

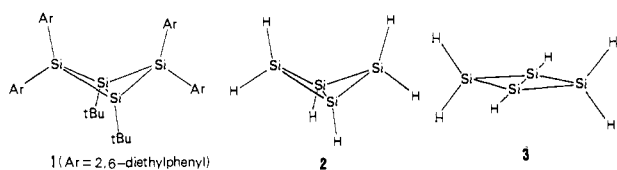
The Structure and Barrier to Inversion of Tetrasilabicyclo[1.1.0]butane. Comparison to Bicyclo[1.1.0]butane

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Abstract: The equilibrium geometry of tetrasilabicyclo[1.1.0]butane, as determined by full gradient optimization at the RHF level of theory by using 6-31G* basis set, has C_{2v} symmetry. The two Si-Si bond lengths are 2.304 and 2.370 Å, the latter being the bond connecting the bridgehead atoms. The dihedral angle between the two rings is 122.9°. The corresponding bonds of the transition structure for ring inversion, which has D_{2h} symmetry, are 2.295 and 2.805 Å, respectively. The barrier to ring inversion is calculated to be 75 kJ mol⁻¹ after correction for correlation energy differences up to MP3 and inclusion of zero-point vibrational energies. The bond connecting the bridgehead atoms is not broken but changes from a bent σ bond at the equilibrium geometry to a π bond in the transition structure. By contrast, bicyclo[1.1.0]butane suffers bond rupture during inversion, the transition structure being most probably a triplet diradical. The inversion barrier, estimated to be about 300 kJ mol⁻¹, is higher than that required for the sigmatropic rearrangement to butadiene. The origin of the differences between the C and Si analogues is discussed.

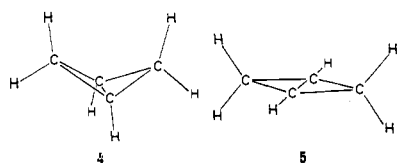
Interest in the properties and preparation of strain decyclic polysilanes has increased substantially in recent years. Examples of the preparation and characterization of cyclotrisilanes, both symmetrically¹ and unsymmetrically² substituted, have appeared. More recently, the preparation and characterization of a spiro-[2.2]pentasilane has been reported,³ and the first example of the tetrasilabicyclo[1.1.0]butane system, 1,3-di-*tert*-butyl-2,2,4,4-tetrakis(2,6-diethylphenyl)tetrasilabicyclo[1.1.0]butane (**1**) has



been synthesized,⁴ and its structure determined by X-ray crystallography.⁵ The latter compound is highly reactive, considering the bulky substituents that are present, undergoing facile air oxidation and rapid addition by both electrophiles and nucleophiles across the central Si-Si bond.⁴ In addition, this bicyclic tetrasilane is a fluxional molecule—dynamic NMR studies⁴ reveal that the cage inverts rapidly above room temperature. The barrier for this process has been estimated⁴ to be greater than or equal to 62 kJ mol⁻¹.

While this work was in progress, a theoretical study by Dabisch and Schoeller (DS) of the parent tetrasilane system **2** appeared.⁶ An unusually long central bond, 2.850 Å, and a considerably flattened ring system, $\theta = 142.6^\circ$, compared to the corresponding values in **1**, were obtained by geometry optimization at the 4-31G basis set level. These results, which are considerably at odds with those reported herein as well as with the experimental structure of **1**, are discussed further below. Other geometries, particularly the planar structure **3**, which would be involved in the ring flapping, were not explored by DS.⁶

The chemical properties of **1** may be compared to those observed in bicyclo[1.1.0]butane, **4**, and derivatives of **4**, where the central



bridging bond, while subject to electrophilic attack,⁷ is less reactive and has higher thermodynamic stability. The parent hydrocarbon **4** undergoes a [$\sigma_2s + \sigma_2a$] sigmatropic rearrangement to 1,3-butadiene⁸ with an activation energy of 193 kJ mol⁻¹. The rearrangement is Lewis acid catalyzed.⁹ Both the catalyzed⁹ and uncatalyzed¹⁰ processes are believed to be initiated by rupture of the 1,2 bond, rather than the 1,3 bond.

The inversion barrier of **4** has not been determined experimentally but has been estimated theoretically^{11,12} to be ca. 120 kJ mol⁻¹. The theoretical estimate¹¹ is based on structures optimized with a smaller (3-21G) basis set but with explicit inclusion of some electron correlation via the generalized valence bond (GVB)¹³ method. The effect of electron correlation is minor at the equilibrium geometry but is reported to lead to significant lowering of the energy and alteration of the geometry of the planar species **5** and to result in a "biradicaloid" description for **5**. The calculated inversion barrier is close to the observed inversion barrier

(1) (a) Masamune, S.; Hanzawa, Y.; Bally, T.; Blount, J. F. *J. Am. Chem. Soc.* **1982**, *104*, 1150-1153. (b) Masamune, S.; Tobita, H.; Murakami, S. *Ibid.* **1983**, *105*, 6524-6525. (c) Watanabe, H.; Okawa, T.; Kato, M.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1983**, 781-782. (d) Watanabe, H.; Kougo, Y.; Nagai, Y. *Ibid.* **1984**, 66-67. (e) Masamune, S.; Murakami, S.; Snow, J. T.; Tobita, H.; Williams, D. J. *Organometallics* **1984**, *3*, 333-334. (f) Schafer, A.; Weidenbruch, M.; Peters, K.; v. Schnering, H. G. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 302-303.

(2) (a) Murakami, S.; Collins, S.; Masamune, S. *Tetrahedron Lett.* **1984**, *25*, 2131-2134. (b) Dewar, J. C.; Murakami, S.; Snow, J. T.; Collins, S.; Masamune, S. *J. Chem. Soc., Chem. Commun.* **1985**, 892-894.

(3) Boudjouk, P.; Sooriyakumaran, R. *J. Chem. Soc., Chem. Commun.* **1984**, 777-778.

