	3198.8	3222.7	3382.9	3384.8			



2,2-Disilylcyclopentane-1,3-diyl (3)  
3A'' ROHF/6-31G\* C<sub>s</sub> Geometry

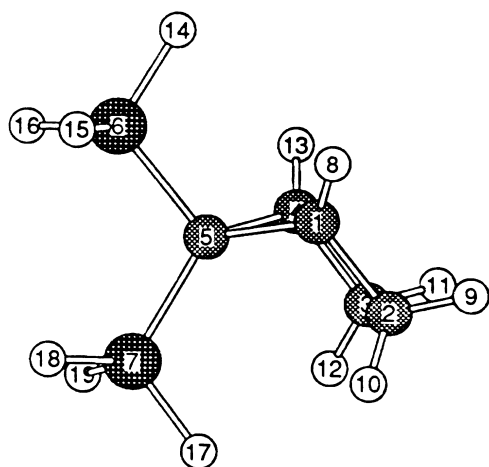
ROHF/6-31G*	-774.056452
E <sub>nuc</sub>	436.861370
ZPE (kcal/mol)	95.37
C <sub>v</sub> <sup>298</sup> (cal/mol-K)	33.67
S <sup>298</sup> (cal/mol-K)	94.85
CASPT2/6-31G*	-774.888262

Bond Lengths (Å) and Angles (°)

(1-2)	1.513	(1-5)	1.507	(1-8)	1.075
(2-6)	1.905	(2-7)	1.910	(4-5)	1.548
(4-10)	1.087	(4-11)	1.088	(5-12)	1.087
(5-13)	1.088	(6-14)	1.475	(6-15)	1.479
(6-16)	1.479	(7-17)	1.478	(2-1-5)	112.6
(2-1-8)	122.3	(5-1-8)	121.9	(1-2-3)	102.1
(1-2-6)	110.4	(1-2-7)	110.7	(6-2-7)	112.2
(3-4-5)	105.5	(3-4-10)	111.1	(3-4-11)	111.3
(5-4-10)	111.7	(5-4-11)	111.1	(10-4-11)	106.2
(1-5-12)	111.1	(1-5-13)	111.3	(4-5-12)	111.7
(4-5-13)	111.1	(2-6-14)	110.0	(2-6-15)	110.4
(2-6-16)	110.4	(14-6-15)	108.8	(14-6-16)	108.8
(15-6-16)	108.3	(2-7-17)	109.6	(2-7-18)	110.7
(2-7-19)	110.7	(17-7-18)	108.6	(17-7-19)	108.6
(18-7-19)	108.6	(5-1-2-3)	-12.8	(5-1-2-6)	-130.2
(5-1-2-7)	105.0	(8-1-2-3)	-172.7	(8-1-2-6)	69.9
(8-1-2-7)	-54.9	(2-1-5-4)	8.3	(2-1-5-12)	129.6
(2-1-5-13)	-112.3	(8-1-5-4)	168.3	(8-1-5-12)	-70.5
(8-1-5-13)	47.7	(1-2-6-14)	56.1	(1-2-6-15)	-64.1
(1-2-6-16)	176.2	(3-2-6-15)	-176.2	(3-2-6-16)	64.1
(7-2-6-14)	180.0	(7-2-6-15)	59.9	(7-2-6-16)	-59.9
(1-2-7-17)	-56.2	(1-2-7-18)	63.5	(1-2-7-19)	-176.0
(3-2-7-18)	176.0	(3-2-7-19)	-63.5	(6-2-7-18)	-60.2
(6-2-7-19)	60.2	(2-3-4-10)	-129.6	(2-3-4-11)	112.3
(9-3-4-10)	70.5	(9-3-4-11)	-47.7	(3-4-5-1)	0.0
(3-4-5-12)	-120.9	(3-4-5-13)	120.7	(10-4-5-1)	120.9
(10-4-5-12)	0.0	(10-4-5-13)	-118.4	(11-4-5-1)	-120.7
(11-4-5-12)	118.5				

Frequencies (cm<sup>-1</sup>)

-85.3	73.2	109.8	167.5	168.9	216.3	225.1	296.0	391.6
435.9	437.2	617.1	682.4	708.7	709.2	774.7	844.0	851.4
913.4	972.2	1010.2	1021.1	1033.9	1037.6	1038.3	1043.6	1047.4
1052.5	1062.3	1151.9	1213.8	1230.6	1357.6	1407.5	1411.8	1472.1
1510.8	1625.5	1651.5	2354.1	2358.8	2364.1	2365.8	2370.9	2380.0
3182.5	3198.9	3208.0	3230.2	3361.2	3363.4			



5,5-Disilylbicyclo[2.1.0]pentane (7)  
<sup>1</sup>A (2/2) CASSCF/6-31G\* C<sub>1</sub> Geometry

(2/2) CASSCF/6-31G*	-774.095359
E <sub>nuc</sub>	444.919966
ZPE (kcal/mol)	98.72
C <sub>v</sub> <sup>298</sup> (cal/mol-K)	32.23
S <sup>298</sup> (cal/mol-K)	90.37
CASPT2/6-31G*	-774.937598

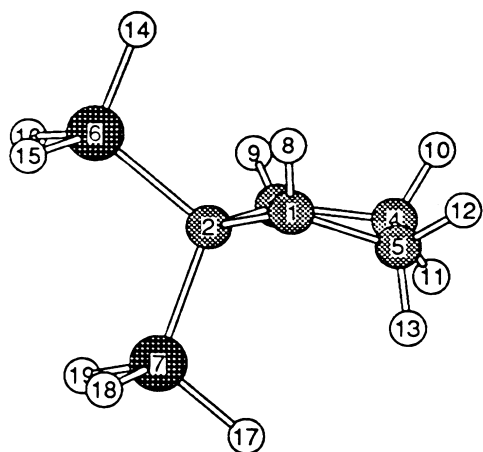
Bond Lengths (Å) and Angles (°)

