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THE ELECTRONIC STRUCTURE OF ORGANOSILICON COMPOUNDS

III *. ITERATIVE MAXIMUM OVERLAP CALCULATIONS ON SOME CYCLIC AND POLYCYCLIC SILANES

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Summary

The electronic structures of a large number of cyclic and polycyclic silanes were investigated by the iterative maximum overlap approximation (IMOA) approach. The angular strain energy in small silacarbocycles is discussed in terms of the hybrid sp^n contents and the deviation angles from Si—C and C—C bond vectors. Several subtle changes following insertion of two spiro-annelated cyclopropyl rings to silacyclopropane are rationalized in terms of a considerable rehybridization of the silicon and spiro-junction carbon atoms. The calculated geometries are compared with available experimental data. Theoretical estimates of bond and dihedral angles are in good accordance with the measured values. The calculated interatomic distances are, however, less accurate. The calculated heats of formation of the examined compounds and the J(Si—H) and J(Si—C) spin—spin coupling constants for the directly bonded nuclei are briefly discussed. The calculated heats of formation are consistent with those derived by the MINDO/3 method.

Introduction

Cyclic organosilanes have been much studied in recent years and the elusive silacyclopropane and related molecules containing silacyclopropane rings were recently successfully synthesized by Seyferth and his coworkers [1,2]. Since strained systems have an important role in chemistry because of their excep-

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* For part II see ref. 7.

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tionally high reactivity we performed maximum overlap approximation (MOA) calculations on some small cyclic and polycyclic silanes. This method proved very useful in discussing angular strain in hydrocarbons [3,4], and the hybrid orbitals and the deviation angles obtained by the MOA method can be expected to shed some light on the bonding in silacarbocycles. In the first part of our work the MOA method was applied to molecules possessing characteristic Si—C bonds which could be roughly classified as sp^3—sp^2, sp^3—sp, etc. Then, the iterative version of the maximum overlap method (IMOA) for silicon is applied by using the correlation between the calculated S(Si—C) overlap integrals and the corresponding experimental interatomic distances. This approach, which enables prediction of molecular geometry, was employed for all the molecules studied. The calculated bond lengths and bond angles are compared with the available experimental results and the electronic structure of the considered compounds is discussed in terms of the hybrid orbitals.

Outline of the method

The details of the MOA method have been published elsewhere [5]. The method is based on the notion that an atom retains its identity within a molecule. Consequently, it is tacitly assumed that the electronic wavefunctions of an atom are only slightly disturbed. The influence of the neighbouring atoms is reflected in mixing of the nearly degenerate atomic orbitals. The resulting hybrid orbitals possess relevant directional properties. They are of the form:

$$\psi_{Ai} = a_{Ai}(ns) + (1 - a_{Ai}^2)^{1/2}(np)_i \qquad (1)$$

where A is the host nucleus, n stands for the principal quantum number and a_{Ai} denotes a mixing parameter ranging generally from 0 to 1. It is supposed that the hybrid orbitals placed on the same atom are mutually orthogonal. This condition provides additional equations which should be fulfilled:

$$a_{Ai}a_{Aj} + (1 - a_{Ai}{}^2)^{1/2}\,(1 - a_{Aj}{}^2)^{1/2}\cos\vartheta_{ij} = 0 \qquad (2)$$

where ϑ_{ij} is an angle between the symmetry axes of the hybrids Ψ_{Ai} and Ψ_{Aj}, if there is no bending relative to the internuclear line. This is the case in acyclic molecules. However, in small ring compounds bent bonds necessarily appear and the interhybrid angle does not coincide with the geometrical one. They are related by the following formula:

$$\vartheta_{Aij,BC} = \vartheta_{ABC} + \delta_{iB} + \delta_{jC} \qquad (3)$$

The geometrical angle is denoted here by ϑ_{ABC}. The deviation angles of the hybrids Ψ_{Ai} and Ψ_{Bj} from the straight lines $\overline{AB}$ and $\overline{AC}$ passing through the nuclei in question are given by δ_{iB} and δ_{jC}, respectively. Thus the (np) orbitals can be resolved into the components parallel and perpendicular to the bond components:

$$(np)_{Ai} = \cos\delta_{iB}(np)_{\parallel} + \sin\delta_{iB}(np)_{\perp} \qquad (4)$$

and one can distinguish between the σ and π type of overlap, or in the words σ and π types of interaction. The hybridization parameters a_{Ai} are varied until a maximum is attained for the sum of bond overlaps:

$$E_b = \sum_{A-B} k_{AB} S_{AB} \qquad (5)$$

the summation being extended over all the bonds in a molecule. The constants k_{AB} are the weighting factors which take into account the difference in bond energy for different bonds. Expression 5 is based on Mulliken's analysis of the resonance energy term $-2\beta/(1 + S)$ which appears in the molecular orbitals treatment of diatomic molecules [6]. It turned out that the heats of atomization could be calculated with a satisfactory accuracy if the resonance integral β were set equal to

$$\beta = -(1/2)\, PSI \qquad (6)$$

where P is an empirical parameter, S is the overlap integral between the atomic orbitals contributing in bond formation and I is their average ionization potential. The energy of the covalent bond A—B is given then by

$$E_{AB} = P_{AB}\, S_{AB}\, I_{AB}/(1 + S_{AB}) \qquad (7)$$

It appears that the adjustable empirical parameter P_{AB} is approximately a constant, being roughly unity for most σ bonds. If the overlap integral S_{AB} is neglected in the denominator in formula 7, and the product $P_{AB} I_{AB}$ is written as a new constant, k_{AB}, one obtains relationship 5. We shall further assume that the parameters k_{AB} depend only on the nature of the constituent atoms A and B and some special bonding features, e.g. existence of bent bonds (vide infra). In other words, we shall try to keep the number of adjustable parameters at a minimum. The choice of these weighting factors was thoroughly discussed in the previous paper [7]. We here give their values (in kcal mol^{-1}): k(C—C) 121, k(C—H) 136, k(C—Si) 103.4, k(Si—Si) 65.9 and k(Si—H) 105.9. The atomic basis set is formed by using Clementi double ζ atomic wave-functions [8]. The optimization of the hybridization parameters and bond angles is based on the simplex algorithm [9].

