

## THE STRUCTURE OF SILYL CYCLOPENTADIENES

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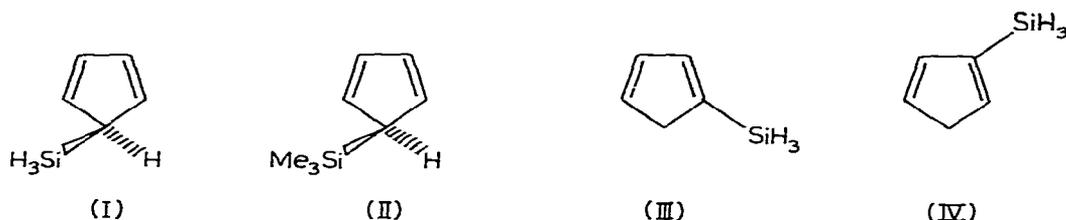
### Summary

Calculations have been made in the MNDO approximation of the structures and energies of three isomeric forms of  $(\eta^1\text{-C}_5\text{H}_5)\text{SiR}_3$  ( $\text{R} = \text{H}, \text{Me}$ ) and of  $(\eta^5\text{-C}_5\text{H}_5)\text{SiR}_3$ , together with potential energy curves for the folding of the  $\text{C}_5$  ring in  $5\text{-R}_3\text{SiC}_5\text{H}_5$ : all the  $\eta^1$  species have planar  $\text{C}_5$  rings at equilibrium. In addition (1,2) and (1,3) shift mechanisms have been investigated for migration of both  $\text{SiH}_3$  and hydrogen in  $(\eta^1\text{-C}_5\text{H}_5)\text{SiH}_3$ : the lowest energy pathway in each case is the (1,2) shift mechanism; structures and energies of the transition states are reported.

### Introduction

The structures reported [1,2] for silyl cyclopentadienes  $\text{R}_3\text{SiC}_5\text{H}_5$  ( $\text{R} = \text{H}$  or  $\text{Me}$ ) are puzzling. Bentham and Rankin [2] found for  $5\text{-SiH}_3\text{C}_5\text{H}_5$  (I) [3] a structure in which the monohapto  $\text{C}_5\text{H}_5$  ring is planar, subject only to the assumption of overall  $\text{C}_s$  molecular symmetry: by contrast, Veniaminov et al. [1] found for  $5\text{-Me}_3\text{SiC}_5\text{H}_5$  (II) a structure containing a non-planar  $\text{C}_5\text{H}_5$  ring, in which the dihedral angle between the planes  $\text{C}(1)\text{C}(2)\text{C}(3)\text{C}(4)$  and  $\text{C}(1)\text{C}(5)\text{C}(4)$  is  $158^\circ \pm 4^\circ$  in such a sense, hereafter called "cis", that the ring folding brings the silicon atom closer to the centre of the  $\text{C}_5\text{H}_5$  ring. This discrepancy in ring conformation is repeated also in the germyl analogues: in  $5\text{-Me}_3\text{GeC}_5\text{H}_5$ , the folding angle has been reported as  $156^\circ$  [4], whereas in  $5\text{-H}_3\text{GeC}_5\text{H}_5$ , the folding angle is zero in the gas phase [5], and no more than  $4.1^\circ \pm 0.6^\circ$  in the crystalline state [5], where the ring is subject to intermolecular forces. Ab initio calculations have been made [6] of the energies of various conformers of  $5\text{-SiH}_3\text{C}_5\text{H}_5$ , but with all geometrical parameters other than the fold angle of the ring kept constant: these calculations showed that the cis ring-folded conformer was more stable than the form containing a planar  $\text{C}_5\text{H}_5$  ring,

contrary to experiment [6].



We have now completed a study of  $\text{SiH}_3\text{C}_5\text{H}_5$  and  $\text{Me}_3\text{SiC}_5\text{H}_5$  using the MNDO method, and we report here the calculated structures and energies of these molecules at equilibrium for  $\eta^1$  rings, and also for the analogous  $\eta^5$  compounds: in addition we report potential energy curves for the folding of the ring in both  $(\eta^1\text{-C}_5\text{H}_5)\text{SiH}_3$  and  $(\eta^1\text{-C}_5\text{H}_5)\text{SiMe}_3$ .

Silyl cyclopentadienes (and their germyl analogues) exhibit fluxional behaviour in solution [7–10]. While  $^1\text{H}$  NMR has generally been unable to provide a definitive distinction between the two possible mechanisms for the fluxional exchange, via either 1,2 shifts or 1,3 shifts, (although ruling out random shifts),  $^{13}\text{C}$  NMR provides a clear demonstration that the exchange proceeds via 1,2 shifts [10]. We have investigated both 1,2 and 1,3 shifts using MNDO and find evidence only for successive 1,2 shifts: the structure of the transition state is reported here, together with the geometry of the shift pathway.

In solution, 5- $\text{SiH}_3\text{C}_5\text{H}_5$  (I) has been found [10] to undergo rapid prototropic rearrangement to form 1- $\text{SiH}_3\text{C}_5\text{H}_5$  (III) and 2- $\text{SiH}_3\text{C}_5\text{H}_5$  (IV), probably by successive 1, 2 hydrogen shifts: these isomers are at present structurally uncharacterised, and we report here calculated structures and energies for the isomers III and IV.

## Method

All computations were made using MNDO [11] implemented on a VAX 11/780 computer. For the calculation of equilibrium structures of  $\eta^1$  species no geometric assumptions of any kind were imposed, but for  $\eta^5$  species, local  $C_{5v}$  symmetry was imposed on the  $\text{C}_5\text{H}_5$  rings, even though the overall symmetry of the molecule, treated as a rigid entity, can be no more than  $C_s$ . However for both  $(\eta^5\text{-C}_5\text{H}_5)\text{SiR}_3$  species, the calculated barriers for internal rotation of the two symmetric tops is less than  $0.1 \text{ kJ mol}^{-1}$ , so that these molecules are more properly represented as non-rigid, belonging to a point group of order 30.

In the calculation of the potential energy curves for ring folding, the atom C(5) was fixed in a series of positions such that the dihedral angle in the ring varied by  $5^\circ$  increments on both sides of  $180^\circ$  (planarity), and the molecular energy was then optimised with respect to all the remaining geometrical variables without the imposition of any structural or symmetry constraint.