(4) Masamune, S.; Kabe, Y.; Collins, S.; Williams, D. J.; Jones, R. *J. Am. Chem. Soc.* **1985**, *107*, 5552-5553.

(5) Jones, R.; Williams, D. J.; Kabe, Y.; Masamune, S. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 173-175.

(6) Dabisch, T.; Schoeller, W. W. *J. Chem. Soc., Chem. Commun.* **1986**, 896-898.

(7) (a) Wiberg, K. B. *Rec. Chem. Progr. (Kresge-Hooker Sci. Lib)* **1966**, *26*, 143. (b) Wiberg, K. B.; Lampman, G. M. *Tetrahedron Lett.* **1963**, *30*, 2173.

(8) (a) Frey, H. M.; Stevens, I. D. *Trans. Faraday Soc.* **1965**, *61*, 90-94. (b) Srinivasan, R.; Levi, A. A.; Haller, I. J. *Phys. Chem.* **1965**, *69*, 1775-1777.

(9) Paquette, L. A.; Wilson, S. E.; Henzel, R. P. *J. Am. Chem. Soc.* **1972**, *94*, 7771-7788, and references therein.

(10) Dewar, M. J. S.; Kirschner, S. *J. Am. Chem. Soc.* **1975**, *97*, 2931-2932.

(11) Budzelaar, P. H. M.; Kraka, E.; Cremer, D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1986**, *108*, 561-567.

(12) Gassmann, P. G.; Greenlee, M. L.; Dixon, D. A.; Richtsmeier, S.; Gougoutas, J. *J. Am. Chem. Soc.* **1983**, *105*, 5865-5874.

(13) Goddard, W. A., III.; Dunning, T. H., Jr.; Hunt, W. J.; Hay, P. J. *Acc. Chem. Res.* **1973**, *6*, 368-376.

*University of Waterloo.

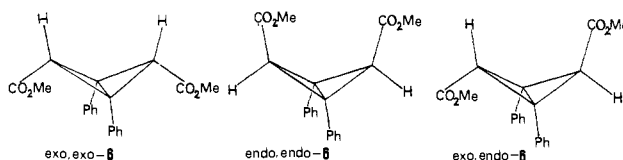
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Table I. Calculated Energies and Inversion Barrier 6-31G* Basis Set

structure ^a	E_{RHF}^b (E_{UHF})	E_{MP2}^b (E_{UMP2})	E_{MP3}^b	ZPVE ^c	
2	(¹ A ₁)	-1159.077392	-1159.405960	-1159.451959	148.1
	(³ B ₁)	(-1158.949602)	(-1159.260320)		
2⁺⁻	(² A ₁)	(-1158.814950)	(-1159.115588)		
	(² B ₁)	(-1159.007632)	(-1159.347300)		
3	(¹ A _g)	-1159.423259	146.7		
	(³ B _{2u})	(-1159.056209)	(-1159.352158)		
	(¹ B _{2u}) ^f	(-1158.925911) ^f	(-1159.221760) ^f		
	(³ B _{2g})	(-1158.929061)	(-1159.254568)		
	(¹ B _{2g}) ^f	(-1158.913523) ^f	(-2259.239030) ^f		
		98 ^h	72 ^h	75 ^h	74 ^{d,h}
4	(¹ A ₁)	-154.871767 ^e	-155.388987	-155.416896	216.1 ^e
5	(¹ A _g)	-154.722809	-155.269689	-155.295234	235.0
	(¹ A _g)	-154.690584			
	(³ B _{2u})	(-154.813690)	(-155.281456)		
	(¹ B _{2u})	(-154.636136) ^f	(-155.103902) ^f		
		389 ⁱ	313, ⁱ (282) ^g	328 ⁱ	345 ^{d,i}

^aState symmetries are shown in parentheses. ^bHartrees. ^ckJ mol⁻¹. ^dIncludes $E_{\text{MP3}} + 0.9 \times \text{ZPVE}$. ^eReference 28. ^fEstimated by the addition of twice the exchange integral to the energy of the corresponding triplet state: **3**, $K_{4b1u,2b3g} = 0.065199$, $K_{3b1g,2b3g} = 0.007769$; **5**, $K_{2b1u,1b3g} = 0.088777$. ^g $E(\text{5}, ^3\text{B}_{2u}) - E(\text{4})$. ^h $E(\text{3}) - E(\text{2})$. ⁱ $E(\text{5}) - E(\text{4})$.

for the 1,3-diphenyl-2,4-dicarbomethoxy derivative¹⁴ **6**, $\Delta H^\ddagger = 109$ kJ mol⁻¹. We have reinvestigated the structure and ring



inversion of **4** as part of the study of **2** and report below that the barrier to inversion in **4** is probably not as low as previously calculated nor as might be inferred from the experimental results for **6**.¹⁴

We present below the results of a comprehensive study of tetrasilabicyclo[1.1.0]butane **2** and **3** and of bicyclo[1.1.0]butane (**4** and **5**) at a comparable level of theory. These allow parallels and contrasts to be drawn between features of Si-Si bonds and C-C bonds in strained systems. Three-dimensional orbital plots of the higher bonding and lower antibonding molecular orbitals of the two systems serve to illustrate the comparisons being drawn.

Computational Method

The electronic structures and geometries of **2** and **3** as well as **4** and **5** were determined by full geometry optimization within RHF¹⁵ theory and by using the internal 6-31G* basis set of the GAUSSIAN 82 system of programs.¹⁶ Use of polarization functions has been shown to be necessary in order to obtain accurate geometries and frequencies for compounds involving second row elements.¹⁷ Bonds which are too long result if polarization functions are omitted.^{6,17,18} In addition, it has been shown that use of a core description with six contracted Gaussians as in the 6-31G* basis set is required as a starting point for post Hartree-Fock calculations.^{19,20}

(14) (a) Woodward, R. B.; Dalrymple, D. L. *J. Am. Chem. Soc.* **1969**, *91*, 4612-4613. (b) D'yakonov, I. A.; Razen, V. V.; Komendantov, M. I. *Tetrahedron Lett.* **1966**, *1127*, 1135-1140.