(1-2)	1.530	(1-4)	1.527	(1-5)	1.522
(1-8)	1.077	(2-3)	1.555	(2-9)	1.084
(2-10)	1.083	(3-4)	1.532	(3-11)	1.083
(3-12)	1.085	(4-5)	1.519	(4-13)	1.076
(5-6)	1.884	(5-7)	1.888	(6-14)	1.478
(6-15)	1.477	(6-16)	1.478	(7-17)	1.475
(7-18)	1.479	(7-19)	1.478	(2-1-4)	90.6
(2-1-5)	112.7	(2-1-8)	123.9	(4-1-5)	59.8
(4-1-8)	129.0	(5-1-8)	121.1	(1-2-3)	89.5
(1-2-9)	111.7	(1-2-10)	117.1	(3-2-9)	111.5
(3-2-10)	117.7	(9-2-10)	108.4	(2-3-4)	89.4
(2-3-11)	112.1	(2-3-12)	117.3	(4-3-11)	112.5
(4-3-12)	116.5	(11-3-12)	108.1	(1-4-3)	90.5
(1-4-5)	60.0	(1-4-13)	129.1	(3-4-5)	111.8
(3-4-13)	124.1	(5-4-13)	121.6	(1-5-4)	60.2
(1-5-6)	112.3	(1-5-7)	125.8	(4-5-6)	113.1
(4-5-7)	123.3	(6-5-7)	112.5	(5-6-14)	109.6
(5-6-15)	111.0	(5-6-16)	110.7	(14-6-15)	108.6
(14-6-16)	108.8	(15-6-16)	108.1	(5-7-17)	114.1
(5-7-18)	109.0	(5-7-19)	109.8	(17-7-18)	107.8
(17-7-19)	108.2	(18-7-19)	107.8	(4-1-2-3)	-1.1
(4-1-2-9)	112.0	(4-1-2-10)	-122.2	(5-1-2-3)	56.1
(5-1-2-9)	169.2	(5-1-2-10)	-65.0	(8-1-2-3)	-140.9
(8-1-2-9)	-27.9	(8-1-2-10)	97.9	(2-1-4-3)	1.1
(2-1-4-5)	116.2	(2-1-4-13)	-135.8	(5-1-4-3)	-115.1
(5-1-4-13)	108.0	(8-1-4-3)	137.6	(8-1-4-5)	-107.3
(8-1-4-13)	0.7	(2-1-5-4)	-76.6	(2-1-5-6)	178.6
(2-1-5-7)	35.0	(4-1-5-6)	-104.8	(4-1-5-7)	111.6
(8-1-5-4)	119.9	(8-1-5-6)	15.2	(8-1-5-7)	-128.4
(1-2-3-4)	1.1	(1-2-3-11)	115.3	(1-2-3-12)	-118.7
(9-2-3-4)	-112.1	(9-2-3-11)	2.1	(9-2-3-12)	128.1
(10-2-3-4)	121.7	(10-2-3-11)	-124.1	(10-2-3-12)	1.9
(2-3-4-1)	-1.1	(2-3-4-5)	-58.7	(2-3-4-13)	139.1
(11-3-4-1)	-114.9	(11-3-4-5)	-172.5	(11-3-4-13)	25.3
(12-3-4-1)	119.5	(12-3-4-5)	61.9	(12-3-4-13)	-100.4
(1-4-5-6)	103.4	(1-4-5-7)	-115.4	(3-4-5-1)	77.2
(3-4-5-6)	-179.4	(3-4-5-7)	-38.2	(13-4-5-1)	-120.0
(13-4-5-6)	-16.6	(13-4-5-7)	124.6	(1-5-6-14)	40.1
(1-5-6-15)	-79.9	(1-5-6-16)	160.1	(4-5-6-14)	-25.8
(4-5-6-15)	-145.8	(4-5-6-16)	94.2	(7-5-6-14)	-171.3
(7-5-6-15)	68.7	(7-5-6-16)	-51.3	(1-5-7-17)	-13.4
(1-5-7-18)	107.1	(1-5-7-19)	-134.9	(4-5-7-17)	61.7
(4-5-7-18)	-177.8	(4-5-7-19)	-59.9	(6-5-7-17)	-156.9
(6-5-7-18)	-36.4	(6-5-7-19)	81.5		

Contd.

Frequencies ( $\text{cm}^{-1}$ )

76.7	138.4	172.4	199.5	206.7	240.3	351.3	380.7	484.4
648.6	683.2	714.3	720.5	830.0	844.7	880.0	929.9	944.8
1017.3	1025.0	1038.6	1040.8	1045.4	1051.4	1055.0	1055.9	1063.6
1099.1	1110.7	1200.1	1249.5	1307.3	1334.8	1381.4	1389.0	1427.8
1487.1	1635.4	1662.2	2355.3	2360.3	2363.9	2366.0	2374.9	2386.9
3228.7	3244.1	3271.3	3292.0	3361.1	3349.8			

Transition State from **3** to **7**  
 $^1\text{A}$  (2/2) CASSCF/6-31G\*  $\text{C}_1$  Geometry

(2/2) CASSCF/6-31G*	-774.047145
$E_{\text{nuc}}$	437.921987
ZPE (kcal/mol)	95.98
$C_v^{298}$ (cal/mol-K)	33.03
$S^{298}$ (cal/mol-K)	90.60
CASPT2/6-31G*	-774.875503