Results and discussion

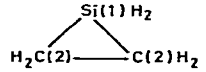
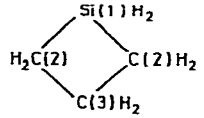
The MOA method was applied to methyl-substituted silanes, vinylsilane, trimethylsilylacetylene, silacyclopropane and silacyclobutane. The calculated hybridization parameters and the corresponding overlap integrals are listed in Table 1. The C—Si interatomic distances are seen to be larger if the p-character of the hybrids forming the bond in question is increased. The cyclopropene is an exception to that rule. Its C—Si bond length of 1.826 Å is unusually short. This feature can be rationalized in terms of the extremely large bending of the hybrid orbitals describing three-membered rings [10,11]. The least-squares fit method yields the following correlation between the C—Si bond distances and the corresponding overlap integrals

$$d(\text{C—Si}) = [-0.775\, S(\text{C—Si})^{\sigma}(b) - 0.113\, S(\text{C—Si})^{\pi}(b) + 2.366]\,\text{Å} \qquad (8)$$

where $S(\text{C—Si})^{\sigma}(b)$ and $S(\text{C—Si})^{\pi}(b)$ refer, respectively, to the σ and π type of overlap in the strained C—Si bond. If the C—Si bond is axially symmetric, the

TABLE 1

THE HYBRIDIZATION PARAMETERS AND THE CORRESPONDING OVERLAP INTEGRALS FOR SOME CHARACTERISTIC Si—C BONDS AS CALCULATED BY THE MAXIMUM OVERLAP APPROXIMATION

Molecule	Bond A—B	Hybridization n_A—n_B	Overlapping		Deviation angles (°)	Exp. bond lengths (Å)
			σ	π		
$H_3Si(1)$—$C(2)H=C(3)H_2$	Si(1)—C(2)	2.70—2.10	0.665	0	—	1.853 [32]
	C(2)—C(3)	1.72—1.68	0.764	0	—	1.347
	Si(1)—H	3.11—0	0.727	0	—	1.475
	C(2)—H	2.22—0	0.736	0	—	1.094
	C(3)—H	2.19—0	0.736	0	—	1.097
$(H_3C(4))_3Si(1)$—$C(2)\equiv C(3)H$	Si(1)—C(2)	3.06—1.11	0.699	0	—	1.825 [33]
	Si(1)—C(4)	2.98—3.11	0.635	0	—	1.865
	C(2)—C(3)	0.90—0.79	0.856	0	—	1.20
	C(3)—H	1.26—0	0.775	0	—	1.05
	C(4)—H	2.97—0	0.720	0	—	1.10
 	Si(1)—C(2)	3.50—3.64	0.540	0.046	δ_{12} 28.8	1.826[a]
	C(2)—C(2)	3.43—3.43	0.621	0.013	δ_{21} 26.5	1.520
	Si(1)—H	2.60—0	0.729	0	δ_{22} 14.5	1.480
	C(2)—H	2.56—0	0.734	0	—	1.082
 	Si(1)—C(2)	3.19—3.11	0.607	0.010	δ_{12} 13.8	1.895 [34]
	C(2)—C(3)	3.48—3.26	0.624	0.001	δ_{21} 12.6	1.600
	Si(1)—H	2.83—0	0.857	0	δ_{23} 5.6	1.496
	C(2)—H	2.75—0	0.706	0	δ_{32} 3.8	1.143
	C(3)—H	2.77—0	0.706	0	—	1.143
CH_3SiH_3	C—Si	3.16—2.66	0.637	0	—	1.867 [35]
	C—H	2.95—0	0.723	0	—	1.093
	Si—H	3.13—0	0.723	0	—	1.485
$(CH_3)_2SiH_2$	C—Si	3.15—2.79	0.636	0	—	1.871 [35]
	C—H	2.95—0	0.722	0	—	1.093
	Si—H	3.24—0	0.722	0	—	1.485
$(CH_3)_3SiH$	C—Si	3.14—2.89	0.634	0	—	1.873 [35]
	C—H	2.95—0	0.722	0	—	1.09
	Si—H	3.37—0	0.720	0	—	1.48
$(CH_3)_4Si$	C—Si	3.18—3.00	0.629	0	—	1.888 [35]
	C—H	2.94—0	0.720	0	—	1.10

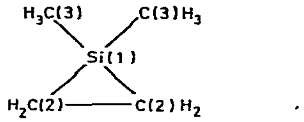
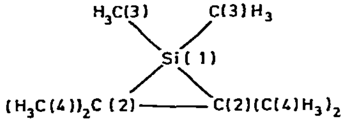
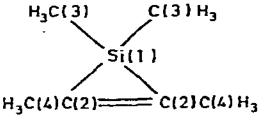
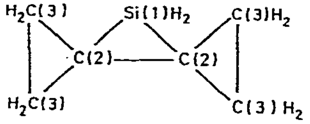
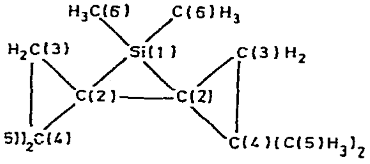
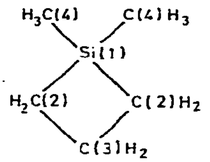
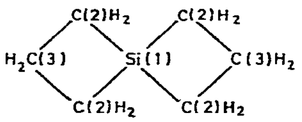
[a] Based on the geometry determined for dimethyldispiro(bicyclo[4.1.0]heptane-7,2′-silacyclopropane-3′,7″-bicyclo[4.1.0]heptane) [18].