For 1,2 and 1,3 shift pathways the reaction coordinate was chosen as the distance between the migrating atom and its destination: all geometrical variables were then optimised for a series of values of this reaction coordinate which was constrained to become progressively shorter. If the scan was con-

TABLE I  
POINT GROUPS AND MOLECULAR ENERGIES

Molecule	Point group	$\Delta H_f^\theta$ (kJ mol <sup>-1</sup> )
C <sub>5</sub> H <sub>6</sub>	C <sub>2v</sub>	133.9
1-SiH <sub>3</sub> C <sub>5</sub> H <sub>5</sub>	C <sub>s</sub>	90.6
2-SiH <sub>3</sub> C <sub>5</sub> H <sub>5</sub>	C <sub>s</sub>	90.9
5-SiH <sub>3</sub> C <sub>5</sub> H <sub>5</sub>	C <sub>s</sub>	106.3
1-Me <sub>3</sub> SiC <sub>5</sub> H <sub>5</sub>	C <sub>s</sub>	-216.3
2-Me <sub>3</sub> SiC <sub>5</sub> H <sub>5</sub>	C <sub>s</sub>	-216.6
5-Me <sub>3</sub> SiC <sub>5</sub> H <sub>5</sub>	C <sub>s</sub>	-197.1
1-CH <sub>3</sub> C <sub>5</sub> H <sub>5</sub>	C <sub>s</sub>	90.3
2-CH <sub>3</sub> C <sub>5</sub> H <sub>5</sub>	C <sub>s</sub>	90.4
5-CH <sub>3</sub> C <sub>5</sub> H <sub>5</sub>	C <sub>s</sub>	115.5
( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )H	C <sub>5v</sub>	632.2
( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )SiH <sub>3</sub>	see text	351.7
( $\eta^5$ -C <sub>5</sub> H <sub>5</sub> )SiMe <sub>3</sub>	see text	92.7

ducted in the reverse sense, the migrating atom tended to be lost from the system entirely. Calculated point groups and molecular energies are given in Table 1.

## Results

### Equilibrium structures

Reaction of the anion C<sub>5</sub>H<sub>5</sub><sup>-</sup> with a molecular halide RX will generally give rise initially to one of two structures in each of which there is one hydrogen atom per carbon: these are the pentahapto species ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)R in which the group R is symmetrically bonded to the ring and the monohapto species 5-R-C<sub>5</sub>H<sub>5</sub>, analogous to I and II. When R = H, SiH<sub>3</sub> or SiMe<sub>3</sub>, the monohapto species is found experimentally to be the isomer formed. The equilibrium structures (Table 2) calculated for 5-R<sub>3</sub>SiC<sub>5</sub>H<sub>5</sub> (R = H, Me) both have C<sub>s</sub> symmetry in which the C<sub>5</sub> fragment is planar. The agreement between the structure calculated and that observed [2] for 5-H<sub>3</sub>SiC<sub>5</sub>H<sub>5</sub> is good. The major disagreements are in the Si-C distance, which is well known always to be calculated some 2-4% too short by MNDO (here 2%) and the C(2)-C(3) distance, which was fixed at 1.436 Å in the experimental determination but is calculated here as 1.473 Å: it is interesting that in the analogous 5-GeH<sub>3</sub>C<sub>5</sub>H<sub>5</sub> the experimental analysis [5], which is more complete than that for 5-SiH<sub>3</sub>C<sub>5</sub>H<sub>5</sub>, found this distance to be 1.468(22) Å, identical with the calculated value within experimental uncertainty.

By contrast the agreement between the observed [1] and calculated structures for 5-Me<sub>3</sub>SiC<sub>5</sub>H<sub>5</sub> is poor: the experimental structure analysis is based on a number of assumptions which may not be justifiable. Firstly two of the three independent bonded distances in the C<sub>5</sub> ring were assumed to be equal in magnitude, which is plainly incorrect, as they generally differ by ca. 0.1 Å; secondly the silicon atom was assumed to be rigorously tetrahedral; and thirdly the internal ring angle at C(5) was fixed at 109°, whereas in 5-MH<sub>3</sub>C<sub>5</sub>H<sub>5</sub> (M = Si, Ge) it is found to be 100.3(2)°. Possibly as a consequence of these assumptions, and of others unspecified concerning the other internal angles of the ring,

TABLE 2

OBSERVED AND CALCULATED GEOMETRIES FOR 5-R<sub>3</sub>SiC<sub>5</sub>H<sub>5</sub> (R = H or Me)

	5-H <sub>3</sub> SiC <sub>5</sub> H <sub>5</sub>		5-Me <sub>3</sub> SiC <sub>5</sub> H <sub>5</sub>		
	Observed	Calculated	Observed	Calculated	
<i>d</i> (C(5)–Si)(Å)	1.881(10)	1.845	1.90(1)	1.871	
<i>d</i> (C(5)–C(1))(Å)	1.500(13)	1.515	1.53(3)	1.515	
<i>d</i> (C(1)–C(2))(Å)	1.389(13)	1.364	1.40(2)	1.364	
<i>d</i> (C(2)–C(3))(Å)	1.436(fixed)	1.473	1.40(2)	1.472	
<i>d</i> (Si–H)(Å)	<i>a</i>	1.438	—	—	
<i>d</i> (Si–C)(Å)	—	—	1.90(1)	1.859	
<i>d</i> (C(5)–H)(Å)	} mean	1.111	1.11(2)	1.113	
<i>d</i> (C(1)–H)(Å)		<i>d</i> (C–H)	1.082	1.11(2)	1.082
<i>d</i> (C(2)–H)(Å)		1.109(18)Å	1.082	1.11(2)	1.082
<(C(5)–C(1)–C(2))( <sup>o</sup> )	112.0(10)	110.0	<i>a</i>	110.3	
<(C(1)–C(2)–C(3))( <sup>o</sup> )	107.9(6)	108.9	<i>a</i>	108.8	
<(C(1)–C(5)–C(4))( <sup>o</sup> )	100.3(15)	102.1	109(fixed)	101.8	
<(C(1)–C(5)–Si)( <sup>o</sup> )	106.6(6)	112.1	109(3)	114.0	
<(C(5)–Si–H)( <sup>o</sup> )	<i>a</i>	{ 111.5(×1) 109.7(×2)	—	—	
<(C(5)–Si–C)( <sup>o</sup> )	—		—	109.5(fixed)	{ 111.8(×1) 109.2(×2)

<sup>a</sup> Not reported. <sup>b</sup> Assumed equal.

the authors [1] concluded that the C<sub>5</sub> ring was non-planar, as they did also for 5-Me<sub>3</sub>GeC<sub>5</sub>H<sub>5</sub> [4]. Our calculations indicate a planar C<sub>5</sub> ring at equilibrium, and suggest that the geometry of the ring is almost identical in 5-H<sub>3</sub>SiC<sub>5</sub>H<sub>5</sub> and 5-Me<sub>3</sub>SiC<sub>5</sub>H<sub>5</sub>, in contrast to the experimental reports [1,2,4,5]. We return to the question of the puckering of the ring below.