(15) Roothaan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69-89.

(16) (a) Binkley, J. S.; Frisch, M. J.; DeFrees, D. J.; Raghavachari, K.; Whiteside, R. A.; Schlegel, H. B.; Fluder, E. M.; Pople, J. A. Department of Chemistry, Carnegie-Mellon University, Pittsburgh, PA. (b) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657-2664. (c) Hehre, W. J.; Ditchfield, R.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1970**, *52*, 2769-2773. (d) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 939-947.

(17) Pietro, W. J.; Francl, M. M.; Hehre, W. J.; DeFrees, D. J.; Pople, J. A.; Binkley, J. S. *J. Am. Chem. Soc.* **1982**, *104*, 5039-5048.

(18) Clabo, D. A., Jr.; Schaeffer, H. F., III. *J. Am. Chem. Soc.* **1986**, *108*, 4344-4346.

(19) (a) Dykstra, C. E.; Schaeffer, H. F., III. In *The Chemistry of Ketenes and Allenes*; Patai, S., Ed.; Wiley: New York, 1980; p 1. (b) DeFrees, D. J.; Levi, B. A.; Pollack, S. K.; Hehre, W. J.; Binkley, J. S.; Pople, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4085-4089.

(20) No geometry optimizations were attempted with incorporation of electron correlation.

Table II. Ionization Potentials^a for Si₄H₆ and C₄H₆ (in eV)

Si ₄ H ₆ 2		C ₄ H ₆ 4		
orbital	IP	orbital	IP _{calcd} ^b	IP _{exp} ^c
13a ₁ (HOMO)	8.07	7a ₁	9.69	9.4
3a ₂	8.72	1a ₂	11.69	11.3
7b ₁	10.52	3b ₁	12.37	11.7
8b ₂	11.54	4b ₂	13.93	13.0
7b ₂	13.43	6a ₁	15.87	
12a ₁	13.52	3b ₂	16.06	
11a ₁	14.37	5a ₁	18.90	
10a ₁	17.07	2b ₁	21.37	
6b ₁	17.21	4a ₁	21.37	
6b ₂	19.11	2b ₂	25.29	
9a ₁	22.47	3a ₁	33.22	

^aBy Koopmans' theorem, IP = - ϵ_i . ^bThis work. ^cReference 24.

Table III. Vibrational Frequencies for **2** and **3**^a (in cm⁻¹)

equilibrium structure 2		transition structure 3	
symmetry	frequency	symmetry	frequency
1a ₁	126.7	1b _{1u}	304.5i
2a ₁	340.8	2b _{1u}	67.7
3b ₁	394.2	3a _g	291.4
4a ₂	403.6	4b _{2u}	431.4
5a ₁	432.3	5b _{3b}	452.0
6b ₂	505.6	6a _g	500.8
7b ₁	517.0	7b _{1g}	503.9
8a ₁	534.8	8b _{3u}	551.4
9a ₂	535.7	9b _{1u}	552.2
10b ₂	556.6	10a _u	607.7
11a ₂	593.3	11b _{3g}	646.2
12a ₁	613.9	12b _{1g}	672.7
13b ₁	640.8	13b _{2g}	685.1
14a ₂	709.8	14b _{2u}	711.6
15b ₂	727.4	15b _{1g}	720.7
16b ₁	766.3	16b _{3u}	836.9
17b ₂	1017.9	17b _{3u}	1092.1
18a ₁	1043.4	18a _g	1125.2
19b ₂	2373.4	19b _{1u}	2332.1
20a ₁	2378.3	20b _{2g}	2332.2
21a ₁	2382.4	21b _{2u}	2343.7
22b ₂	2383.6	22a _g	2345.7
23b ₁	2388.0	23b _{3u}	2351.4
24a ₁	2396.3	24a _g	2364.3

^aThe calculated values are expected to be about 10% too high—see ref 30.

Force constant matrices were obtained by numerical differentiation of analytically determined gradients in the case of **2** and **3** and by full analytic differentiation in the case of **4** and **5**. These were used to perform harmonic frequency analyses in order to verify that **2** and **4** are equilibrium geometries and that **3** and **5**, each with 1 imaginary frequency, are true transition structures.

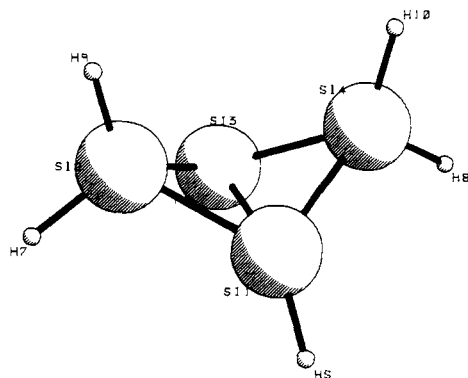


Figure 1. PLUTO plot of the 6-31G* optimized geometry of **2**, point group C_{2v} . Bond lengths (Å): Si₁-Si₃, 2.370; Si₁-Si₂, 2.304; Si₁-H₅, 1.471; Si₂-H₇, 1.474; Si₂-H₉, 1.474. Bond angles (deg): Si₂-Si₁-Si₄, 97.8; H₅-Si₁-Si₄, 131.1; H₅-Si₁-Si₃, 139.9; H₇-Si₂-H₉, 110.6; H₇-Si₂-Si₁, 124.6; Si₂-Si₂-Si₃, 61.9. Dihedral angle (deg): Si₂-Si₁-Si₃-Si₄, 122.9.