overlap $S(C—Si)^{\pi}(b)$ is zero and the second term in formula 8 disappears. The shortening of the C—Si interatomic distance is taken into account in the separate empirical coefficient of the $S(C—Si)^{\pi}(b)$ overlap integral. It assumes a value of —2.639 Å. The established relationship 8 enables the prediction of bond lengths in silanes in an iterative fashion. The calculation is started by assuming reasonable interatomic distances, and the maximum overlap procedure is carried out. The resulting overlap integrals are substituted in formula 8 along with the relevant correlations for C—C, C=C and C—H bonds published elsewhere [5]. Thus a new set of bond lengths is derived and a new cycle is executed. After that the whole procedure is continued until the self-consistency between the input and output bond distances is obtained. This is the essence of the iterative maximum overlap (IMOA) method. It follows that the IMOA method is the maximum overlap type of calculation constrained to obey empirical bond length/bond overlap correlations. The IMOA approach was applied to a number of silacarbocyclic compounds and the calculated hybridization parameters, deviation angles of hybrids from the straight lines connecting neighbouring nuclei and the bond overlap integrals are listed in Table 2. Since the experimental geometries for allylsilane and tetravinylsilane have recently become available [12,13] we also give the IMOA results for these two molecules. It will be seen that the silicon atom undergoes a considerable rehybridization in small three- and four-membered rings. The hybrid orbitals describing ring bonds possess very high *p*-character. Consistent with the increased *p*-character of the hybrids in the small rings are their large deviation angles and low *S*(Si—C) and *S*(C—Si) overlap integrals. These features represent a simple quantum-mechanical explanation of the Baeyer angular strain [3,4]. It is noteworthy that the hybrid orbitals of the silicon atom have larger *p*-contents and slightly higher deviation angles in silacyclopropane and silacyclobutane than does the carbon atom of the Si—C bond. Furthermore, the average *p*-character as well as the deviation angles are higher for Si—C bonds than for the homonuclear C—C bond in small silacarbocycles. Thus we conclude that the Si—C bond is highly strained and consequently very reactive, and this is consistent with the experimental observations. It was found that Si—C bonds of the silacyclopropanes, e.g. hexamethylsilirane, dimethyldispiro(bicyclo[4.1.0]heptane-7,2′-silacyclopropane-3,7″-bicyclo[4.1.0]heptane) and methyl derivatives of 7-siladispiro[2.0.2.1]heptane are unusually reactive. They react instantly and exothermally with atmospheric oxygen, water, alcohols, ammonia and carbon tetrachloride [1,2]. This is apparently a consequence of the relatively weak Si—C bond as reflected in the low overlap of the respective hybrid orbitals and the shift of the electron charge density to the outside of the ring where it is exposed to electrophilic attack. It is interesting that the C—C bent bond in silacyclopropane is substantially stronger than that in cyclopropane. The deviation angle of the Ψ(CC) hybrids is dramatically changed from the cyclopropane value of 22.9° [5] to only 14.5° (Table 1). Our results are similar to those of Mollere and Hoffmann [14], who used the extended Hückel theory (EHT) [15]. They found that EHT overlap population of C—C bond in silacyclopropane is greater than that in the parent hydrocarbon, while the Si—C population is considerably smaller. It is worthwhile comparing IMOA and EHT results for spiro compounds. Mollere and Hoffmann [14] found that insertion of two spiro-annulated cyclopropyl groups results in a slight fall of the C—C overlap population in the heterocycle involving the Si atom. On the contrary, the Si—C overlap population is augmented by 16% over its original silacyclopropane value, and now exceeds that of the C—C bond in the analogous carbocycle. It was found that the enhancement of the overlap population and thus of the Si—C bond strength is due to hyperconjugative interaction between the highest occupied Walsh orbitals of the cyclopropyl rings and unoccupied silicon *d*-orbitals of appropriate symmetry. Exclusion of silicon *d*-orbitals from the basis set diminished the above mentioned increase in Si—C overlap population to only ~6%. This residual effect was ascribed to the acceptor capacity of the Si—H antibonding orbitals. It is beyond the scope of this paper to discuss the

(Continued on p. 302)

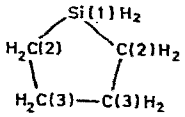
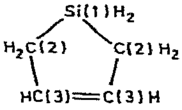
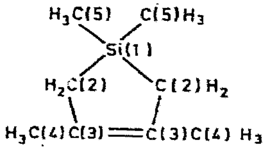
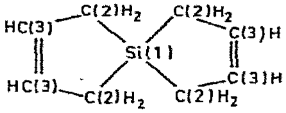
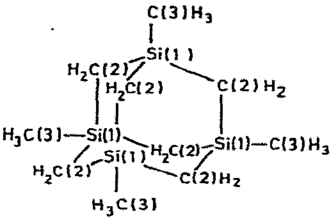
TABLE 2

THE HYBRIDIZATION RATIOS, OVERLAP INTEGRALS AND HYBRIDS' DEVIATION ANGLES FROM THE INTERNUCLEAR STRAIGHT LINES IN SOME CYCLIC AND POLYCYCLIC SILANES AS CALCULATED BY THE IMOA METHOD [a]