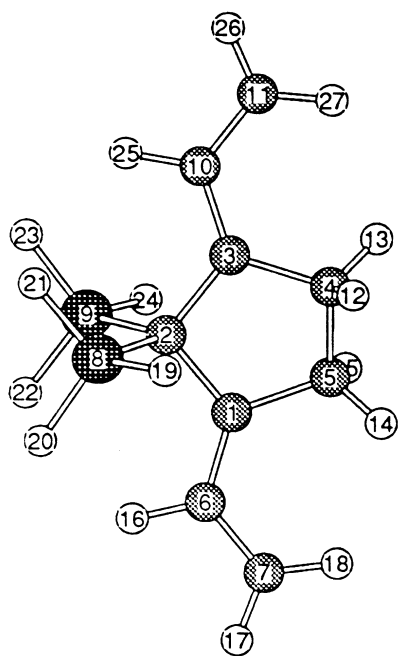
Bond Lengths ( $\text{\AA}$ ) and Angles ( $^\circ$ )

(1-2)	1.533	(1-5)	1.514	(1-8)	1.079
(2-3)	1.530	(2-6)	1.898	(2-7)	1.905
(3-4)	1.517	(3-9)	1.077	(4-5)	1.544
(4-10)	1.086	(4-11)	1.087	(5-12)	1.083
(5-13)	1.086	(6-14)	1.479	(6-15)	1.477
(6-16)	1.477	(7-17)	1.477	(7-18)	1.479
(7-19)	1.478	(2-1-5)	109.1	(2-1-8)	119.5
(5-1-8)	118.1	(1-2-3)	99.0	(1-2-6)	112.3
(1-2-7)	111.8	(3-2-6)	111.9	(3-2-7)	110.3
(6-2-7)	111.1	(2-3-4)	112.0	(2-3-9)	121.7
(4-3-9)	119.5	(3-4-5)	104.7	(3-4-10)	110.2
(3-4-11)	112.2	(5-4-10)	109.8	(5-4-11)	113.3
(10-4-11)	106.6	(1-5-4)	103.5	(1-5-12)	112.3
(1-5-13)	110.7	(4-5-12)	112.3	(4-5-13)	111.0
(12-5-13)	107.1	(2-6-14)	109.6	(2-6-15)	111.0
(2-6-16)	110.4	(14-6-15)	108.7	(14-6-16)	108.6
(15-6-16)	108.5	(2-7-17)	110.6	(2-7-18)	110.7
(2-7-19)	110.0	(17-7-18)	108.5	(17-7-19)	108.3
(18-7-19)	108.6	(5-1-2-3)	-33.4	(5-1-2-6)	-151.7
(5-1-2-7)	82.7	(8-1-2-3)	106.9	(8-1-2-6)	-11.4
(8-1-2-7)	-136.9	(2-1-5-4)	33.5	(2-1-5-12)	154.9
(2-1-5-13)	-85.5	(8-1-5-4)	-107.5	(8-1-5-12)	13.9
(8-1-5-13)	133.5	(1-2-3-4)	21.3	(1-2-3-9)	-129.6
(6-2-3-4)	139.8	(6-2-3-9)	-11.1	(7-2-3-4)	-96.1
(7-2-3-9)	113.1	(1-2-6-14)	49.3	(1-2-6-15)	-70.7
(1-2-6-16)	168.9	(3-2-6-14)	-61.0	(3-2-6-15)	179.0
(3-2-6-16)	58.6	(7-2-6-14)	175.3	(7-2-6-15)	55.3
(7-2-6-16)	-65.2	(1-2-7-17)	-57.7	(1-2-7-18)	62.6
(1-2-7-19)	-177.3	(3-2-7-17)	51.5	(3-2-7-18)	171.7
(3-2-7-19)	-68.2	(6-2-7-17)	176.1	(6-2-7-18)	-63.6
(6-2-7-19)	56.5	(2-3-4-5)	-2.3	(2-3-4-10)	-120.4
(2-3-4-11)	121.0	(9-3-4-5)	149.2	(9-3-4-10)	31.2
(9-3-4-11)	-87.5	(3-4-5-11)	-18.3	(3-4-5-12)	-139.6
(3-4-5-13)	100.5	(10-4-5-1)	100.1	(10-4-5-12)	-21.3
(10-4-5-13)	-141.2	(11-4-5-1)	-140.8	(11-4-5-12)	97.8
(11-4-5-13)	-22.0				

Contd.

Frequencies ( $\text{cm}^{-1}$ )

-217.8	122.4	142.4	181.0	190.4	204.7	216.3	241.2	402.1
528.1	595.1	634.1	678.3	696.7	732.1	748.0	771.5	883.0
967.2	979.8	1011.0	1016.6	1035.0	1040.2	1045.8	1047.2	1054.4
1065.4	1118.2	1165.5	1177.1	1262.1	1350.3	1402.6	1437.6	1464.6
1481.1	1630.5	1652.4	2359.1	2360.1	2364.0	2372.1	2372.5	2379.2
3201.3	3215.6	3230.4	3269.2	3314.0	3332.2			



2,2-Disilyl-1,3-divinylcyclopentane-1,3-diyl (**4**)  
 $^1\text{A}$  (6/6) CASSCF/6-31G\*  $\text{C}_2$  Geometry

(6/6) CASSCF/6-31G*	-927.910468
$E_{\text{nuc}}$	790.333618
ZPE (kcal/mol)	139.66
$\text{C}^{298}_{\text{v}}$ (cal/mol-K)	51.84
$\text{S}^{298}$ (cal/mol-K)	112.09
CASPT2/6-31G*	-929.233530

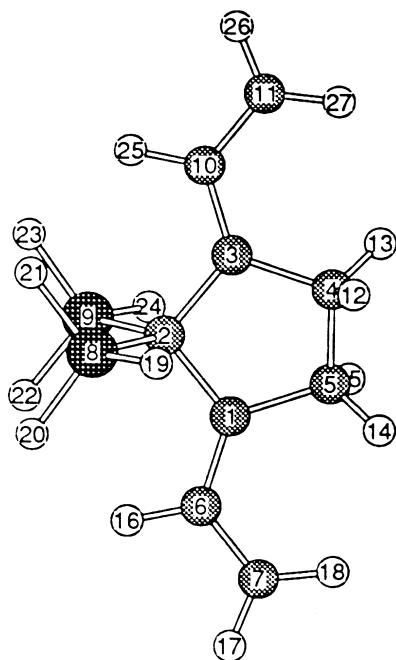
Bond Lengths ( $\text{\AA}$ ) and Angles ( $^\circ$ )