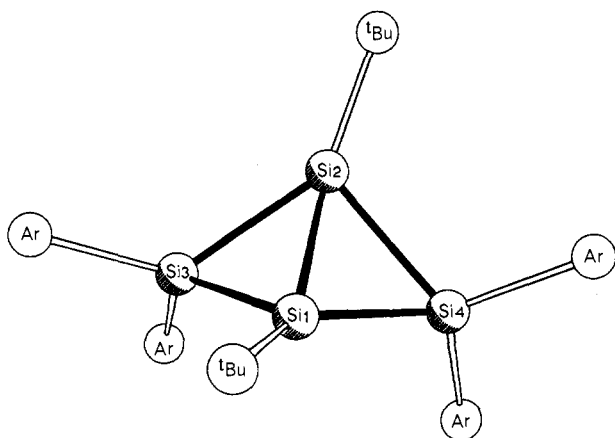


Figure 2. PLUTO plot of the bicyclic cage of compound **1**.^{5,23} Selected bond lengths (Å) with esd's in parentheses: Si₁-Si₃, 2.373 (3); Si₁-Si₂, 2.334 (4); Si₁-Si₄, 2.308 (3); Si₂-Si₃, 2.311 (3); Si₃-Si₄, 2.336 (3). Selected bond angles (deg): C(*tert*-butyl)-Si₁-Si₂, 119.8 (3); C(*tert*-butyl)-Si₁-Si₄, 142.3 (3); Si₄-Si₁-Si₂, 96.9 (1); C(*tert*-butyl)-Si₃-Si₄, 119.5 (3); C(*tert*-butyl)-Si₃-Si₂, 142.3 (3); Si₄-Si₃-Si₂, (96.8 (1); Si₁-Si₄-Si₃, 61.4 (1); Si₁-Si₂-Si₃, 61.4 (1); Ar-Si₂-Ar, 107.8 (3); Ar-Si₄-Ar, 109.8 (3). Dihedral angle (deg): Si₂-Si₁-Si₃-Si₄, 121.

The effects of electron correlation, known to be important for the planar structure **5**,^{11,12} were estimated within the framework of Møller-Plesset perturbation theory truncated to second- (MP2)²¹ or third-order (MP3)²¹ applied to the 6-31G* optimized geometries. Configuration interaction calculations including all singles and doubles were carried out on **5**. In addition, several of the vertically excited lower electronic states of **2-5** were investigated by UHF and UMP2 calculations.²⁰

Molecular orbital plots were obtained by using PSI/77²² modified to accept the 6-31G* basis set.

Results and Discussion

The calculated energies for **2-5**, the ionization potentials for **2** and **4**, and the harmonic frequencies for **2** and **3** are given in Tables I, II, and III, respectively.

Tetrasilabicyclo[1.1.0]butane (2). **Structure and Bonding.** The equilibrium structure of **2** obtained at the 6-31G* level of theory is shown in Figure 1. All of the calculated structural parameters are in good agreement with those observed in the X-ray structure of the highly hindered 1,3-di-*tert*-butyl-2,2,4,4-tetrakis(2,6-diethylphenyl) derivative **1**.⁵ Experimental values for **1** are re-

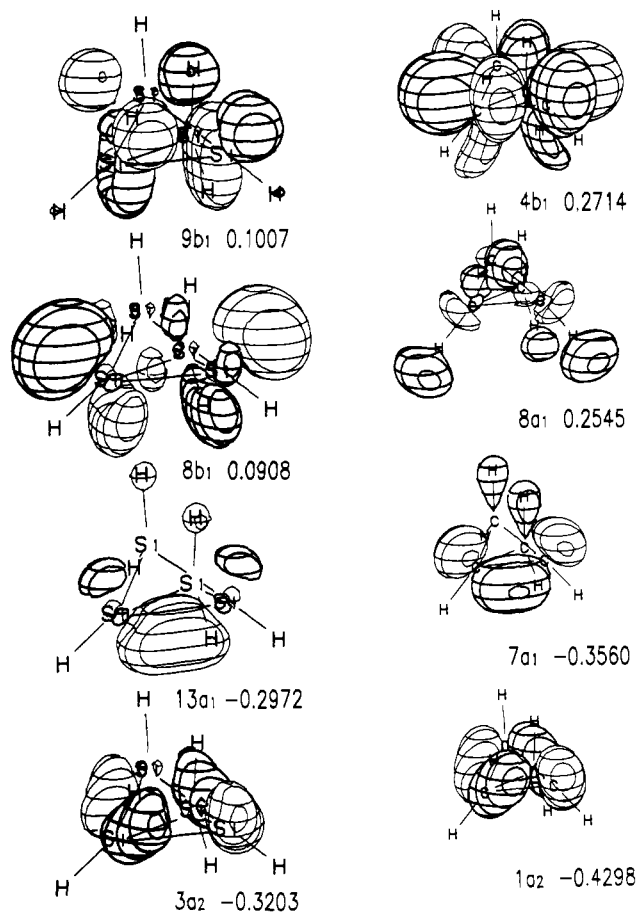


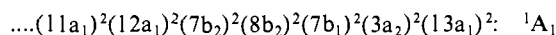
Figure 3. Orbital plots²² of the two highest occupied MO's and two lowest unoccupied MO's of **2** (left) and **4** (right). Contour values: occupied MO's 0.075, unoccupied MO's 0.05.

produced in Figure 2.^{5,23} In particular, the bridgehead Si-Si bond length is almost identical in the two structures, and the fold angles of the two cages differ by less than 2°.

The agreement found between **1** and **2**, even if somewhat fortuitous, suggests that the bonding in **2** is *not* as "unusual" as declared in the recent report by Dabisch and Schoeller⁶ (DS) who found a very long bridging Si-Si bond, 2.850 Å, and flatter (by 20°) ring system in their calculations on **2**. The discrepancies are attributable to deficiencies in the basis set used by DS and are primarily associated with the lack of polarization (3d) functions on the silicon atoms.