Molecule	Bond A—B	Hybridization n_A—n_B	Overlapping		Deviation angles (°)
			σ	π	
	Si(1)—C(2)	3.87—3.53	0.541	0.045	δ_{12} 27.6
	Si(1)—C(3)	2.39—2.95	0.612	0	δ_{21} 26.6
	C(2)—C(2)	3.53—3.53	0.653	0.013	δ_{22} 14.8
	C(2)—H	2.58—0	0.730	0	
	C(3)—H	3.02—0	0.718	0	
	Si(1)—C(2)	3.73—3.37	0.544	0.046	δ_{12} 28.0
	Si(1)—C(3)	2.46—3.15	0.639	0	δ_{21} 27.0
	C(2)—C(2)	3.35—3.35	0.619	0.014	δ_{22} 15.1
	C(2)—C(4)	2.70—3.23	0.660	0	—
	C(3)—H	2.95—0	0.720	0	—
	C(4)—H	2.93—0	0.721	0	—
	Si(1)—C(2)	3.84—2.56	0.546	0.056	δ_{12} 31.0
	Si(1)—C(3)	2.41—3.15	0.639	0	δ_{21} 30.5
	C(2)—C(2)	1.80—1.80	0.723	0.024	δ_{22} 18.8
	C(2)—C(4)	1.76—3.10	0.693	0	—
	C(3)—H	2.95—0	0.720	0	—
	C(4)—H	2.97—0	0.720	0	—
	Si(1)—C(2)	3.46—2.90	0.552	0.049	δ_{12} 29.0
	C(2)—C(2)	2.80—2.80	0.644	0.016	δ_{21} 28.6
	C(2)—C(3)	3.16—3.62	0.589	0.034	δ_{22} 16.3
	C(3)—C(3)	3.75—3.75	0.575	0.023	δ_{23} 23.8
	Si(1)—H	2.63—0	0.729	0	δ_{32} 23.1
	C(3)—H	2.49—0	0.733	0	δ_{33} 23.1
	Si(1)—C(2)	3.73—2.89	0.551	0.048	δ_{12} 28.4
	Si(1)—C(6)	2.47—3.15	0.639	0	δ_{21} 28.5
	C(2)—C(2)	2.82—2.82	0.642	0.016	δ_{22} 16.4
	C(2)—C(3)	3.17—3.63	0.588	0.034	δ_{23} 23.9
	C(2)—C(4)	3.14—3.48	0.592	0.035	δ_{32} 23.2
	C(3)—C(4)	3.69—3.56	0.580	0.034	δ_{34} 23.2
	C(4)—C(5)	2.59—3.21	0.663	0	δ_{42} 23.3
	C(3)—H	2.50—0	0.732	0	—
	C(5)—H	2.93—0	0.720	0	—
	C(6)—H	2.95—0	0.720	0	—
	Si(1)—C(2)	3.51—3.37	0.597	0.010	δ_{12} 14.1
	Si(1)—C(4)	2.59—3.14	0.637	0	δ_{21} 12.4
	C(2)—C(3)	3.34—3.24	0.641	0.001	δ_{23} 4.9
	C(2)—H	2.64—0	0.727	0	δ_{32} 3.2
	C(3)—H	2.79—0	0.725	0	
	C(4)—H	2.96—0	0.720	0	
	Si(1)—C(2)	3.00—3.41	0.599	0.021	δ_{12} 15.4
	C(2)—C(3)	3.33—3.23	0.641	0.001	δ_{21} 12.9
	C(2)—H	2.69—0	0.727	0	δ_{23} 4.9
	C(3)—H	2.80—0	0.724	0	δ_{32} 2.9

(Continued)

TABLE 2 (*Continued*)

Molecule	Bond A—B	Hybridization n_A—n_B	Overlapping σ	Overlapping π	Deviation angles (°)
	Si(1)—C(2)	2.95—3.07	0.631	0.001	δ_{12} 4.2
	C(2)—C(3)	3.30—3.10	0.648	0	δ_{21} 0.3
	C(3)—C(3)	3.10—3.10	0.650	−0.001	δ_{23} 5.3
	Si(1)—H	3.05—0	0.726	0	δ_{32} −2.1
	C(2)—H	3.03—0	0.723	0	δ_{33} −4.5
	C(3)—H	2.91—0	0.721	0	
	Si(1)—C(2)	2.96—3.27	0.623	0.003	δ_{12} 7.4
	C(2)—C(3)	3.09—2.31	0.674	0	δ_{21} 6.2
	C(3)—C(3)	1.65—1.65	0.770	0	δ_{23} 2.5
	Si(1)—H	3.04—0	0.725	0	δ_{32} 1.6
	C(2)—H	2.84—0	0.723	0	δ_{33} 0.7
	C(3)—H	2.12—0	0.744	0	
	Si(1)—C(2)	3.04—3.14	0.627	0.002	δ_{12} 6.1
	Si(1)—C(5)	2.96—3.29	0.629	0	δ_{21} 5.4
	C(2)—C(3)	3.36—2.24	0.671	0	δ_{23} 2.7
	C(3)—C(3)	1.62—1.62	0.772	0	δ_{32} 1.7
	C(3)—C(4)	2.23—3.12	0.676	0	δ_{33} 0.5
	C(2)—H	2.97—0	0.724	0	
	C(4)—H	2.96—0	0.720	0	
	C(5)—H	2.91—0	0.721	0	
	Si(1)—C(2)	3.00—3.25	0.626	0.002	δ_{12} 6.4
	C(2)—C(3)	3.06—2.26	0.677	0	δ_{21} 5.6
	C(3)—C(3)	1.66—1.66	0.769	0	δ_{23} 2.2
	C(2)—H	2.86—0	0.723	0	δ_{32} 1.4
	C(3)—H	2.15—0	0.743	0	δ_{33} 0.4
	Si(1)—C(2)	2.99—3.08	0.633	0	δ_{12} 0
	Si(1)—C(3)	3.04—3.15	0.631	0	δ_{21} −0.2
	C(2)—H	2.92—0	0.721	0	—
	C(3)—H	2.95—0	0.720	0	—
$H_3Si(1)$—$C(2)H_2$—$C(3)H{=}C(4)H_2$	Si(1)—C(2)	2.69—3.09	0.637	0	—
	C(2)—C(3)	3.11—2.26	0.676	0	—
	C(3)=C(4)	1.66—1.68	0.769	0	—
	Si(1)—H	3.12—0	0.725	0	—
	C(2)—H	2.91—0	0.721	0	—
	C(3)—H	2.15—0	0.743	0	—
	C(4)—H	2.19—0	0.742	0	—
$Si(1)[C(2)H{=}C(3)H_2]_4$	Si(1)—C(2)	3.00—2.14	0.660	0	—
	C(2)=C(3)	1.70—1.68	0.767	0	—
	C(2)—H	2.21—0	0.740	0	—
	C(3)—H	2.19—0	0.741	0	—