(1-2)	1.521	(1-5)	1.514	(1-6)	1.400
(2-8)	1.908	(4-5)	1.535	(4-12)	1.089
(4-13)	1.084	(6-7)	1.385	(6-16)	1.077
(7-17)	1.073	(7-18)	1.074	(8-19)	1.475
(8-20)	1.476	(8-21)	1.476	(2-1-5)	109.6
(2-1-6)	125.5	(5-1-6)	124.7	(1-2-3)	104.7
(1-2-8)	110.7	(1-2-9)	108.6	(8-2-9)	113.4
(3-4-5)	105.2	(3-4-12)	109.6	(3-4-13)	112.5
(5-4-12)	110.4	(5-4-13)	112.2	(12-4-13)	107.0
(1-6-7)	125.8	(1-6-16)	117.5	(7-6-16)	116.8
(6-7-17)	120.6	(6-7-18)	122.4	(17-7-18)	117.0
(2-8-19)	109.3	(2-8-20)	111.2	(2-8-21)	110.4
(19-8-20)	109.0	(19-8-21)	109.1	(20-8-21)	107.9
(5-1-2-3)	-7.9	(5-1-2-8)	-124.7	(5-1-2-9)	110.3
(6-1-2-3)	176.6	(6-1-2-8)	59.8	(6-1-2-9)	-65.2
(2-1-5-4)	20.3	(2-1-5-14)	142.8	(2-1-5-15)	-98.3
(6-1-5-4)	-164.1	(6-1-5-14)	-41.7	(6-1-5-15)	77.2
(2-1-6-7)	176.5	(2-1-6-16)	-3.2	(5-1-6-7)	1.7
(5-1-6-16)	-178.1	(1-2-8-19)	59.6	(1-2-8-20)	-60.7
(1-2-8-21)	179.6	(3-2-8-19)	-54.7	(3-2-8-20)	-175.1
(3-2-8-21)	65.2	(9-2-8-19)	-178.1	(9-2-8-20)	61.5
(9-2-8-21)	-58.2	(3-4-5-1)	-24.4	(3-4-5-14)	-147.1
(3-4-5-15)	93.7	(12-4-5-14)	-29.0	(12-4-5-15)	-148.2
(13-4-5-14)	90.3	(1-6-7-17)	179.7	(1-6-7-18)	-1
(16-6-7-17)	-5	(16-6-7-18)	179.7		

Contd.

Frequencies ( $\text{cm}^{-1}$ )

67.3	100.3	103.2	116.0	138.2	170.5	171.2	194.6	206.9
243.0	264.7	297.7	361.6	385.3	386.7	414.1	565.9	583.1
585.1	633.5	641.9	643.8	706.3	707.9	708.2	715.5	727.3
845.0	926.7	960.0	975.3	993.1	999.2	1020.4	1035.0	1041.2
1047.6	1050.4	1051.6	1064.9	1091.6	1096.8	1124.6	1223.1	1237.1
1255.2	1258.6	1309.8	1368.4	1380.9	1433.6	1484.3	1500.5	1560.6
1562.3	1623.3	1641.5	1652.5	1655.9	2366.3	2373.2	2376.0	2377.4
2379.3	2385.1	3182.0	3185.9	3256.0	3261.9	3336.3	3336.7	3348.5
3348.7	3435.3	3435.5						

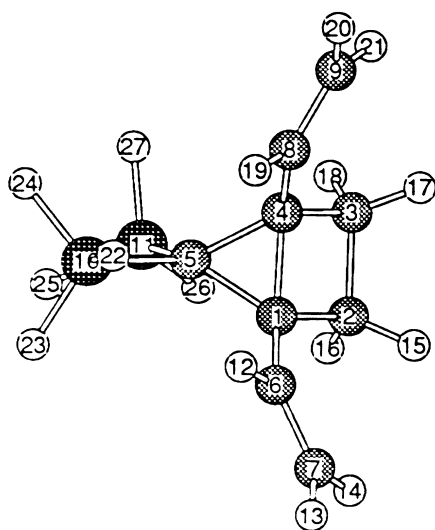


2,2-Disilyl-1,3-divinylcyclopentane-1,3-diyl (**4**)  
 $^3\text{B}$  (6/6) CASSCF/6-31G\*  $\text{C}_2$  Geometry

(6/6) CASSCF/6-31G*	-927.909187
$E_{\text{nuc}}$	789.220679
CASPT2/6-31G*	-929.230239

Bond Lengths ( $\text{\AA}$ ) and Angles ( $^\circ$ )