The experimental structure for **1** (Figure 2) indicates a slight alteration of the Si-Si bonds about the periphery of the ring. It is possible that crystal packing forces or the disposition of the bulky substituents of **1** result in the distortion to C_2 symmetry. The results of the frequency calculation (*vide infra*) indicate that distortions of the bicyclic cage are energetically facile. In particular, one of the lower energy modes (403.6 cm⁻¹) of a_2 symmetry allows distortion of the cage in a manner that mimics the structure of **1**.

The electronic configuration of **2** is



The frontier molecular orbitals (MO's), 13a₁ and 3a₂, as well as the two lowest unoccupied MO's are shown in Figure 3 together with the corresponding MO's of **4**. The energies of the higher MO's, expressed as ionization potentials obtained by Koopmans' theorem, are presented in Table II along with experimental²⁴ and

(21) (a) Møller, C.; Plesset, M. S. *Phys. Rev.* **1934**, *46*, 618-622. (b) Pople, J. A.; Binkley, J. S.; Seeger, R. *Int. J. Quantum Chem. Symp.* **1976**, *10*, 1-19.

(22) Jorgensen, W. A. *QCPE* **1977**, *11*, 340.

(23) We thank Professor Masamune for disclosing these results prior to publication—see ref 5.

(24) (a) Bischof, P.; Gleiter, R.; Müller, E. *Tetrahedron* **1976**, *32*, 2769-2771. (b) Gleiter, R. *Top. Curr. Chem.* **1979**, *86*, 197.

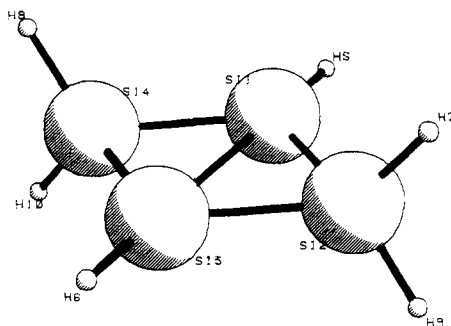


Figure 4. PLUTO plot of the 6-31G* optimized geometry of **3**, point group D_{2h} . Bond lengths (Å): Si₁-Si₃, 2.805; Si₁-Si₂, 2.295; Si₁-H₅, 1.480; Si₂-H₁, 1.479. Bond angles (deg): Si₂-Si₁-Si₄, 104.6; H₇-Si₂-H₉, 106.1; H₇-Si₂-Si₁, 118.4; Si₁-Si₂-Si₃, 75.3.

theoretical values obtained for **4**. The ordering of the four highest valence MO's of **2** is the same as in **4** while the corresponding energies are uniformly higher (IP's are lower) as expected on the basis of the lower electronegativity of Si vs. C.

In both **1** and **2**, the sum of the bond angles about the bridgehead silicon atoms, excluding the bridging bond, is nearly 360° (359.0° and 359.96° in structures **1** and **2**, respectively). This characteristic, which also pertains to **4** (359.1°), indicates that the average hybridization about the bridgehead atoms is approximately sp². As a consequence, the bridging bond is formed from the nonaligned overlap of essentially unhybridized p orbitals.²⁵ This feature and the consequences that ensue from 2p-2p vs. 3p-3p overlap are discussed further below. There is a direct relationship between the strength of the bridging bond (overlap of the p orbitals), its length, and the fold angle of the rings, as has been discussed in the case of derivatives and analogues of **4**.^{11,12,26} Electron-accepting substituents in a position to delocalize electron density from the bridgehead bond lead to considerable lengthening of the bond and flattening of the rings.¹¹ Of particular interest in the present context are the corresponding geometric features of the three stereoisomers of **6** whose structures have been determined by X-ray analysis.¹² The endo-endo isomer, in which the planes of the phenyl groups are perpendicular to the 2p orbitals which constitute the bridging bond, has a notably lengthened bond (1.558 vs. 1.497 Å in **4**) and wider flap angle (127.2° vs. 121.7° in **4**). In the other two isomers, endo-exo-**6** and exo-exo-**6**, steric interactions between the exo carbomethoxy group(s) and the phenyl groups prevent the conjugated geometry and consequent electron delocalization from the central bond. The skeletal geometry of the former is very similar to **4**, while the corresponding features of the latter are altered in the opposite direction as a consequence of the conjugation of the perimeter bonds with the two carbomethoxy groups.²⁷ In **1**, the bridgehead *tert*-butyl groups are nonconjugating, and the 2,2,4,4-aryl groups are twisted out of conjugation.⁵ By analogy with the structural similarity of **4** and endo-exo-**6**, one expects structural similarity between **1** and **2**, as is observed in the present study but not by DS,⁶ for reasons stated above.

Inversion Barriers. The transition structure corresponding to the inversion of the bicyclic ring of **2** has been identified as **3**. Structure **3** was optimized within the constraints of the point group D_{2h} . Harmonic frequency analysis reveals that **3** has a single imaginary frequency, and thus is a true transition structure at the present level of theory. The geometry of **3** is shown in Figure 4, and the harmonic frequencies are presented in Table III. Inspection of structures **2** and **3** reveals that inversion involves a