Both 5-H<sub>3</sub>SiC<sub>5</sub>H<sub>5</sub> and 5-Me<sub>3</sub>SiC<sub>5</sub>H<sub>5</sub> undergo rearrangement via hydrogen migration to yield the 1 and 2 isomers [10, 12, 13]. The calculated  $\Delta H_f^\ddagger$  values (Table 1) show that these isomers are in fact more stable than the corresponding 5-R<sub>3</sub>SiC<sub>5</sub>H<sub>5</sub> species. The 5 isomers are formed initially since there is an easy pathway from C<sub>5</sub>H<sub>5</sub><sup>−</sup> as indicated above: only after substitution to form the 5 isomer has occurred can the prototropic shifts occur. Geometrical data for these isomers are given in Table 3, and the three  $\eta^1$  isomers of C<sub>5</sub>H<sub>5</sub>SiH<sub>3</sub> are shown in Fig. 1: as for the 5 isomers, the 1 and 2 isomers contain planar C<sub>5</sub> rings.

Although silicon and germanium have so far only been observed to form  $\eta^1$ -cyclopentadienides,  $\eta^5$  derivatives are known for beryllium [14–18], and for tin and lead [19]. Consequently, it is of interest to consider  $\eta^5$  derivatives also for silicon: the molecular energies (Table 1) indicate that although when R = H the energy difference between 5-RC<sub>5</sub>H<sub>5</sub> and the pentahapto isomer is 498.3 kJ mol<sup>−1</sup>, this is reduced to 245.4 for R = SiH<sub>3</sub> and to only 189.8 kJ mol<sup>−1</sup> for R = SiMe<sub>3</sub>: while this is still a substantial difference it is possible that for a suitably substituted SiX<sub>3</sub> derivative and a suitable C<sub>5</sub>Y<sub>5</sub> ring, the energy difference could be sufficiently small for the ( $\eta^5$ -C<sub>5</sub>Y<sub>5</sub>)SiX<sub>3</sub> isomer to be accessible.

The major structural parameters for the pentahapto molecules are recorded in Table 4. The C–C distance within the ring decreases as the axial substituent varies H > SiH<sub>3</sub> > SiMe<sub>3</sub>, as at the same time the C–H distance increases. From H to SiH<sub>3</sub> to SiMe<sub>3</sub>, these parameters approach the values in the isolated C<sub>5</sub>H<sub>5</sub><sup>−</sup>

TABLE 3  
 GEOMETRICAL DATA FOR ( $\eta^1$ -C<sub>5</sub>H<sub>5</sub>)SiR<sub>3</sub> ISOMERS

(a) ( $\eta^1$ -C <sub>5</sub> H <sub>5</sub> )SiH <sub>3</sub>	1-SiH <sub>3</sub> C <sub>5</sub> H <sub>5</sub>	2-SiH <sub>3</sub> C <sub>5</sub> H <sub>5</sub>	5-SiH <sub>3</sub> C <sub>5</sub> H <sub>5</sub>
$d(C(5)-C(1))(\text{Å})$	1.526	1.522	1.515
$d(C(1)-C(2))(\text{Å})$	1.365	1.364	1.364
$d(C(2)-C(3))(\text{Å})$	1.476	1.484	1.473
$d(C(3)-C(4))(\text{Å})$	1.360	1.360	1.364
$d(C(4)-C(5))(\text{Å})$	1.520	1.517	1.515
$\angle(C(5)-C(1)-C(2))(^{\circ})$	108.2	110.9	110.0
$\angle(C(1)-C(2)-C(3))(^{\circ})$	110.3	107.4	108.9
$\angle(C(2)-C(3)-C(4))(^{\circ})$	108.7	110.1	108.9
$\angle(C(3)-C(4)-C(5))(^{\circ})$	109.7	109.6	110.0
$\angle(C(4)-C(5)-C(1))(^{\circ})$	103.1	101.9	102.1
$d(Cn-Si)(\text{Å})$	1.791	1.793	1.845
$\angle(Si-Cn-C(n+1))(^{\circ})$	128.1	123.0	112.1
(b) ( $\eta^1$ -C <sub>5</sub> H <sub>5</sub> )SiMe <sub>3</sub>	1-Me <sub>3</sub> SiC <sub>5</sub> H <sub>5</sub>	2-Me <sub>3</sub> SiC <sub>5</sub> H <sub>5</sub>	5-Me <sub>3</sub> SiC <sub>5</sub> H <sub>5</sub>
$d(C(5)-C(1))(\text{Å})$	1.527	1.520	1.515
$d(C(1)-C(2))(\text{Å})$	1.366	1.364	1.364
$d(C(2)-C(3))(\text{Å})$	1.476	1.485	1.472
$d(C(3)-C(4))(\text{Å})$	1.360	1.360	1.364
$d(C(4)-C(5))(\text{Å})$	1.519	1.518	1.515
$\angle(C(5)-C(1)-C(2))(^{\circ})$	107.9	111.2	110.3
$\angle(C(1)-C(2)-C(3))(^{\circ})$	110.6	107.2	108.8
$\angle(C(2)-C(3)-C(4))(^{\circ})$	108.5	110.2	108.8
$\angle(C(3)-C(4)-C(5))(^{\circ})$	109.6	109.6	110.3
$\angle(C(4)-C(5)-C(1))(^{\circ})$	103.4	101.8	101.8
$d(Cn-Si)(\text{Å})$	1.813	1.814	1.871
$\angle(Si-Cn-C(n+1))(^{\circ})$	127.2	123.0	114.0