(1-2)	1.529	(1-5)	1.512	(1-6)	1.397
(2-8)	1.909	(4-5)	1.534	(4-12)	1.088
(4-13)	1.084	(6-7)	1.388	(6-16)	1.077
(7-17)	1.073	(7-18)	1.073	(8-19)	1.476
(8-20)	1.477	(8-21)	1.477	(9-23)	1.477
(9-24)	1.476	(2-1-5)	110.2	(2-1-6)	125.1
(5-1-6)	124.6	(1-2-3)	103.6	(1-2-8)	110.9
(1-2-9)	109.0	(8-2-9)	112.9	(3-4-5)	105.2
(3-4-12)	109.9	(3-4-13)	112.3	(5-4-12)	110.3
(5-4-13)	112.2	(12-4-13)	107.0	(1-6-7)	125.8
(1-6-16)	117.5	(7-6-16)	116.7	(6-7-17)	120.6
(6-7-18)	122.4	(17-7-18)	117.0	(2-8-19)	109.4
(2-8-20)	111.3	(2-8-21)	110.3	(19-8-20)	108.9
(19-8-21)	109.0	(20-8-21)	107.9	(2-9-23)	111.3
(2-9-24)	109.4	(22-9-23)	107.9	(22-9-24)	109.0
(23-9-24)	108.9	(5-1-2-3)	-7.8	(5-1-2-8)	-124.7
(5-1-2-9)	110.4	(6-1-2-3)	176.1	(6-1-2-8)	59.3
(6-1-2-9)	-65.7	(2-1-5-4)	20.0	(2-1-5-14)	142.3
(2-1-5-15)	-98.7	(6-1-5-4)	-163.9	(6-1-5-14)	-41.6
(6-1-5-15)	77.3	(2-1-6-7)	176.7	(2-1-6-16)	-3.1
(5-1-6-7)	1.2	(5-1-6-16)	-178.6	(1-2-8-19)	58.9
(1-2-8-20)	-61.5	(1-2-8-21)	178.8	(3-2-8-19)	-54.6
(3-2-8-20)	-174.9	(3-2-8-21)	65.3	(9-2-8-19)	-178.4
(9-2-8-20)	61.3	(9-2-8-21)	-58.5	(1-2-9-23)	-174.9
(1-2-9-24)	-54.6	(3-2-9-23)	-61.5	(3-2-9-24)	58.9
(8-2-9-23)	61.3	(8-2-9-24)	-178.4	(3-4-5-1)	-23.9
(3-4-5-14)	-146.3	(3-4-5-15)	94.6	(12-4-5-14)	-27.8
(12-4-5-15)	-146.9	(13-4-5-14)	91.4	(1-6-7-17)	179.5
(1-6-7-18)	-4	(16-6-7-17)	-7	(16-6-7-18)	179.5



5,5-Disilyl-1,3-divinylbicyclo[2.1.0]pentane (**8**)  
<sup>1</sup>A (6/6) CASSCF/6-31G\* C<sub>1</sub> Geometry

(6/6) CASSCF /6-31G*	-927.910580
E <sub>nuc</sub>	801.777608
ZPE(kcal/mol)	141.93
C <sub>v</sub> <sup>298</sup> (cal/mol-K)	50.01
S <sup>298</sup> (cal/mol-K)	112.06

Bond Lengths (Å) and Angles (°)

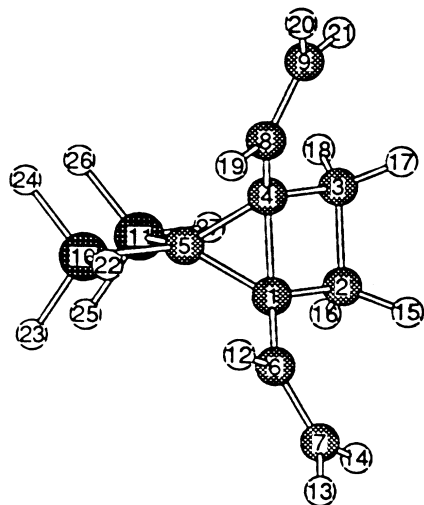
(1-2)	1.531	(1-4)	1.549	(1-5)	1.532
(1-6)	1.483	(2-3)	1.550	(2-15)	1.083
(2-16)	1.082	(3-4)	1.535	(3-17)	1.083
(3-18)	1.085	(4-5)	1.528	(4-8)	1.483
(5-10)	1.895	(5-11)	1.900	(6-7)	1.341
(6-12)	1.077	(7-13)	1.075	(7-14)	1.075
(8-9)	1.341	(8-19)	1.076	(9-20)	1.075
(9-21)	1.075	(10-22)	1.474	(10-23)	1.476
(10-24)	1.477	(11-25)	1.478	(11-26)	1.474
(11-27)	1.477	(2-1-4)	90.1	(2-1-5)	111.0
(2-1-6)	123.3	(4-1-5)	59.5	(4-1-6)	130.6
(5-1-6)	123.0	(1-2-3)	90.0	(1-2-15)	111.3
(1-2-16)	117.2	(3-2-15)	111.1	(3-2-16)	117.8
(15-2-16)	108.5	(2-3-4)	90.0	(2-3-17)	111.8
(2-3-18)	117.4	(4-3-17)	112.4	(4-3-18)	116.4
(17-3-18)	108.0	(1-4-3)	89.9	(1-4-5)	59.7
(1-4-8)	131.1	(3-4-5)	109.6	(3-4-8)	123.3
(5-4-8)	124.0	(1-5-4)	60.8	(1-5-10)	117.7
(1-5-11)	124.7	(4-5-10)	119.3	(4-5-11)	121.1
(10-5-11)	107.4	(1-6-7)	124.4	(1-6-12)	117.0
(7-6-12)	118.6	(6-7-13)	121.1	(6-7-14)	122.2
(13-7-14)	116.6	(4-8-9)	124.4	(4-8-19)	117.0
(9-8-19)	118.6	(8-9-20)	121.1	(8-9-21)	122.3
(20-9-21)	116.6	(5-10-22)	114.3	(5-10-23)	109.5
(5-10-24)	108.8	(22-10-23)	107.9	(22-10-24)	108.0
(23-10-24)	108.3	(5-11-25)	108.8	(5-11-26)	114.5
(5-11-27)	109.6	(25-11-26)	107.5	(25-11-27)	107.9
(26-11-27)	108.3	(4-1-2-3)	-1.5	(4-1-2-15)	111.2
(4-1-2-16)	-123.2	(5-1-2-3)	55.6	(5-1-2-15)	168.3
(5-1-2-16)	-66.1	(6-1-2-3)	-142.8	(6-1-2-15)	-30.1
(6-1-2-16)	95.5	(2-1-4-3)	1.5	(2-1-4-5)	114.5
(2-1-4-8)	-135.0	(5-1-4-3)	-113.0	(5-1-4-8)	110.5
(6-1-4-3)	138.0	(6-1-4-5)	-109.1	(6-1-4-8)	1.4
(2-1-5-4)	-77.1	(2-1-5-10)	173.0	(2-1-5-11)	32.3
(4-1-5-10)	-109.9	(4-1-5-11)	109.4	(6-1-5-4)	121.3
(6-1-5-10)	11.4	(6-1-5-11)	-129.4	(2-1-6-7)	-21.5
(2-1-6-12)	158.3	(4-1-6-7)	-146.1	(4-1-6-12)	33.7
(5-1-6-7)	137.9	(5-1-6-12)	-42.3	(1-2-3-4)	1.5
(1-2-3-17)	115.8	(1-2-3-18)	-118.5	(15-2-3-4)	-111.4
(15-2-3-17)	2.9	(15-2-3-18)	128.5	(16-2-3-4)	122.6
(16-2-3-17)	-123.1	(16-2-3-18)	2.6	(2-3-4-1)	-1.5
(2-3-4-5)	-59.1	(2-3-4-8)	140.2	(17-3-4-1)	-115.2
(17-3-4-5)	-172.8	(17-3-4-8)	26.5	(18-3-4-1)	119.4
(18-3-4-5)	61.8	(18-3-4-8)	-98.9	(1-4-5-10)	107.2
(1-4-5-11)	-115.2	(3-4-5-1)	77.8	(3-4-5-10)	-174.9
(3-4-5-11)	-37.3	(8-4-5-1)	-121.6	(8-4-5-10)	-14.4
(8-4-5-11)	123.3	(1-4-8-9)	146.6	(1-4-8-19)	-33.3
(3-4-8-9)	22.0	(3-4-8-19)	-158.0	(5-4-8-9)	-136.0
(5-4-8-19)	44.0	(1-5-10-22)	43.6	(1-5-10-23)	-77.5
(1-5-10-24)	164.3	(4-5-10-22)	-26.7	(4-5-10-23)	-147.8
(4-5-10-24)	94.0	(11-5-10-22)	-169.5	(11-5-10-23)	69.4
(11-5-10-24)	-48.8	(1-5-11-25)	115.4	(1-5-11-26)	-4.9
(1-5-11-27)	-126.9	(4-5-11-25)	-170.6	(4-5-11-26)	69.1
(4-5-11-27)	-52.8	(10-5-11-25)	-28.7	(10-5-11-26)	-148.9
(10-5-11-27)	89.1	(1-6-7-13)	180.0	(1-6-7-14)	-3
(12-6-7-13)	0.2	(12-6-7-14)	179.9	(4-8-9-20)	179.9
(4-8-9-21)	0.4	(19-8-9-20)	-1	(19-8-9-21)	-179.7