role of d-orbitals in silicon chemistry * which may well compensate for the inadequacies of the minimum basis set as well as for the inherent approximations of the EHT method. We seek only to provide an alternative explanation for the so-called residual (vide supra) Si—C strengthening effect in spiro compounds. For this purpose we compare the hybrid orbitals in silacyclopropane and 7-siladispiro[2.0.2.1]heptane (Tables 1 and 2). The HCH angle of methylene groups in silacyclopropane is an independent geometrical parameter which can be optimized by the maximum overlap criterion. The hybrids Ψ(CH) describing C—H bonds, assuming the perfect orbital following, are very flexible, and acquire the favourable $sp^{2.56}$ composition. The local symmetry of the carbon atom formed by its nearest neighbours is given by the strongly deformed tetrahedron. In contrast, the CCC angle of the spiro-annulated cyclopropyl ring is rigid because three carbon atoms form an almost equilateral triangle. The neighbouring atoms of the spiro-junction carbon also are arranged on the vertices of the perturbed tetrahedron. However, the perturbation is much weaker than at the corresponding carbon in spirocyclopropane. It is not surprising that the Ψ(CC) hybrid orbitals of the C(2) carbon in 7-siladispiro[2.0.2.1]heptane are roughly of the sp^3 form. Thus Si—C bonds in the spiro compound and silacyclopropane are described by $sp^{3.46}$—$sp^{2.90}$ and $sp^{3.50}$—$sp^{3.64}$ hybridization states, respectively. The former bond has greater average s-character and larger overlap which should lead to an increase in the bond strength. We conclude, therefore, that the augmented Si—C bond energy in silaspiro compounds is due to the rehybridization of the spirojunction carbon atom. An additional stabilization is, of course, possible by the hyperconjugative interaction of Si—H antibonding orbitals and Walsh orbitals of the cyclopropyl rings ** which form pseudo π orbitals as suggested by Mollere and Hoffmann [14]. Since the hybrid orbitals are to a high degree transferable we expect that the results follow the same pattern in related spiro compounds e.g. the spiro-annulated norcaranylidene systems synthesized by Lambert and Seyferth [1]. Their electronic structure was recently discussed exclusively in terms of d-σ and Walsh π orbitals σ hyperconjugation [18]. It should be pointed out that there is a very large difference in thermal stability between hexamethylsilirane and 7-siladispiro[2.0.2.1.]heptane methyl derivatives. The half-life of the latter is about 7 days at 65°C while the half-life of the hexamethylsilacyclopropane in THF solution is only 5 h at 63°C [19]. This finding can be at least partly explained in terms at rehybridization of the spirojunction carbon atoms, following the same chain of arguments as above. Indeed, the central ring involving the heteroatom in the dispiro compound possess substantially higher s-orbital content than its counterpart in hexamethylsilirane (Table 2). Further strengthening of the Si—C bond is expected in the tetramethylsilacyclopropene ring, where the Ψ(CSi) hybrid located on the ring carbon atom and directed toward silicon is of the $sp^{2.56}$ form. The hybrid orbitals describing the four-membered ring in 1,1-dimethylsilacyclobutane are all above the canonical sp^3 hybridization state. The corresponding overlap integrals are

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* The reader is referred to a review article [16].

** In our interpretation it is the interaction between the Si—H antibonding orbitals and $sp^{3.16}$ hybrids which are directed from C(2) toward C(3) in the cyclopropyl ring. The near equivalence of the Walsh orbitals and hybrid orbitals forming C—C bonds in cyclopropane was discussed [17].

*** For an extensive review the reader is referred to ref. 21.

smaller than, for example, in ethane and silane [5,7]. The deviation angles are roughly 13° and 4° for Si—C and C—C bonds, respectively, indicating a moderate amount of the angular strain. This is consistent with the experimental results of Sommer and Baum [20] who prepared the first silacyclobutane. They found that the endocyclic Si—C bonds of 1,1-dimethylsilacyclobutane are more reactive than those of the larger silacarbocycles. An enhancement of the Si—C bond strength could be predicted for 4-silaspiro[3.3]heptane, where the sp^3 hybridization of the central Si atom is determined by the symmetry. An increase in the average *s*-character and in Si—C overlap is found as expected, although the increase of the latter is small. A review of the relevant data for silacyclopentane shows absence of any significant amount of angular strain. It is interesting that the hybrid orbitals at the site C(3) are bent inside the molecule. The deviation angles of the hybrids belonging to the C(2)—C(3) bond alternate in sign forming thus an *anti*-bent bond. However, the absolute values of these angles are very small, and could be artifacts of the method applied. There is an increase in the strength of the C(2)—C(3) bond in silacyclopentene due to the neighbouring double bond. A small amount of strain could be ascribed to Si—C bonds due to the hybrids' deviations of δ_{12} 7.4° and δ_{21} 6.2°. It is instructive to compare the double bonds in tetramethylsilacyclopropene and silacyclopentene. While the former provides an example of a strained double bond with considerable hybrids' deviation angles of 18.8°, the latter is completely strain-free showing high percentage of *s*-orbitals ($sp^{1.65}$—$sp^{1.65}$) and an appreciable overlap of 0.770. It can be compared with similar localized C=C double bonds found in 1,1-dimethyl-1-sila-3-cyclopentane, 5-silaspiro[4.4]nona-2,7-diene, allylsilane and tetravinylsilane. Although it is generally assumed that the double bond is described by sp^2 hybridization, one observes a large shift in *s*-character toward the *sp* canonical state. This is not surprising because the sp^2 hybridization assumes D_{3h} symmetry of the local field formed by the nearest neighbours. In fact the D_{3h} local symmetry is completely destroyed for carbon atoms forming a C=C double bond and all three hybrids differ widely, which is in accord with C_s symmetry. This flexibility of the variable hybridization model enables a fair description of many physical and chemical properties of localized bonds [21]. Another almost strain-free molecule is 1,3,5,7-tetramethyltetrasilaadamantane. The hybridization parameters are very close to sp^3 value and their deviation angles are practically zero. The main features of the electronic structure of this molecule should be very close to those of adamantane [22]. The Si(1)—C(2) bond is near to the sp^3—sp^3 type. On the other hand, an example of an sp^3—sp^2 bond between silicon and carbon is found in tetravinylsilane. Other data presented in Table 2 speak for themselves.