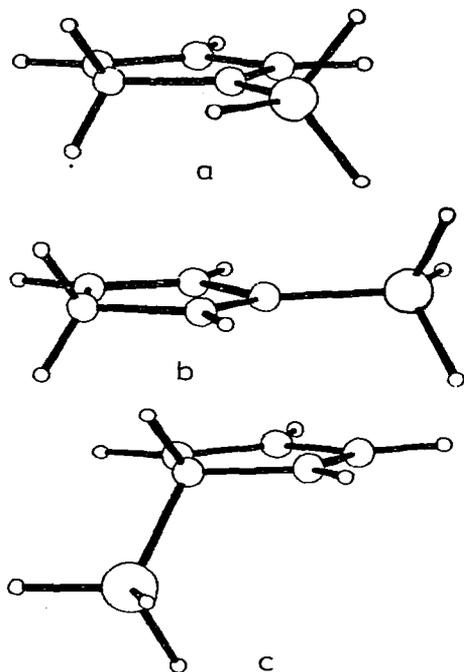


Fig. 1. The molecular structures of: (a) 1-SiH<sub>3</sub>C<sub>5</sub>H<sub>5</sub>, (b) 2-SiH<sub>3</sub>C<sub>5</sub>H<sub>5</sub>, (c) 5-SiH<sub>3</sub>C<sub>5</sub>H<sub>5</sub>.

TABLE 4

GEOMETRICAL PARAMETERS FOR  $(\eta^5\text{-C}_5\text{H}_5)\text{X}$  ( $\text{X} = \text{H}, \text{SiH}_3, \text{SiMe}_3$ )

	$(\eta^5\text{-C}_5\text{H}_5)\text{H}$	$(\eta^5\text{-C}_5\text{H}_5)\text{SiH}_3$	$(\eta^5\text{-C}_5\text{H}_5)\text{SiMe}_3$	$\text{C}_5\text{H}_5^-$
$d(\text{C}-\text{C})(\text{\AA})$	1.4351	1.4344	1.4300	1.4180
$d(\text{C}-\text{H})(\text{\AA})$	1.0796	1.0815	1.0816	1.0827
$\langle(\text{C}-\text{C}-\text{H})(^\circ)$	125.98	125.85	125.80	126.00
$\delta(\text{C}-\text{C}-\text{C}-\text{H})(^\circ)$	179.79	174.11	173.19	180.00
$h_1(\text{\AA})^a$	1.1989	1.9640	2.0902	—
$h_2(\text{\AA})^b$	0.0032	0.0900	0.1041	0.0000
$d(\text{C}\dots\text{H,Si})(\text{\AA})$	1.7110	2.3122	2.4184	—
$d(\text{Si}-\text{H,C})(\text{\AA})$	—	1.4521	1.8786	—
$\langle(\text{X}-\text{Si}-\text{H,C})(^\circ)$	—	111.61	112.91	—

<sup>a</sup> Distance of H or Si from X. <sup>b</sup> Distance of  $\text{C}_5$  plane from  $\text{H}_5$  plane. <sup>c</sup> X is point at centre of  $\text{C}_5$  ring.

ion, suggesting that of the pentahapto species here considered,  $(\eta^5\text{-C}_5\text{H}_5)\text{H}$  is the least ionic in the bonding of the ring to the axial substituent and  $(\eta^5\text{-C}_5\text{H}_5)\text{-SiMe}_3$  is the most ionic. That the most ionic species is that which is the most stable relative to its  $\eta^1$  isomers, and the least ionic is that which is the least stable relative to the  $\eta^1$  isomer may be significant, but studies of a wider range of cyclopentadienides are required before an evaluation of this relationship is possible.

The molecular structures calculated for  $(\eta^5\text{-C}_5\text{H}_5)\text{SiR}_3$  ( $\text{R} = \text{H}, \text{Me}$ ) are shown in Fig. 2.

### Ring-folding

Although complete geometry optimisation for  $5\text{-R}_3\text{SiC}_5\text{H}_5$ , as well as for  $\text{C}_5\text{H}_6$ , indicates that the  $\text{C}_5$  rings are accurately planar, we have sought to investigate further the question of possible ring folding in these molecules by determining the molecular energy as a function of the dihedral angle,  $\theta$ , between the two planes  $\text{C}(1)\text{C}(2)\text{C}(3)\text{C}(4)$  and  $\text{C}(4)\text{C}(5)\text{C}(1)$ . When the ring is planar,  $\theta = 180^\circ$ : values of  $\theta$  less than  $180^\circ$  indicate in our specification the "cis" configuration, and values greater than  $180^\circ$  the "trans" as defined in ref.

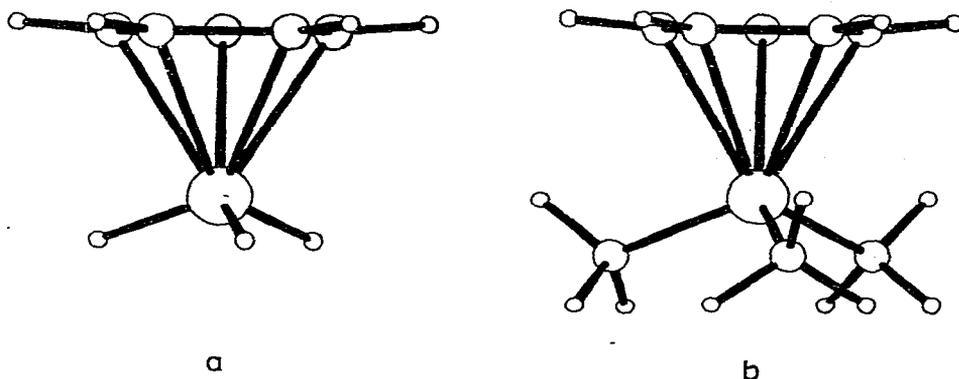


Fig. 2. The molecular structures of: (a)  $(\eta^5\text{-C}_5\text{H}_5)\text{SiH}_3$ , (b)  $(\eta^5\text{-C}_5\text{H}_5)\text{SiMe}_3$ .