Contd.

Frequencies ( $\text{cm}^{-1}$ )

64.8	78.9	91.6	108.8	142.2	174.0	201.4	223.2	246.2
258.8	278.8	286.3	356.8	390.1	438.3	486.0	529.2	619.9
646.2	662.7	676.3	708.6	726.2	782.5	790.0	860.6	865.5
866.7	884.7	964.1	981.9	1024.7	1035.9	1039.5	1041.5	1045.6
1051.5	1054.7	1060.1	1069.3	1080.0	1101.4	1120.0	1212.3	1231.6
1338.2	1342.8	1348.4	1369.5	1420.4	1432.2	1452.6	1458.5	1583.5
1598.0	1639.8	1668.2	1780.9	1786.0	2361.1	2364.9	2372.1	2378.7
2384.8	2392.4	3228.7	3248.1	3276.7	3297.0	3331.2	3332.6	3346.0
3357.6	3414.2	3414.5						

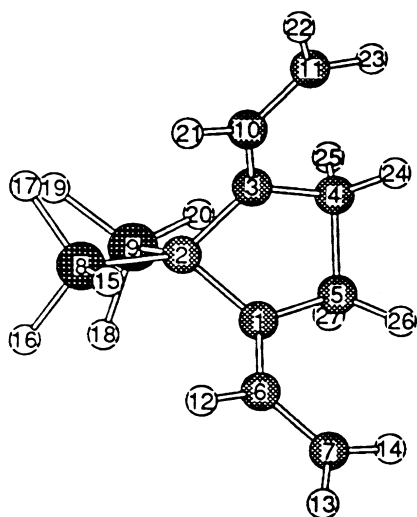


5,5-Disilyl-1,3-divinylbicyclo[2.1.0]pentane (**8**)  
 $^1\text{A}$  (6/6) CASSCF/6-31G\*  $C_s$  Geometry

(6/6) CASSCF/6-31G*	-927.909903
$E_{\text{nuc}}$	801.389379
CASPT2/6-31G*	-929.234090

Bond Lengths (Å) and Angles ( $^\circ$ )