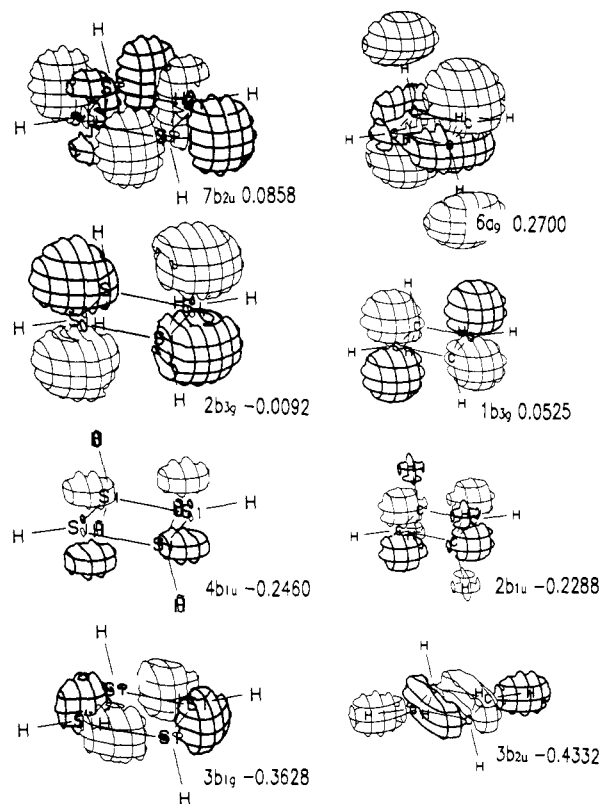


Figure 5. Orbital plots²² of the two highest occupied MO's and two lowest unoccupied MO's of **3** (left) and **5** (right). Contour values: occupied MO's 0.075, unoccupied MO's 0.05.

substantial lengthening of the Si₁-Si₃ bond, in accord with the discussion in the previous section. The lowest frequency fundamental of **2**, 126.7 cm⁻¹, involves flapping of the rings. The second, 340.8 cm⁻¹, has the same symmetry, a_g , and corresponds to stretching of the Si₁-Si₃ bond. The reaction coordinate to ring inversion arises from excitation of these two normal modes. The normal coordinate of **3** which has the imaginary frequency is of b_{1u} symmetry and involves almost exclusively an in-phase out-of-plane bending of the bridgehead Si-H bonds.

The two highest occupied and two lowest unoccupied molecular orbitals of **3** are shown in Figure 5 together with those of the analogous C₄H₆ structure **5**. The highest occupied molecular orbital of **3** is a weak π bond which does not have an underlying σ bond. The most favorable geometric deformation of **3**, the reaction coordinate vector off the transition structure, results in tipping the 3p orbitals of the bridgehead silicon atoms toward each other in order partially to reestablish the bent σ bond between Si₁ and Si₃.

The lowest unoccupied orbital of **3** is the π^* combination of the 3p orbitals and is calculated to have a slightly negative energy. The low energy of this orbital suggests that it may play an important role in the bonding of **3**; i.e., it is necessary to take into account electron correlation to describe the bonding, as in the case of **5**.^{11,12} Examination of the data in Table I reveals that incorporation of electron correlation by MP2 (or MP3) perturbation theory leads to a substantial decrease in the energy difference between **2** and **3**. A similar treatment of several of the lower electronically excited states of **3** suggest that only the triplet $\pi\pi^*$ state of symmetry B_{2u} is comparable in energy (69 kJ mol⁻¹ higher, without geometry optimization) to the closed shell structure **3** with state symmetry 1A_g . It appears probable that **3** (1A_g) is still the lowest electronic state and thus is the true transition structure for ring flapping of **2**. In this sense, the persila system is unlike the all-carbon system. The differences are discussed below.

The calculated value of the imaginary frequency, 304.5i cm⁻¹, suggests rather low curvature of the potential surface in the vicinity of the transition structure. The "floppiness" of **3** is reinforced by the very low value of the lowest real frequency, 67.7 cm⁻¹, which

(25) Newton, M. D.; Schulman, J. M. *J. Am. Chem. Soc.* **1972**, *94*, 767-773.

(26) Paddon-Row, M. N.; Houk, K. N.; Dowd, P.; Garner, P.; Schappert, R. *Tetrahedron Lett.* **1981**, *22*, 4799-4802.

(27) This conjugative effect is widely observed in cyclopropane derivatives. See, for example: (a) Childs, R. F.; Faggiani, R.; Lock, C. J. L.; Mahendran, M.; Zweep, S. D. *J. Am. Chem. Soc.* **1986**, *108*, 1692-1693. (b) Allen, F. H. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1980**, *B36*, 81-96. (c) Allen, F. H. *Ibid.* **1981**, *B37*, 890-900.

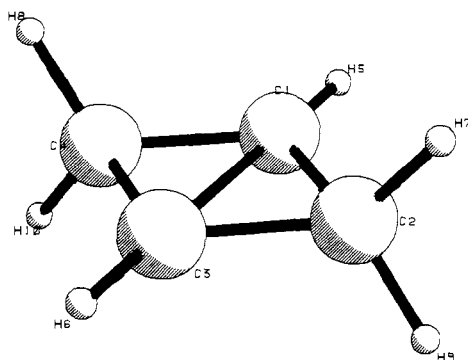


Figure 6. PLUTO plot of the 6-31G* optimized geometry of **5**, point group D_{2h} . Bond lengths (Å): C₁-C₃, 1.859; C₁-C₂, 1.493; C₁-H₅, 1.083; C₂-H₇, 1.101. Bond angles (deg): C₂-C₁-C₄, 103.0; H₇-C₂-H₃, 105.6; H₇-C₂-C₁, 118.2; C₁-C₂-C₃, 77.0.

has the same symmetry and corresponds to the motion that renders the skeleton nonplanar, with the bridgehead hydrogen atoms moving in the direction which would not lead to the equilibrium structure **2**.

In summary, the best estimate for the barrier to ring inversion is 75 kJ mol⁻¹ (Table I) after correction for correlation energy differences up to MP3 level. Correction for ZPVE difference between **2** and **3** is included also but is very small. A lower bound for the inversion barrier, 62 kJ mol⁻¹, has been determined for **2** by dynamic NMR spectroscopy. The value for the barrier is somewhat overestimated at the RHF 6-31G* level because structure **3** is not as well-described at the RHF level.