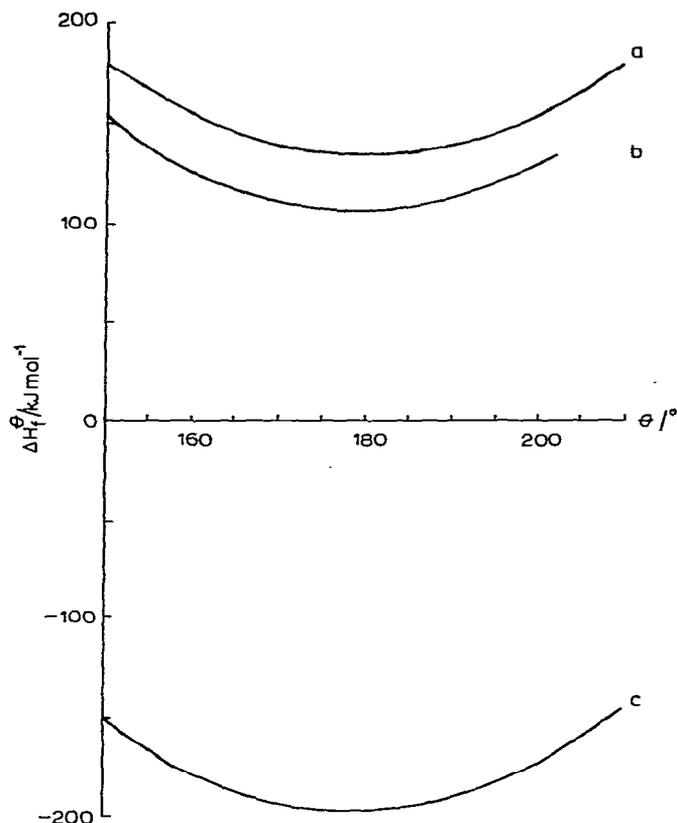


Fig. 3. Potential energy curves for ring folding in: (a)  $\text{C}_5\text{H}_6$ , (b)  $5\text{-H}_3\text{SiC}_5\text{H}_5$ , (c)  $5\text{-Me}_3\text{SiC}_5\text{H}_5$ .

6. The potential energy curves are shown in Fig. 3: that for  $\text{C}_5\text{H}_6$  is necessarily symmetrical about  $\theta = 180^\circ$ , while those for  $5\text{-R}_3\text{SiC}_5\text{H}_5$  are almost symmetrical, and all have but a single clearly defined minimum. Furthermore, the forms of the three potential energy curves are extremely similar, and virtually superposable, indicating that for these substituents (H,  $\text{H}_3\text{Si}$ ,  $\text{Me}_3\text{Si}$ ) at least, the ring folding potential is essentially independent of the substituent. The required energies for folding the ring from the planar configuration  $\theta = 180^\circ$ , to that deduced in the experimental study [1] of  $5\text{-Me}_3\text{SiC}_5\text{H}_5$ ,  $\theta = 158^\circ$ , are as follows:  $\text{C}_5\text{H}_6$ ,  $24.1 \text{ kJ mol}^{-1}$ ;  $5\text{-H}_3\text{SiC}_5\text{H}_5$ ,  $24.2 \text{ kJ mol}^{-1}$ ; and  $5\text{-Me}_3\text{SiC}_5\text{H}_5$ ,  $28.2 \text{ kJ mol}^{-1}$ . In  $(\eta^1\text{-C}_5\text{H}_5)\text{BeH}$ , the value is  $24.5 \text{ kJ mol}^{-1}$ . In view of these findings, it must be concluded that the reported [1] structure of  $5\text{-Me}_3\text{SiC}_5\text{H}_5$  is incorrect in its conclusion of a folded ring, and that most probably the folded ring reported for  $5\text{-Me}_3\text{GeC}_5\text{H}_5$  [4] is also incorrect.

There remains, however, the *ab initio* study of these molecules [6], which concluded that the *cis* folded structure was the most stable for  $5\text{-SiH}_3\text{C}_5\text{H}_5$  and the *trans* folded structure the least stable. In this study all the energies quoted are total energies which were not related to  $\Delta H_f^\theta$ : a number of different basis sets were employed and, although for a given structure the energy varied with basis set by up to  $275 \text{ kJ mol}^{-1}$ , for a given fixed basis set the relative energies

of the various conformations were almost constant with *trans* less stable than planar by some  $51.1 \text{ kJ mol}^{-1}$  and planar less stable than *cis* by  $2.5 \text{ kJ mol}^{-1}$ , both much smaller than the basis set variation. Because fixed geometries were assumed for all calculations, the differences of energy consequent on ring folding reported [6] are meaningless. Even very plausible assumed geometries can often have  $\Delta H_f^\theta$  values above the optimised value of several hundred  $\text{kJ mol}^{-1}$ , and our own calculations indicate changes in the remainder of the ring geometry on folding. If the geometry of  $5\text{-R}_3\text{SiC}_5\text{H}_5$  is fully optimised for  $\theta = 180^\circ$ , for example, and the ring is then folded to  $\theta = 1.58^\circ$ , but with all the other parameters held at the values appropriate for  $\theta = 180^\circ$ , errors are introduced into  $\Delta H_f^\theta$  of ca.  $5 \text{ kJ mol}^{-1}$ . Similarly if random variations of  $\pm 0.01 \text{ \AA}$  or  $\pm 0.05^\circ$  are introduced into the parameters of a completely optimised structure,  $\Delta H_f^\theta$  will again increase by ca.  $5 \text{ kJ mol}^{-1}$ . With much larger uncertainties on bond angles and dihedral angles quite possible when using assumed geometries, the scope for error in molecular energies is correspondingly greater.

### Molecular rearrangements

We consider first the question of  $\text{R}_3\text{Si}$  shifts, and subsequently prototropic rearrangements. Two mechanisms for the shift of  $\text{H}_3\text{Si}$  were investigated, the 1,2 shift and the 1,3 shift: for the 1,2 shift the reaction pathway is symmetrical, having a maximum in which the silicon atom is equidistant from two carbon atoms and for which the energy is  $99.1 \text{ kJ mol}^{-1}$  above the equilibrium energy for  $5\text{-SiH}_3\text{C}_5\text{H}_5$ ; this is not comparable with the solution activation energy as it represents an isolated molecule in the absence of solvation. The principal structural parameters for this transition state, which is depicted in Fig. 4, are listed in Table 5: the reaction pathway is shown in Fig. 5. For the 1,3 shift mecha-