(1-2)	1.533	(1-4)	1.551	(1-5)	1.531
(1-6)	1.483	(2-3)	1.549	(2-15)	1.083
(2-16)	1.083	(5-10)	1.898	(5-11)	1.900
(6-7)	1.341	(6-12)	1.076	(7-13)	1.075
(7-14)	1.075	(10-22)	1.474	(10-23)	1.476
(11-25)	1.478	(11-27)	1.472	(2-1-4)	90.0
(2-1-5)	110.6	(2-1-6)	123.0	(4-1-5)	59.6
(4-1-6)	130.6	(5-1-6)	123.6	(1-2-3)	90.0
(1-2-15)	111.7	(1-2-16)	116.9	(3-2-15)	111.5
(3-2-16)	117.6	(15-2-16)	108.3	(1-5-4)	60.9
(1-5-10)	117.9	(1-5-11)	123.3	(10-5-11)	107.5
(1-6-7)	124.3	(1-6-12)	117.1	(7-6-12)	118.6
(6-7-13)	121.1	(6-7-14)	122.3	(13-7-14)	116.6
(5-10-22)	114.2	(5-10-23)	109.2	(22-10-23)	107.9
(23-10-24)	108.2	(5-11-25)	109.1	(5-11-27)	114.8
(25-11-26)	107.9	(25-11-27)	107.8	(4-1-2-3)	0.0
(4-1-2-15)	113.2	(4-1-2-16)	-121.3	(5-1-2-3)	57.2
(5-1-2-15)	170.4	(5-1-2-16)	-64.1	(6-1-2-3)	-141.4
(6-1-2-15)	-28.2	(6-1-2-16)	97.3	(2-1-4-3)	0.0
(2-1-4-5)	114.0	(2-1-4-8)	-136.1	(5-1-4-8)	109.8
(6-1-4-8)	0.0	(2-1-5-4)	-77.2	(2-1-5-10)	174.6
(2-1-5-11)	35.5	(4-1-5-10)	-108.2	(4-1-5-11)	112.7
(6-1-5-4)	121.5	(6-1-5-10)	13.3	(6-1-5-11)	-125.8
(2-1-6-7)	-22.5	(2-1-6-12)	157.5	(4-1-6-7)	-146.7
(4-1-6-12)	33.3	(5-1-6-7)	136.5	(5-1-6-12)	-43.5
(1-2-3-4)	0.0	(1-2-3-17)	113.4	(1-2-3-18)	-120.7
(15-2-3-17)	0.0	(15-2-3-18)	125.9	(16-2-3-18)	0.0
(1-5-10-22)	35.0	(1-5-10-23)	-85.9	(1-5-10-24)	155.9
(11-5-10-22)	180.0	(11-5-10-23)	59.1	(1-5-11-25)	83.8
(1-5-11-26)	-158.5	(1-5-11-27)	-37.3	(10-5-11-25)	-58.8
(10-5-11-27)	180.0	(1-6-7-13)	180.0	(1-6-7-14)	0.0
(12-6-7-13)	0.0	(12-6-7-14)	180.0		



Transition State for **4** to **8**  
<sup>1</sup>A (6/6) CASSCF/6-31G\* C<sub>1</sub> Geometry

(6/6) CASSCF/6-31G*	-927.887590
E <sub>nuc</sub>	793.950289
ZPE (kcal/mol)	139.82
C <sub>v</sub> <sup>298</sup> (cal / mol-K)	50.04
S <sup>298</sup> (cal/mol-K)	112.49

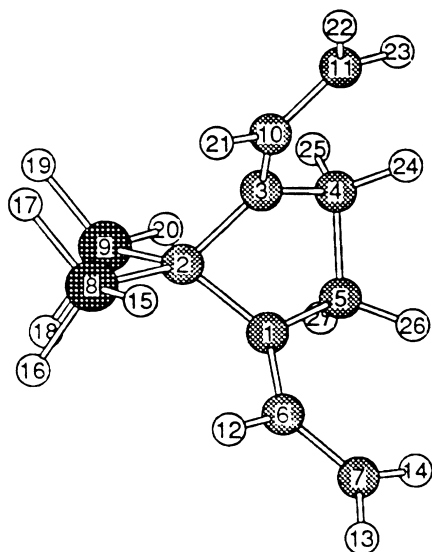
Bond Lengths (Å) and Angles (°)

(1-2)	1.519	(1-5)	1.520	(1-6)	1.431
(2-3)	1.520	(2-8)	1.908	(2-9)	1.919
(3-4)	1.521	(3-10)	1.432	(4-5)	1.540
(4-24)	1.082	(4-25)	1.086	(5-26)	1.081
(5-27)	1.088	(6-7)	1.362	(6-12)	1.076
(7-13)	1.074	(7-14)	1.074	(8-15)	1.474
(8-16)	1.477	(8-17)	1.475	(9-18)	1.478
(9-19)	1.478	(9-20)	1.474	(10-11)	1.362
(10-21)	1.077	(11-22)	1.074	(11-23)	1.074
(2-1-5)	109.0	(2-1-6)	126.4	(5-1-6)	124.3
(1-2-3)	85.3	(1-2-8)	116.6	(1-2-9)	115.2
(3-2-8)	115.8	(3-2-9)	117.0	(8-2-9)	106.4
(2-3-4)	109.8	(2-3-10)	126.0	(4-3-10)	123.9
(3-4-5)	100.0	(3-4-24)	111.4	(3-4-25)	113.2
(5-4-24)	110.3	(5-4-25)	114.6	(24-4-25)	107.3
(1-5-4)	99.7	(1-5-26)	112.2	(1-5-27)	112.7
(4-5-26)	110.9	(4-5-27)	114.2	(26-5-27)	107.1
(1-6-7)	126.0	(1-6-12)	117.4	(7-6-12)	116.6
(6-7-13)	120.4	(6-7-14)	122.9	(13-7-14)	116.6
(2-8-15)	113.1	(2-8-16)	108.9	(2-8-17)	109.4
(15-8-16)	108.6	(15-8-17)	108.3	(16-8-17)	108.5
(2-9-18)	109.0	(2-9-19)	109.9	(2-9-20)	113.0
(18-9-19)	108.6	(18-9-20)	108.4	(19-9-20)	107.8
(3-10-11)	126.0	(3-10-21)	117.4	(11-10-21)	116.5
(10-11-22)	120.5	(10-11-23)	122.9	(22-11-23)	116.7
(5-1-2-3)	-55.9	(5-1-2-8)	-172.5	(5-1-2-9)	61.8
(6-1-2-3)	119.1	(6-1-2-8)	2.5	(6-1-2-9)	-123.2
(2-1-5-4)	39.8	(2-1-5-26)	157.3	(2-1-5-27)	-81.6
(6-1-5-4)	-135.3	(6-1-5-26)	-17.8	(6-1-5-27)	103.3
(2-1-6-7)	179.1	(2-1-6-12)	1.1	(5-1-6-7)	-6.6
(5-1-6-12)	175.4	(1-2-3-4)	54.3	(1-2-3-10)	-119.6
(8-2-3-4)	171.7	(8-2-3-10)	-2.2	(9-2-3-4)	-61.6
(9-2-3-10)	124.5	(1-2-8-15)	44.5	(1-2-8-16)	-76.4
(1-2-8-17)	165.2	(3-2-8-15)	-53.6	(3-2-8-16)	-174.5
(3-2-8-17)	67.1	(9-2-8-15)	174.4	(9-2-8-16)	53.6
(9-2-8-17)	-64.8	(1-2-9-18)	55.5	(1-2-9-19)	174.5
(1-2-9-20)	-65.1	(3-2-9-18)	153.5	(3-2-9-19)	-87.6
(3-2-9-20)	32.8	(8-2-9-18)	-75.3	(8-2-9-19)	43.7
(8-2-9-20)	164.1	(2-3-4-5)	-35.6	(2-3-4-24)	-152.2
(2-3-4-25)	86.7	(10-3-4-5)	138.4	(10-3-4-24)	21.8
(10-3-4-25)	-99.3	(2-3-10-11)	-179.9	(2-3-10-21)	-2.1
(4-3-10-11)	7.0	(4-3-10-21)	-175.2	(3-4-5-1)	-2.3
(3-4-5-26)	-120.7	(3-4-5-27)	118.1	(24-4-5-1)	115.2
(24-4-5-26)	-3.3	(24-4-5-27)	-124.5	(25-4-5-1)	-123.6
(25-4-5-26)	117.9	(25-4-5-27)	-3.3	(1-6-7-13)	-177.5
(1-6-7-14)	1.1	(12-6-7-13)	0.6	(12-6-7-14)	179.1
(3-10-11-22)	177.4	(3-10-11-23)	-1.1	(21-10-11-22)	-4
(21-10-11-23)	-179.0				