Parallel calculations on the inversion process in **4** reveal that the planar structure **5** (Figure 6), with symmetry $1A_g$, is also a true transition structure, having a single imaginary frequency, 828.8i, of symmetry b_{1u} . This result is entirely parallel to that found for **3** and is also consistent with the results of Gassman and co-workers,¹² obtained by using an approximate MO method (PRDDO) but with inclusion of some electron correlation via GVB. However, geometry optimization from a point near the D_{2h} structure **5** led directly to **4**, rather than to the second minimum¹² found by Gassman et al. While this result does not preclude the existence of the second minimum on the closed shell singlet potential energy surface, it does render it unlikely. The present results also differ from those of previous workers^{11,12} with respect to the extent of stabilization predicted for the planar closed-shell structure when correlation is included in the calculation. As with the tetrasilic systems **2** and **3**, the energy difference between planar structure **5** and the equilibrium geometry **4** is reduced only by about 25% relative to the RHF value when correlation effects are accounted for up to MP3 level of theory. Whereas in the case of **2** and **3** this resulted in a barrier close to that observed for **1**, the barrier predicted in this way in the case of **4** and **5**, 345 kJ mol⁻¹, is still much larger than observed¹⁴ for **6**. As we do not have facilities to perform GVB or MCSCF calculations, we have investigated **5** by CI calculations including all singly and doubly excited configurations relative to the RHF configuration. The results are essentially the same as the MP3 results²⁹ shown in Table I. It seems unlikely that geometry optimization with correlated wave functions will substantially alter the high value for the barrier to inversion via a closed-shell transition state. Calculations of alternative open shell electronic states of **5** suggest that the triplet state of B_{2u} symmetry (i.e., $2b_{1u} \rightarrow 1b_{3g}$ or $\pi \rightarrow \pi^*$) is close in energy to **5** (Table I), i.e., 31 kJ mol⁻¹ lower. The difference would increase somewhat with geometry optimization. Thus an upper bound for the inversion barrier for **4**, via an open shell triplet diradical state of symmetry B_{2u} , is 282 kJ mol⁻¹. This value is still substantially higher than that observed experimentally for

6¹⁴ or required for the isomerization of **4** to 1,3-butadiene.⁸ Inversion in the parent hydrocarbon **4** may not be a feasible process according to the present study. Hopefully, this result will provoke experiments with suitably deuteriated bicyclobutanes. It remains to rationalize the unambiguous observation that **6** does undergo ring inversion hindered by a much lower barrier than is estimated for **4**. The answer must lie in the effects of the substituents. π -conjugating substituents at the bridgehead positions can interact with the p atomic orbitals that make up the bridging bond (Figure 3 or 5). Electron withdrawal would directly weaken the bond by depleting it of electrons. Electron donation would have the same effect by populating the σ^* antibonding orbital. The electron-withdrawing carbomethoxy groups situated at C₂ and C₄ indirectly strengthen the central bond by withdrawing electrons from the a₂ orbital thereby reducing the transannular repulsion due to this orbital. Evidently, the ability to interact directly with the bridging bond carries more weight, and one may speculate whether the bicyclic ring would have any stability if the phenyl groups at C₁ and C₃ had carried electron-donating or -withdrawing substituents.

Vibrational Frequencies of 2 and 3. The results of the harmonic frequency analysis of **2** and **3** are presented in Table III. At the present level of theory (RHF, 6-31G*), it is known that the calculated frequencies are too high by about 10%.³⁰ While the values presented in Table III and discussed in the following text have not been "corrected", the reader should bear in mind that this systematic error exists. One should expect six skeletal deformation modes from the four atom bicyclic skeleton. As mentioned above, the lowest two fundamental frequencies of **2** involve flapping of the skeleton and stretching of the weak bond which joins the bridgehead silicon atoms. The remaining four skeletal fundamentals are extensively mixed with deformations of the Si-Si-H angles. In Si₂H₆, the Si-Si stretching frequency, calculated to be 465 cm⁻¹ at the same level of theory, is similar to the frequencies for rocking of the SiH₃ groups, 417 and 697 cm⁻¹ for combinations of e_u and e_g symmetry, respectively. Thus the remaining four skeletal deformations of **2** which involve predominantly stretches of "normal" Si-Si bonds are expected to be mixed with deformations of bond angles to the substituents and are found to be so. Normal coordinates 3 and 4, of b₁ and a₂ symmetry, and frequencies 394.2 and 403.6 cm⁻¹, respectively, involve substantial deformations of the bicyclo[1.1.0] skeleton as well as motions of the attached hydrogen atoms. The remaining skeletal deformations are mixed into normal coordinates 8 and 10, with symmetries a₁ and b₂ and frequencies 534.7 and 556.6 cm⁻¹, respectively. While it is unlikely that the parent molecule **2** will be synthesized, the preceding analysis should assist in the understanding and analysis of the vibrational spectroscopy of derivatives such as **1**.

The first two normal modes of **3** have been discussed above in connection with the reaction coordinate for ring inversion of **2** (and **1**). Normal modes **3** and **4**, with symmetries a_g and b_{2u} and frequencies 291.4 and 431.4 cm⁻¹, respectively, are essentially pure skeletal deformations with little independent motion of the attached hydrogen atoms. Mode 3 predominantly involves the stretch of the bridgehead to bridgehead bond. Mode 4 involves stretching of the other Si-Si bonds and concurrent bending of the angles at the bridgehead positions. Skeletal deformations are involved in all normal modes up to and including number 8. Mode 7, with b_{1g} symmetry, corresponds to mode 4 of **1** in that it results in a lowering of the molecular symmetry to C_{2h}.

Conclusions

In summary, the calculations described herein provide substantial insight into the bonding and chemical reactivity of the recently synthesized tetrasilabicyclo[1.1.0]butane system **1**. The inversion of the bicyclic cage of **2** has been determined to be an energetically facile process which probably does not involve rupture of the bridging bond, as would be the case in bicyclo[1.1.0]butane

(28) Wiberg, K. B.; Bonneville, G.; Dempsey, R. *Isr. J. Chem.* **1983**, *23*, 85-92.

(29) Configuration interaction calculations including all single and double excitations (CISD) gave essentially the same results as MP3 after the size consistency correction (SCC): $E_{\text{CISD}} = -155.215893$; after SCC -155.309597 .