Bond lengths and angles

Rationalization of molecular geometry is the first aim of theoretical chemistry. It is, in the same time, the first step in understanding the electronic structure of molecules. Indeed, many characteristics of chemical bonding are reflected in interatomic distances and their spatial arrangement. In our approach the changes in CC and SiC localized bond distances are ascribed to the variation of hybridization states of the participating atoms [5]. Delocalized systems can be encompassed by including the Hückel method for π electrons [23]. The bond lengths and angles calculated by the IMOA method are compared with available experimental data in Table 3. MINDO/3 results by Dewar et al. [24] are also included. Inspection of the results shows that the bond angles are in very good accordance with experiment. The agreement with measurements for bond distances is, however, only fair, and falls behind the accuracy obtained for hydrocarbons [5,23]. No doubt this is a consequence of the small set of the representative molecules available for parametrization (Table 1). Therefore, the predicted bond lengths of the compounds listed in Table 3 must be considered as tentative estimates. On the other hand, the available experimental data refer mostly to electron diffraction and X-ray measurements, while the empirical parameters for CC and CH bonds taken from hydrocarbons are related more closely to microwave values. It is not surprising that there is a good agreement with experiment for silacyclopentane where the structure was determined by microwave spectroscopy [25]. Needless to say, future experimental work and a more abundant set of consistent data on Si—C bond distances will lead to better parametrization of the IMOA method and consequently to greater reliability of this approach. One of the striking features of the results is the increase in the C—C bond length in the silacyclopropane ring relative to the hydrocarbon value (1.510 Å). Such a lengthening was explained by the back-donation of the heteroatom into the antibonding "π^*" localized orbital of the C—C moiety [18]. This interpretation was based on the Dewar—Chatt model of the π bonding of olefins to transition metals [26—28]. In our variable hybridization model this increase is ascribed to a decrease in the deviation angle δ_{22}, which falls from the cyclopropane value (22.9°) to 14.5°. Therefore it turns out that the characteristic shortening of highly strained C—C bonds in three-membered rings [11] is substantially smaller for silacyclopropane than for cyclopropane. One can also easily explain the increased bending of the two CH_2 groups away from the heteroatom on the same footing. For this purpose we shall consider the angle between the CC bond vector and the axis bisecting the HCH angle (Fig. 1) denoted by β. The latter is given by the sum of the angles δ_{22} and α

$$\beta = \alpha + \delta_{22} \qquad (9)$$

By using spherical trigonometry one readily obtains the relationship:

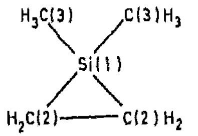
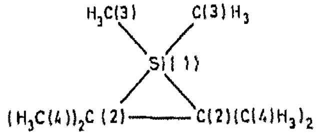
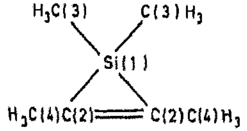
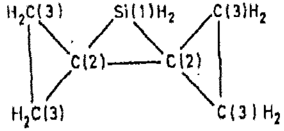
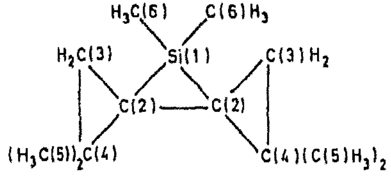
$$\cos\alpha = \cos\vartheta(C_2 14, H_1 C_2)/\cos(\vartheta(C_2 12, H_1 H_2)/2) \qquad (10)$$

Simple arithmetic yields $\beta = 142.5°$ for silacyclopropane, which should be compared with the cyclopropane value of 150°. Thus the "bent back" angle for silacyclopropane is 7.5°. It is roughly equal to the difference in δ_{22} bending angles between these two molecules (22.9° — 14.5° = 8.4°). Therefore, it follows that the "bent back" effect is a consequence of a decrease in Ψ(C—C) hybrid bending in silacyclopropane. The C—C bond of the central ring in dispiro compounds is slightly shortened due to a small increase in δ_{22} bending angle and in *s*-character. The same conclusion applies to Si—C bond lengths in 7-dispiro-[2.0.2.1]heptane and 1,1,5,5,7,7-hexamethyl-7-siladispiro[2.0.2.1]heptane. The calculated geometries of acyclic molecules allylsilane and tetravinylsilane are in good agreement with the experimental data. The electron diffraction data for C—H bond distances in tetravinylsilane are somewhat too long for the sp^2-H type of covalent bonding. This is, however, a general feature of the electron

(Continued on p. 308)

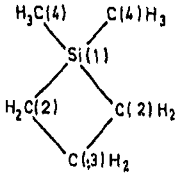
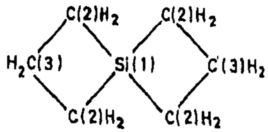
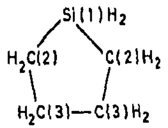
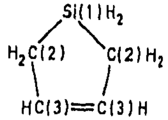
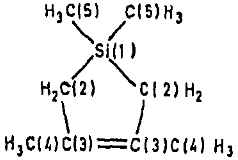
TABLE 3

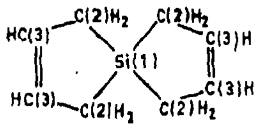
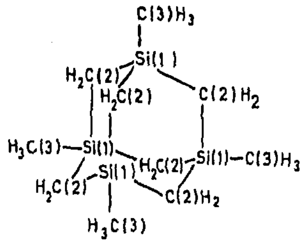
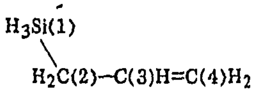
THE CALCULATED INTERATOMIC DISTANCES AND BOND ANGLES IN SOME CYCLIC AND POLYCYCLIC SILANES BY THE ITERATIVE MAXIMUM OVERLAP METHOD