Contd.

Frequencies ( $\text{cm}^{-1}$ )

-355.6	61.6	65.9	88.9	146.9	154.6	164.4	202.2	209.8
220.3	250.1	271.8	305.9	357.9	372.1	394.4	539.7	598.0
612.3	617.2	619.3	647.2	683.3	716.6	741.5	792.1	794.1
813.6	893.2	908.2	977.8	1008.9	1009.6	1017.7	1034.1	1045.5
1048.4	1050.9	1055.9	1063.4	1080.3	1102.5	1130.3	1228.1	1271.3
1331.5	1344.1	1359.3	1380.9	1388.7	1391.5	1454.3	1486.8	1562.4
1575.7	1633.9	1659.9	1688.0	1696.1	2362.2	2365.8	2376.2	2382.2
2385.1	2391.3	3198.5	3219.4	3273.1	3293.8	3337.5	3340.9	3350.1
3353.1	3429.1	3429.5						

Transition State for **4 to 8** $^1\text{A}$  (6/6) CASSCF/6-31G\*  $C_s$  Geometry

(6/6) CASSCF/6-31G*	-927.887548
$E_{\text{nuc}}$	793.925256
CASPT2/6-31G*	-929.213157

Bond Lengths ( $\text{\AA}$ ) and Angles ( $^\circ$ )

(1-2)	1.519	(1-5)	1.520	(1-6)	1.432
(2-8)	1.908	(2-9)	1.918	(4-5)	1.539
(4-24)	1.081	(4-25)	1.087	(6-7)	1.362
(6-12)	1.076	(7-13)	1.074	(7-14)	1.074
(8-15)	1.474	(8-16)	1.476	(9-18)	1.478
(9-20)	1.474	(2-1-5)	109.6	(2-1-6)	126.2
(5-1-6)	124.1	(1-2-3)	85.2	(1-2-8)	116.0
(1-2-9)	116.2	(8-2-9)	106.6	(3-4-5)	99.8
(3-4-24)	111.8	(3-4-25)	113.0	(5-4-24)	110.6
(5-4-25)	114.4	(24-4-25)	107.3	(1-6-7)	126.0
(1-6-12)	117.4	(7-6-12)	116.6	(6-7-13)	120.5
(6-7-14)	122.9	(13-7-14)	116.6	(2-8-15)	112.9
(2-8-16)	109.2	(15-8-16)	108.5	(16-8-17)	108.4
(2-9-18)	109.5	(2-9-20)	113.0	(18-9-19)	108.7
(18-9-20)	108.1	(5-1-2-3)	-55.1	(5-1-2-8)	-171.7
(5-1-2-9)	61.8	(6-1-2-3)	119.6	(6-1-2-8)	3.0
(6-1-2-9)	-123.5	(2-1-5-4)	37.8	(2-1-5-26)	154.8
(2-1-5-27)	-84.1	(6-1-5-4)	-137.0	(6-1-5-26)	-20.1
(6-1-5-27)	101.0	(2-1-6-7)	179.3	(2-1-6-12)	1.4
(5-1-6-7)	-6.7	(5-1-6-12)	175.4	(1-2-8-15)	48.8
(1-2-8-16)	-71.9	(1-2-8-17)	169.6	(9-2-8-15)	180.0
(9-2-8-16)	59.2	(1-2-9-18)	71.5	(1-2-9-19)	-169.4
(1-2-9-20)	-49.0	(8-2-9-18)	-59.5	(8-2-9-20)	180.0
(3-4-5-1)	0.0	(3-4-5-26)	-117.8	(3-4-5-27)	120.9
(24-4-5-26)	0.0	(24-4-5-27)	-121.2	(25-4-5-27)	0.0
(1-6-7-13)	-177.4	(1-6-7-14)	1.1	(12-6-7-13)	0.5
(12-6-7-14)	179.0				