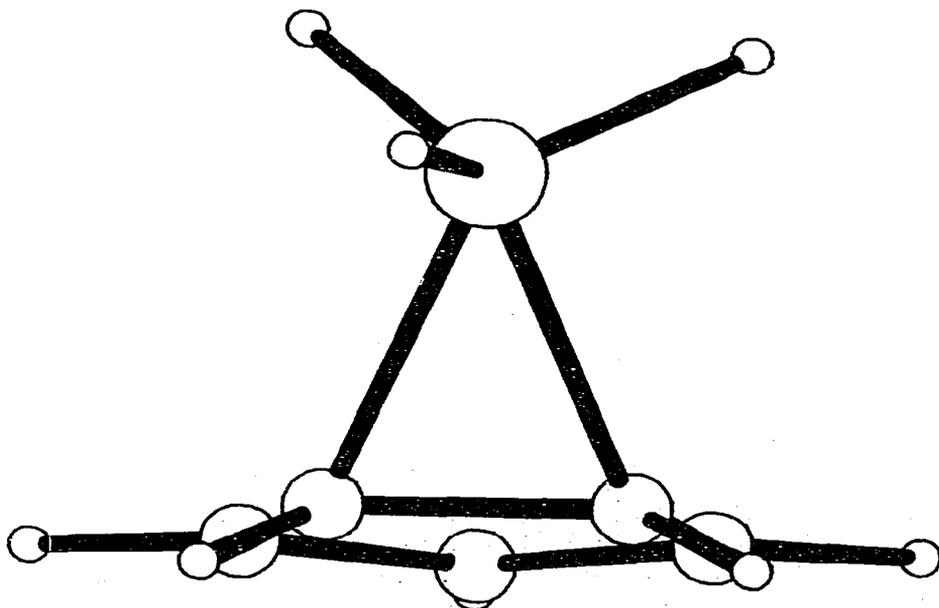


Fig. 4. The structure of the transition state for the 1,2 shift of  $\text{SiH}_3$  in  $5\text{-H}_3\text{SiC}_5\text{H}_5$ .

TABLE 5

GEOMETRICAL PARAMETERS FOR THE TRANSITION STATE IN THE 1,2 SiH<sub>3</sub> SHIFT IN 5-SiH<sub>3</sub>C<sub>5</sub>H<sub>5</sub>

$d(C_a-C_a')(\text{\AA})(\times 1)$	1.506
$d(C_a-C_b)(\text{\AA})(\times 2)$	1.429
$d(C_b-C_c)(\text{\AA})(\times 2)$	1.414
$\angle(C_a'-C_a-C_b)^\circ(\times 2)$	106.3
$\angle(C_a-C_b-C_c)^\circ(\times 2)$	109.0
$\angle(C_b-C_c-C_b)^\circ(\times 1)$	109.4
$d(\text{Si}-C_a)(\text{\AA})(\times 2)$	2.043
$d(\text{Si}-C_b)(\text{\AA})(\times 2)$	2.960
$d(\text{Si}-C_c)(\text{\AA})(\times 1)$	3.391

nism the reaction pathway is again symmetrical since it is found to consist simply of two successive 1,2 shifts. While a direct 1,3 shift pathway may exist, the lowest energy pathway for H<sub>3</sub>Si shifts is a succession of 1,2 shifts: this is consistent with the results of variable temperature <sup>13</sup>C NMR spectroscopy [10].

For the hydrogen migrations, again two mechanisms were investigated: in the 1,2 shift mechanism, the hydrogen migrates stepwise from C(5) to C(1), and then from C(1) to C(2), while in the 1,3 mechanisms, the hydrogen moves directly from C(5) to C(2). NMR evidence [10,12] suggests that the stepwise pathway is followed. Since, unlike the shift of the SiH<sub>3</sub> group, rearrangements involving hydrogen migration are non-degenerate, the reactions pathways here are not symmetrical. For the 5 → 1 hydrogen shift, the transition state has  $\Delta H_f^\theta$  of +282.2 kJ mol<sup>-1</sup> representing a gas-phase activation enthalpy of +175.9 kJ mol<sup>-1</sup> for the forward direction. The structure of the transition state is shown in Fig. 6(a), and the important geometrical parameters are listed in Table 6: in the 1 → 2 shift,  $\Delta H_f^\theta$  for the transition state is +277.1 kJ mol<sup>-1</sup>, here representing an activation enthalpy of +187.1 kJ mol<sup>-1</sup>. This transition state is shown in Fig. 6(b). Just as for the SiH<sub>3</sub> shift, attempts to investigate a 1,3 shift mecha-

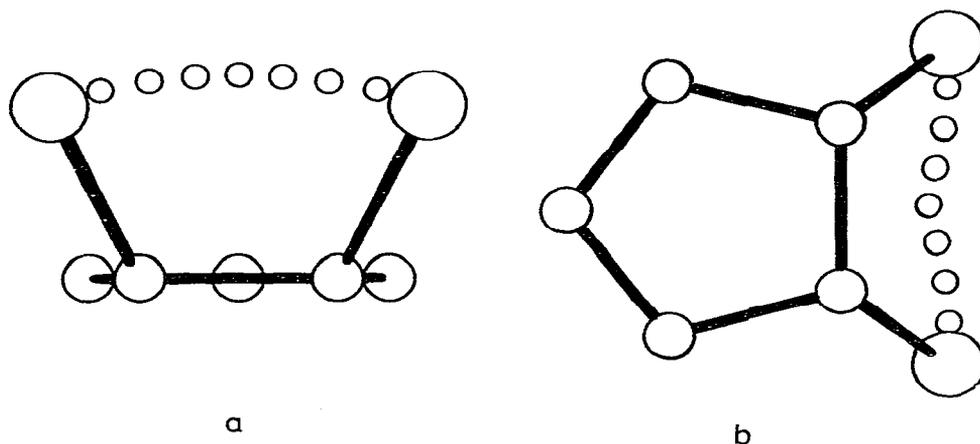


Fig. 5. The reaction pathway for the 1,2 shift of SiH<sub>3</sub> in 5-H<sub>3</sub>SiC<sub>5</sub>H<sub>5</sub>, (a) viewed parallel to the ring, (b) viewed perpendicular to the ring.