(30) Pople, J. A.; Schlegel, H. B.; Krishnan, R.; DeFrees, D. J.; Binkley, J. S.; Frisch, M. J.; Whiteside, R. A.; Hout, R. F.; Hehre, W. J. *Int. J. Quant. Chem. Symp.* **1981**, *15*, 269-278.

4 itself. This result provides additional support for the hypothesis advanced to account for the dynamic NMR behavior of the more heavily substituted system. The close agreement between the calculated structure for 2 and that observed for 1 suggests that the substituents in the latter compound serve mainly to protect the reactive polysilane cage and do not strongly perturb its electronic structure. This analysis indicates that other calculations at this level of theory may be reliably used to predict the structure and properties of more strained polysilanes that have not yet yielded to synthesis. Further studies along these lines are in progress.

Parallel calculations on bicyclo[1.1.0]butane 4 suggest that the formal process of ring inversion entails rupture of the bridging bond and a barrier higher than that which opposes sigmatropic rearrangement to 1,3-butadiene.

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The Lowest Excited Triplet State of Triphenyl-, Diphenylchloro-, and Phenylchlorocarbenium Ions and Their Isoelectronic Boron Compounds. An Optical and ODMR Spectroscopic Investigation Combined with MO Calculations

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Abstract: The lowest excited triplet states of triphenyl-, diphenylchloro-, and phenylchlorocarbenium ions ($\text{CPh}_{3-m}\text{Cl}_m^+$) and of the respective isoelectronic boron compounds ($\text{BPh}_{3-m}\text{Cl}_m$) have been investigated by optical emission and ODMR spectroscopic methods in order to compare the triplet properties of the isoelectronic molecules in these two series as well as the change of triplet characteristics within each of the two series. The phosphorescence spectra, the triplet zero-field splitting parameters D and E , and the triplet spin sublevel selective deactivation rates were measured. Most of the experimental data were interpreted by an analysis of the triplet wave functions of these molecules in terms of intra-ring, inter-ring, charge-transfer ($\text{Ph}_{3-m} \rightarrow \text{XCl}_m$ ($X = \text{B}, \text{C}^+$)), and reverse-charge-transfer ($\text{XCl}_m \rightarrow \text{Ph}_{3-m}$) excitations. The wave functions were obtained by a π -SCF-CI-MO calculation. The carbenium ions showed low structured phosphorescence spectra, low-energy phosphorescence bands, and low D values whereas the boron compounds were characterized by well-structured phosphorescence spectra with typical benzenoid vibrational frequencies, high-energy O-O bands, and high D values. This indicates a non-benzene-like (delocalized) character of the T_1 states of the carbenium ions in contrast to a benzene-like (localized) character of the T_1 states of the boron compounds. This interpretation is in good agreement with the calculations which showed strong inter-ring and charge-transfer excitations with negligible intra-ring excitation for the carbenium ions and a strong increase of intra-ring excitation with a complementary decrease in inter-ring and charge-transfer excitations for the boron compounds. The correlation between experimental and calculational results is well reflected by the linear relationship between the measured D values and the calculated amount of intra-ring excitations. The variation of the T_1 properties of the molecules within each of the two series can be well explained by the lower electron-donating ability of the chlorine atoms as compared to the phenyl rings. The selective decay rates of the three triplet zero-field levels of all molecules investigated were analyzed in terms of the internal and external heavy-atom effect and the change of geometry.

1. Introduction

The physical and chemical properties of the organoboranes BR_3 and the isoelectronic carbenium ions CR_3^+ are of considerable interest. The isoelectronic structure of these compounds results in analogous chemical reactions. For example, the reaction with diazoalkanes¹ demonstrates the chemical similarity of BR_3 and CR_3^+ . Furthermore, the analogous properties of BR_3 and CR_3^+ in the lower excited singlet states are expressed in the remarkable similarities of their UV spectra² and the response of the UV transitions to temperature changes.³

Although BR_3 and CR_3^+ are isoelectronic, important differences are encountered too in their physical properties due to the additional positive charge at C^+ in CR_3^+ . An example constitutes the differing values for the ^{13}C chemical shifts for the para carbon atoms of the phenyl rings in BPh_3 and CPh_3^+ .⁴ Nevertheless, the correlations of the ^{13}C chemical shifts for the para carbon atoms⁴ and for the $^{13}\text{C}^+$ and ^{11}B shifts⁵ demonstrated the strong

relationship between these isoelectronic compounds.

So far, correlations between the isoelectronic boron and carbenium compounds were restricted to the ground state S_0 and excited singlet states. Therefore, we started investigations⁶ to compare the properties of the lowest triplet state T_1 of BPh_3 and CPh_3^+ by means of ODMR (optical detection of magnetic resonance) and optical luminescence spectroscopies, which represent the most appropriate techniques.

The chemical and physical properties of BR_3 and CR_3^+ are governed by the ability of the substituents R to compensate the

- (1) (a) Leffler, J. E.; Ramsey, B. G. *Proc. Chem. Soc., London* **1961**, 117.
- (b) Whitlock, H. J. *Am. Chem. Soc.* **1962**, *84*, 3807.
- (2) Ramsey, B. G. *J. Phys. Chem.* **1966**, *70*, 611.
- (3) Miller, D. S.; Leffler, J. E. *J. Phys. Chem.* **1970**, *74*, 2571.
- (4) Nöth, H.; Wrackmeyer, B.; Goetze, R.; Odom, J. D.; Moore, T. F. *J. Organomet. Chem.* **1979**, *173*, 15.
- (5) Spielvogel, B. F.; Nutt, W. R.; Izydore, R. A. *J. Am. Chem. Soc.* **1975**, *97*, 1609.
- (6) Slama, H.; Bräuchle, Chr.; Voitländer, J. *Chem. Phys. Lett.* **1983**, *102*, 307.

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