Molecule	Interatomic distances (Å)			Bond angles (°)		
		Calcd.	Exp.		Calcd.	Exp.
	Si(1)—C(2)	1.829		C(2)Si(1)C(2)	49.9	
	Si(1)—C(3)	1.860		Si(1)C(2)C(2)	65.1	
	C(2)—C(2)	1.540		HC(2)H	112.8	
	C(2)—H	1.091		HC(3)H	109.4	
	C(3)—H	1.102				
	Si(1)—C(2)	1.824		C(2)Si(1)C(2)	49.6	
	Si(1)—C(3)	1.871		Si(1)C(2)C(2)	65.2	
	C(2)—C(2)	1.530		HC(3)H	109.8	
	C(2)—C(4)	1.528		HC(4)H	109.9	
	C(3)—H	1.100				
	C(4)—H	1.100				
	Si(1)—C(2)	1.795		C(2)Si(1)C(2)	43.1	
	Si(1)—C(3)	1.871		Si(1)C(2)C(2)	68.4	
	C(2)—C(2)	1.321		HC(3)H	109.7	
	C(2)—C(4)	1.490		HC(4)H	109.8	
	C(3)—H	1.100				
	C(4)—H	1.101				
	Si(1)—C(2)	1.808	1.826 [a]	C(2)Si(1)C(2)	48.8 [a]	
	C(2)—C(2)	1.494	1.520	Si(1)C(2)C(2)	65.6	
	C(2)—C(3)	1.520	1.511	C(3)C(2)C(3)	59.6	
	C(3)—C(3)	1.500		C(2)C(3)C(3)	60.9	
	C(3)—H	1.089		HSi(1)H	112.3	
				HC(3)H	113.8	
	Si(1)—C(2)	1.811	1.826 [a]	C(2)Si(1)C(2)	48.8	49.2 [a]
	Si(1)—C(6)	1.871	1.857	Si(1)C(2)C(2)	65.6	65.4
	C(2)—C(2)	1.495	1.520	C(3)C(2)C(4)	60.6	60.7
	C(2)—C(3)	1.500	1.511	C(2)C(3)C(4)	59.5	59.6
	C(2)—C(4)	1.495	1.511	C(3)C(4)C(2)	59.8	59.6
	C(3)—C(4)	1.513		HC(3)H	110.1	
	C(4)—C(5)	1.525		HC(5)H	112.6	
	C(3)—H	1.090		HC(6)H	112.6	
	C(5)—H	1.100				
	C(6)—H	1.100				

(Continued)

TABLE 3 (*Continued*)

Molecule	Interatomic distances (Å)			Bond angles (°)		
		Calcd.	Exp.		Calcd.	Exp.
	Si(1)—C(2)	1,902	1,890 [b]	C(2)Si(1)C(2)	78,3	
	Si(1)—C(4)	1,872	1,871	Si(1)C(2)C(3)	90,0	
	C(2)—C(3)	1,549	1,532	C(2)C(3)C(2)	101,6	102,6 [b]
	C(2)—H	1,094		HC(2)H	112,3	
	C(3)—H	1,096		HC(3)H	111,0	
	C(4)—H	1,100		HC(4)H	109,8	
	Si(1)—C(2)	1,900	1,898 [36]	C(2)Si(1)C(2)	78,8	80,6 [36]
	C(2)—C(3)	1,548	1,579	Si(1)C(2)C(3)	89,5	
	C(2)—H	1,094	1,111	C(2)C(3)C(2)	102,2	
	C(3)—H	1,097	1,111	HC(2)H	111,8	112,0
				HC(3)H	111,0	
	Si(1)—C(2)	1,877	1,87 [25]	C(2)Si(1)C(2)	99,2	96,7 [25]
	C(2)—C(3)	1,543	1,54	Si(1)C(2)C(3)	104,0	105,1
	C(3)—C(3)	1,537	1,54	C(2)C(3)C(2)	115,4	113,7
	C(2)—H	1,098	1,09	HSi(1)H	109,1	
	C(3)—H	1,099	1,09	HC(2)H	109,3	
				HC(3)H	110,1	
				τ	165,9	159
	Si(1)—C(2)	1,883	1,894 [37]	C(2)Si(1)C(2)	95,0	95,7 + 1,2 [37]
	C(2)—C(3)	1,511	1,524	Si(1)C(2)C(3)	108,9	109,9
	C(3)—C(3)	1,334	1,329	C(2)C(3)C(3)	118,5	119,0
	C(2)—H	1,098	1,111	HSi(1)H	109,2	
	C(3)—H	1,080	1,111	HC(2)H	110,6	
				HC(3)C(3)	122,4	
				τ	163,2	164,3 ± 7,7
	Si(1)—C(2)	1,880		C(2)Si(1)C(2)	97,4	
	Si(1)—C(5)	1,879		Si(1)C(2)C(3)	100,1	
	C(2)—C(3)	1,515		C(2)C(3)C(3)	119,8	
	C(3)—C(3)	1,332		HC(2)H	109,7	
	C(3)—C(4)	1,510		HC(4)H	109,7	
	C(2)—H	1,096		HC(5)H	110,0	
	C(4)—H	1,100		τ	160,6	
	C(5)—H	1,010				

	Si(1)—C(2)	1.882		Si(1)C(2)C(3)	100.9	
	C(2)—C(3)	1.509		C(2)Si(1)C(2)	96.7	
	C(3)—C(3)	1.335		C(2)C(3)C(3)	119.3	
	C(2)—H	1.098		HC(2)H	110.5	
	C(3)—H	1.080		HC(3)C(3)	122.3	
				τ	163.5	
	Si(1)—C(2)	1.875	1.866 [38]	C(2)Si(1)C(2)	109.5	107.8 [38]
	Si(1)—C(3)	1.877	1.889	Si(1)C(2)Si(1)	110.3	112.7
	C(2)—H	1.099	1.05	HC(3)H		
	C(3)—H	1.100	1.07	HC(2)H		
 $H_3Si(1)$—$H_2C(2)$—$C(3)H{=}C(4)H_2$	Si(1)—C(2)	1.872	1.875 [12]	HSi(1)H	108.7	
	C(2)—C(3)	1.509	1.500	HC(2)H	110.1	
	C(3)=C(4)	1.332	1.325	HC(4)H	117.6	
	C(2)—H	1.099	1.090			
	C(3)—H	1.080	1.090			
	C(4)—H	1.081	1.090			
$Si(1)[C(2)H{=}C(3)H_2]_4$	Si(1)—C(2)	1.855	1.855 [13]	SiCC	121.6	124.0 [13]
	C(2)=C(3)	1.334	1.355	CSiC	109.5	109.5
	C(2)—H	1.083	1.118	SiCH	117.4	118.4
	C(3)—H	1.082	1.118	CCH	121.4	121.4

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[a] Based on the geometry determined for dimethyldispiro(bicyclo[4.1.0]heptane-7,2′-silacyclopropane-3′,7″-bicyclo[4.1.0]heptane) [18]. [b] MINDO/3 geometry [24].