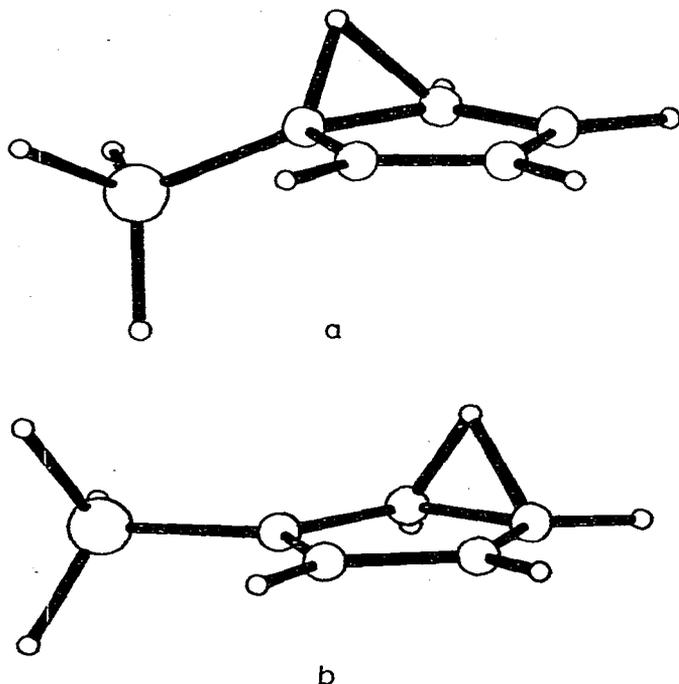


Fig. 6. The structures of the transition states for H migration in  $(\eta^1\text{-C}_5\text{H}_5)\text{SiH}_3$  (a)  $5 \rightarrow 1$ ; (b)  $1 \rightarrow 2$ .

nism merely revealed a pair of successive 1,2 shifts: if a direct 1,3 shift pathway exists, it is of higher energy than the stepwise pathway.

Although, because of solvation, none of these isolated molecule activation enthalpies represents a solution enthalpy, it is nevertheless interesting to find the calculated activation enthalpy for  $\text{SiH}_3$  migration so much less than those

TABLE 6

GEOMETRICAL PARAMETERS FOR THE TRANSITION STATES IN THE HYDROGEN MIGRATIONS IN  $\eta^1\text{-C}_5\text{H}_5\text{SiH}_3$

	(a) $5 \rightarrow 1$	(b) $1 \rightarrow 2$
$d(\text{Si}-\text{C}_a)(\text{\AA})$	1.805	1.787
$d(\text{C}_a-\text{C}_b)(\text{\AA})$	1.503	1.477
$d(\text{C}_b-\text{C}_c)(\text{\AA})$	1.390	1.493
$d(\text{C}_c-\text{C}_d)(\text{\AA})$	1.450	1.390
$d(\text{C}_d-\text{C}_e)(\text{\AA})$	1.382	1.449
$d(\text{C}_e-\text{C}_a)(\text{\AA})$	1.477	1.388
$\angle(\text{C}_a-\text{C}_b-\text{C}_c)(^\circ)$	108.9	106.0
$\angle(\text{C}_b-\text{C}_c-\text{C}_d)(^\circ)$	108.4	107.7
$\angle(\text{C}_c-\text{C}_d-\text{C}_e)(^\circ)$	109.3	108.4
$\angle(\text{C}_d-\text{C}_e-\text{C}_a)(^\circ)$	109.6	110.0
$\angle(\text{C}_e-\text{C}_a-\text{C}_b)(^\circ)$	103.8	107.6
$\angle(\text{Si}-\text{C}_a-\text{C}_b)(^\circ)$	126.3	125.1
$\angle(\text{Si}-\text{C}_a-\text{C}_e)(^\circ)$	120.6	127.8
$d(\text{C}_a-\text{H}^*)(\text{\AA})$	1.182	—
$d(\text{C}_b-\text{H}^*)(\text{\AA})$	—	1.183

for hydrogen migration, since in solution  $\text{SiH}_3$  migration is rapid [9] while hydrogen migration is slow [10]. In  $\text{Me}_3\text{SiC}_5\text{H}_5$  at  $80^\circ\text{C}$ , the rate of  $\text{Me}_3\text{Si}$  migration is [12]  $10^3 \text{ s}^{-1}$ , while that of hydrogen migration is only  $1.4 \times 10^{-3} \text{ s}^{-1}$ , this difference representing a difference in solution activation energies of some  $39.6 \text{ kJ mol}^{-1}$ , as compared with the difference in isolated molecule activation enthalpies calculated here for  $\text{H}_3\text{SiC}_5\text{H}_5$  of  $76.8 \text{ kJ mol}^{-1}$ .

The structures of the two transition states (Table 6) show a number of features in common with the transition state for  $\text{SiH}_3$  migration (Table 5). Within the ring the longest bond in each case is that spanned by the migrating fragment, while the valence angles within the ring are smallest at the two carbons bonded to the migrating fragment: similarly in each case, the shortest bond in the ring is that directly opposite the migration. The transition state for  $\text{SiH}_3$  migration has a plane of symmetry, but the others do not, and in these there is some degree of alternation of bond length around the ring.

### Electronic structure

The electronic structures calculated for the monohapto molecules by MNDO appear to be very similar to those obtained by ab initio methods, although the agreement found here between the calculated eigenvalues and the observed ionisation energies is markedly better than that obtained earlier. Table 7 lists typical values, those for  $\text{C}_5\text{H}_6$  and  $5\text{-SiH}_3\text{C}_5\text{H}_5$ : details of the eigenvalues and eigenvectors of the remaining molecules are available from the authors. For  $5\text{-SiH}_3\text{C}_5\text{H}_5$  in particular the superiority of MNDO is overwhelming. In addition to the improved agreement throughout, which is mirrored also in the isomers of

TABLE 7  
OBSERVED AND CALCULATED EIGENVALUES (eV) IN  $\text{C}_5\text{H}_6$  AND  $5\text{-SiH}_3\text{C}_5\text{H}_5$

	Observed <sup>a</sup>	MNDO	ab initio <sup>a</sup>
(a) $\text{C}_5\text{H}_6$	8.56	9.05	8.88
	10.72	10.84	11.74
	12.2	12.71	13.69
	12.6	12.80	13.38
	13.2	13.35	14.26
	13.8	13.93	15.19
	15.0	14.68	16.63
	16.5	17.14	18.92
	17.5	19.84	19.30
	18.4	20.83	20.15
(b) $5\text{-SiH}_3\text{C}_5\text{H}_5$	8.7	9.03	9.09
	10.2	10.41	11.09
		12.19	12.67
	12.0	12.25	12.72
		12.65	13.18
	12.8	13.09	13.88
	13.9	13.31	14.72
	14.1	13.93	15.56
		14.39	15.65
	16.5	17.06	18.53
17.0	19.17	19.34	
	19.99	19.53	

<sup>a</sup> Ref. 6.

$\text{CH}_3\text{C}_5\text{H}_5$ , MNDO appears to be rather better at predicting the difference in energy between the first two photoelectron bands, which has been used [9] as diagnostic of fluxional character, fast fluxional behaviour having been associated with a small energy difference ( $<1.5$  eV) and slow fluxional behaviour with a large energy difference ( $>2.1$  eV). For  $\text{C}_5\text{H}_6$ , the 5, 1 and 2 isomers of  $\text{CH}_3\text{C}_5\text{H}_5$ , and 5-SiH<sub>3</sub>C<sub>5</sub>H<sub>5</sub> and 5-Me<sub>3</sub>SiC<sub>5</sub>H<sub>5</sub>, respectively, MNDO calculates gaps as follows (eV): 1.79, 1.80, 1.83, 1.62, 1.38, and 1.26; for the first five of these the experimental values are (eV): 2.1, unknown, 2.2, 2.0 and 1.5, while the ab initio values are (eV): 2.86, 2.84, 3.04, 2.50, and 2.00, all further from the experimental values than the MNDO values are. While we have so few MNDO values, it is unwise to read too much into this result; nevertheless it may be that MNDO will prove on further investigation to be a useful diagnostic tool in this context.

The atomic charges calculated by MNDO for 5-SiH<sub>3</sub>C<sub>5</sub>H<sub>5</sub> are very similar to the ab initio values: we note that the SiH<sub>3</sub> group is calculated, even in an *s,p* basis, to be a net electron donor even to such an electron-rich system as cyclopentadiene. When 5-SiH<sub>3</sub>C<sub>5</sub>H<sub>5</sub> is converted into the transition state for the silyl shift, not only do significant changes occur in the geometrical structure, but the electronic structure manifested in the atomic populations and charges also vary appreciably. The silicon atom is somewhat more positive in the transition state, by +0.054 *e*, while the two carbon atoms involved in the shift become much more negative, from -0.182 (C(5)) and -0.102 (C(1)) to -0.195 for each of C<sub>a</sub> and C<sub>a</sub>': other, lesser, changes occur at the other carbon atoms within the ring: C(2) and C(4) becoming less negative, and C(3) more negative. Because of the increased charge separation in the transition state (which is accompanied by an increase in the dipole moment from 0.172 Debye to 0.303 Debye) the solvation of the transition state will be greater than that of the equilibrium structure, and this differential solvation will have a major influence in reducing the high isolated-molecule activation energy to the much smaller solution activation energy. Entirely similar remarks hold for the transition states in the hydrogen migration processes.

In the  $\eta^5$  species, the bonding of the axial substituent when this is H, SiH<sub>3</sub> or SiMe<sub>3</sub> is a simple perturbation of the  $\pi$  molecular orbitals of the C<sub>5</sub> fragment. These orbitals, in the isolated anion C<sub>5</sub>H<sub>5</sub><sup>-</sup> are of symmetries  $A_2''$ ,  $E_1''$  and  $E_2''$  of which  $A_2''$  has  $\sigma$  symmetry with respect to the five-fold axis,  $E_1''$  has  $\pi$ , and  $E_2''$  has  $\delta$  symmetry. In ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)H the axial hydrogen 1s orbital interacts only with  $A_2''$  to form in phase and out of phase combinations of which only the in phase is occupied. In ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)SiH<sub>3</sub> the silicon 3s, 3p<sub>x</sub>, and 3p<sub>y</sub> orbitals contribute mainly to the Si-H bonds: the major interaction between the silicon and the ring involves silicon 3p<sub>z</sub> only; similarly in ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)SiMe<sub>3</sub>, only 3p<sub>z</sub> plays an important role in the silicon-ring interaction. The energies of the four important molecular orbitals 1A<sub>2</sub>'', E<sub>1</sub>'', 2A<sub>2</sub>'', and E<sub>2</sub>'', are recorded in Table 8, together with those in C<sub>5</sub>H<sub>5</sub><sup>-</sup> itself: of these orbitals only 1A<sub>2</sub>'', and E<sub>1</sub>'', are occupied. It is noteworthy that in ( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)X the binding energies of E<sub>1</sub>'', and E<sub>2</sub>'', are extremely sensitive to the net overall charge on the ring, but that the difference between them is almost constant at a value slightly smaller than that for C<sub>5</sub>H<sub>5</sub><sup>-</sup>. On the other hand the separation between 1A<sub>2</sub>'', and 2A<sub>2</sub>'', varies from 12.84 eV when X = H, via 12.20 eV when X = SiH<sub>3</sub>, to only 10.66 eV when X = SiMe<sub>3</sub>. It

TABLE 8

PERTURBATION OF  $\pi$  MOLECULAR ORBITAL ENERGIES (eV) IN  $C_5H_5^-$  BY AXIAL SUBSTITUENTS

$C_5H_5^-$		$(\eta^5-C_5H_5)H$	$(\eta^5-C_5H_5)SiH_3$	$(\eta^5-C_5H_5)SiMe_3$
$E_2''$	+7.938	$E_2''$ +1.252	+0.879	+1.339
$E_1''$	-2.137	$2A_2''$ -0.962	-1.680	-1.617
$A_2''$	-6.110	$E_1''$ -8.428	-8.635	-8.272
		$1A_2''$ -13.802	-13.879	-12.278

was demonstrated earlier on purely geometrical grounds that the bonding in  $(\eta^5-C_5H_5)X$  was least ionic for  $X = H$  and most ionic for  $X = SiMe_3$ , and the axial bonding eigenvalues support the geometrical deductions entirely. For a wholly ionic interaction, the  $1A_2''-E_1''$  gap would be 3.97 eV as found in  $C_5H_5^-$ ; in the present series this latter gap takes the values: 5.37 eV ( $X = H$ ), 5.24 eV ( $X = SiH_3$ ) and 4.01 eV ( $X = SiMe_3$ ).

The  $\pi$  interactions involving the  $E_1''$  orbital of the ring are small; it is important to note that those substituents which form stable  $\eta^5$ -cyclopentadienides are all capable of forming strong  $\pi$  interactions of  $E_1''$  symmetry, involving vacant  $np_\pi$  orbitals in beryllium, tin(II), and lead(II), and  $nd_\pi$  orbitals in transition metals. If silicon is to form stable  $\eta^5$ -cyclopentadienides, a  $\pi$  interaction is essential so that the substituent  $X$  in  $SiX_3$  must be a strong electron sink.

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