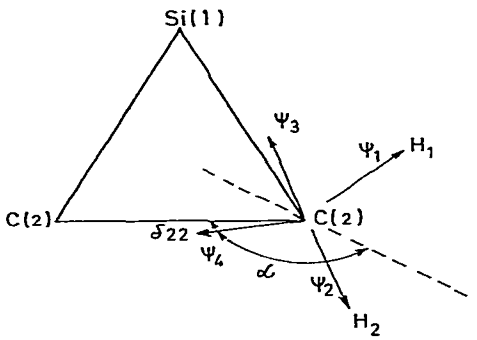

Fig. 1. Schematic representation of the "back bending" angle $\alpha + \delta_{22}$ of the methylene group in silacyclopropane.

diffraction technique, which always yields higher values for C—H interatomic distances than do microwave studies. Finally, the dihedral angles of the five-membered skeletons in silacyclopentane and silacyclopentene are in satisfacory agreement with experiment.

Heats of formation

The standard heat of formation ΔH_f^T of a compound A_mB_n is defined as the change in heat content upon its formation from the constituent atoms:

$$\frac{m}{i} A_i + \frac{n}{j} B_j \rightarrow A_m B_n$$

where the process is carried out isothermally at the constant temperature T. It is tacitly assumed here that the atoms A_i and B_j and also the final product A_mB_n are in their standard thermodynamic states and in the gas phase. The heat of formation is related to the electronic binding energy by the formula:

$$-\Delta H_f^T = E_B - \sum_i \tfrac{1}{2} h\nu_i + \int_0^T C_p \mathrm{d}T \qquad (11)$$

where ν_i is the characteristic frequency of the i-th normal mode of vibration and C_p is the specific heat at constant pressure. The values of ν_i and C_p are, unfortunately, lacking for most cases. Therefore, it is usual to assume that they do not vary too much in a class of similar molecules, and we neglect them in the following discussion. The binding energy is usually broken down into a sum of bond energy contributions, which in turn, are linearly related to overlap integrals [4]. Therefore one can try to fit the experimental heats of formation by the expression:

$$\Delta H_f^{298°} = \sum_{A—B} (k_{AB} S_{AB} + l_{AB}) \qquad (12)$$

where the sum encompasses all directly bonded atoms. The following values for constants k_{AB} and l_{AB} were obtained by the linear least-squares method (at room temperature) (in kcal mol^{-1}): k(SiSi) 289.6, k(SiC) 146.6, k(SiH) —226.2, l(SiSi) —187.4, l(SiC) —90.3, l(SiH) 165.0, k(CH) —18.8, k(C—C)$^\sigma$ (b) —126.9, k(C—C)$^\pi$ (b) 685.4, k(C=C)$^\sigma$ (b) —49.8, k(C=C)$^\pi$ (b) —9.9, l(CH) 9.4 and l(CC) 86.1, where b denotes that the empirical parameters in question refer to bent

TABLE 4

COMPARISON BETWEEN THE IMOA AND MINDO/3 HEATS OF FORMATION FOR SOME SILANES

Molecule	IMOA	MINDO/3
Silacyclobutane	—13.2	—10.6
1,1-Dimethylsilacyclobutane	—35.9	—40.1
4-Silaspiro[3.3]heptane	—5.8	
Silacyclopentane	—14.3	
1,1,3,4-Tetramethyl-1-sila-3-cyclcpentene	—26.1	
1-Sila-3-cyclopentene	10.8	
5-Silaspiro[4.4]nona-2,7-diene	16.4	
1,3,5,7-Tetramethyltetrasilaadamantane	—60.2	
Vinylsilane	14.9	8.6

bonds [7]. Each bond is generally treated as a bent bond. If the particular bond is axially symmetric, the overlap integral $S(\mathrm{CC})^{\pi}$ (b) is zero and its contribution to the heat of formation $\Delta H_f^{298°}$ vanishes. The advantage of this valence bond approach is that one gets some insight into the individual bond contributions to ΔH_f^T. The IMOA heats of formation for some of the silanes studied here are compared with available MINDO/3 results in Table 4. The experimental data are unfortunately nonexistent, to the best of our knowledge. We believe that the IMOA $\Delta H_f^{298°}$ values are quite reliable because of good agreement obtained for acyclic silanes in previous work [7].

The spin—spin coupling constants

The spin—spin coupling constants of the directly bonded nuclei provide a sensitive probe of the *s*-characters of the participating hybrids. Since there are no experimental data we shall only briefly discuss the main features of the IMOA results by using the formulae [7,29]:

$$J(\mathrm{Si—H}) = 725.0[1/(n(\mathrm{Si—H}) + 1)] + 15.9 \text{ Hz}$$

and

$$J(\mathrm{Si—C}) = 555.4[1/(n(\mathrm{Si—C}) + 1)(n(\mathrm{C—Si}) + 1)] + 18.2 \text{ Hz}$$

The Si—C coupling constants span a relatively small range [30] because the silicon atoms in sp^2 and sp^1 states are still elusive. We predict relatively large J(Si—H) values in silacyclopropane and silacyclobutane, they are 217.3 and 205.2 Hz, respectively. The increase over the value found for the sp^3 state in disilane (198.2 Hz) is a consequence of the increased *s*-character of Ψ(Si—H) hybrids. In contrast, the J(Si—C) constants should be considerably smaller in small rings due to the increased *p*-character of the endocyclic bonds. The calculated J(Si—C) values are 44.8 and 50.5 Hz in silacyclopropane and silacyclobutane, respectively. The J(Si—C) coupling constant corresponding to Si(sp^3)—C(sp^2) type of bonding found for tetravinylsilane is 62.4 Hz, and this compares favourably with the experimental value of 66.5 Hz found in trimethylphenylsilane [30]. Analogously, the J(Si—C) coupling constant for the Si—C bond described by sp^3—sp^1 canonical states which appears in 1,1,1-trimethylsilylacetylene is predicted to be 83.0 Hz. It is in excellent agreement with the experimental value of 83.6 Hz for the related compound 1,1,1-trimethylsilylphenylacetylene [30]. Finally, we note that an analysis of *J*(C—H) and *J*(C—C) coupling constants can be made along the same lines by using the available empirical correlations [31].

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