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Electronic Structure of Organosilicon Compounds. 2. Maximum Overlap Approximation Calculations of Hybridization in Some Silanes

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Received November 4, 1976 AIC607985

The electronic structure of some silanes is discussed in terms of the hybridization parameters obtained by the application of the MOA method. The calculated J(Si–H) spin–spin coupling constants and bond angles are in fair agreement with available experimental data. The predicted heats of formation reproduce nicely several experimentally observed features. It was found that the hybrid orbitals describing similar chemical environments are to the high degree transferable. Therefore, the calculated hybridization parameters can serve for an approximate description of higher silanes.

Introduction

Although silicon is in the same column of the periodic system as carbon, the properties of the two elements differ widely. For example, silanes are extremely air sensitive. On the other hand, the Si–O–Si linkage is particularly strong, being one of the most important inorganic structural groups. It is therefore not surprising that in the last two decades considerable attention has been paid to the synthesis and investigation of physical and chemical properties of silicon compounds and particularly of silanes.[1-3] A direct comparison of C–C with Si–Si bonds requires a detailed knowledge of their electronic properties. It is the aim of this paper to report on maximum overlap approximation (MOA) calculations performed on some silanes. Their electronic structure is discussed in terms of the local hybrid orbitals and compared with that of the corresponding hydrocarbon compounds.

Outline of the Calculation

A variable-hybridization model of covalent bonding calculated by the maximum overlap method proved very useful in describing properties of hydrocarbons characterized by localized bonds.[4] Recently, the method was successfully extended to encompass conjugated molecules such as polyenes and their alkylated derivatives.[5] The prerequisite for application of the MOA method is an absence of bonded atoms exhibiting widely different electronegativities. Since the electronegativities (on Pauling's scale) of H, C, and Si are 2.1, 2.5, and 1.8, respectively, one can anticipate that MOA hybrid orbitals will give a fair description of bonding in silanes. It should be also mentioned that the orbital electronegativities of hydrogen, carbon, and silicon, where the latter are in sp^3 hybridization states, are proposed to be 2.21, 2.48, and 2.25, respectively.[6] Furthermore, the group electronegativities of CH_3 and SiH_3 groups are practically the same (vide infra), a fact giving additional justification for the maximum overlap calculations.

The details of the MOA method are given elsewhere.[4] Briefly, the method is based on the intuitive idea that an atom retains its identity within a molecule. Therefore, it is assumed that electronic states of an atom are slightly disturbed and the influence of the neighboring atoms is reflected in mixing of the nearly degenerate atomic levels. Thus hybrid orbitals are formed which possess desirable directional properties. The general form of the hybrid orbital centered on the nucleus A is

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

where n stands for the principal quantum number and a_{Ai} denotes a mixing parameter ranging from 0 to 1. The hybrid orbitals placed on the same atom are orthogonal according to the Pauli principle. This condition imposes a set of equations which determine interhybrid angles

$$a_{Ai}a_{Aj} + (1 - a_{Ai}^2)^{1/2}(1 - a_{Aj}^2)^{1/2} \cos \theta_{ij} = 0 \tag{2}$$

where θ_{ij} is an angle between the symmetry axes of the hybrids Ψ_{Ai} and Ψ_{Aj}. The hybridization parameters a_{Ai} (eq 1 and 2) are not, strictly speaking, determined by the application of the variational theorem. Instead, they are varied until maximum of the bond overlap integrals is achieved

$$E_b = \sum_{A-B} k_{AB}S_{AB} \tag{3}$$

where the summation is extended over all bonds in a molecule. The constant k_{AB} is a weighting factor which takes into account the difference in bond energy for different bonds. Expression 3 deserves some more comments. It is based on Mulliken's analysis of the resonance energy term $-2\beta/(1 + S)$ appearing in the LCAO–MO treatment of simple diatomics.[7] Mulliken has shown that the heats of atomization can be calculated with a good accuracy if the resonance integral is equal to

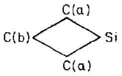
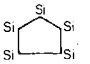
$$\beta = -(1/2)PSI \tag{4}$$

where P is an adjustable empirical parameter, S is the overlap integral between appropriate atomic orbitals participating in a bond formation, and I is their average ionization potential. Then the quantity

$$E_{AB} = P_{AB}S_{AB}I_{AB}/(1 + S_{AB}) \tag{5}$$

is a good measure of the A–B bond energy if the intramolecular charge transfer is not highly pronounced. It turns out that the parameter P does not vary too much being roughly 1 for most σ bonds. If we write the product $P_{AB}I_{AB}$ as a new

Table I. Comparison between the Corresponding Hybridization Parameters in Silanes and Hydrocarbons as Calculated by the MOA Method

Molecule	Bond	X = Si		X = C	
		Hybridizn	Overlap	Hybridizn	Overlap
XH_4	X–H	3.0	0.726	3.0	0.723
XH_3–XH_3	X–X	3.02–3.02	0.678	3.21–3.21	0.648
	X–H	2.99	0.721	2.93	0.718
$H_3X(p)$–$X(s)H_2$–$X(p)H_3$	X(p)–X(s)	3.00–2.97	0.684	3.23–3.16	0.652
	X(p)–H	2.99	0.726	2.93	0.722
	X(s)–H	3.03	0.722	2.85	0.725
X_3C–XH_3	C–X	3.16–2.66	0.637	3.21–3.21	0.648
	C–H	2.95	0.723	2.93	0.718
	X–H	3.13	0.723	2.93	0.718
H_3C–XH_2–CH_3	C–X	3.15–2.79	0.636	3.23–3.16	0.652
	C–H	2.95	0.722	2.93	0.722
	X–H	3.24	0.722	2.85	0.725
$(CH_3)_3X$–H	C–X	3.14–2.89	0.634	3.25–3.05	0.654
	C–H	2.95	0.722	2.92	0.725
	X–H	3.37	0.720	2.86	0.719
$(CH_3)_4X$	C–X	3.18–3.00	0.629	3.24–3.00	0.651
	C–H	2.94	0.720	2.93	0.718
$(CH_3)_3X$–$X(CH_3)_3$	X–X	3.40–3.40	0.667	3.05–3.05	0.650
	C–X	3.24–2.88	0.624	3.22–2.98	0.652
	C–H	2.92	0.721	2.93	0.717
$(CH_3)_3C$–XH_3	C–X	2.92–2.75	0.637	3.24–3.00	0.651
	C–C_{met}	3.03–3.22	0.651		
	C–H	2.93	0.717	2.93	0.718
	X–H	3.09	0.725		
$(H_3C(p)$–$C(s)H_2)_4$	C(s)–X	3.08–3.00	0.631	3.09–3.00	0.656
	C(s)–C(p)	3.20–3.25	0.647	3.16–3.10	0.653
	C(s)–H	2.87	0.721	2.91	0.714
	C(p)–H	2.92	0.720	2.95	0.713
	C(a)–X	3.23–3.27	0.615	3.47–3.47	0.636
	C(a)–C(b)	3.14–3.21	0.632	3.47–3.47	0.636
	C(a)–H	2.83	0.710	2.62	0.739
	C(b)–H	2.81	0.711	2.62	0.739
	X–H	2.76	0.728	2.62	0.739
	X–X	2.99–2.99	0.684	3.28–3.28	0.646
	X–H	3.01	0.722	2.75–2.75	0.736

constant k_{AB} and if the S_{AB} is neglected in the denominator of relation 5, then formula 3 is readily obtained. We shall suppose that the k_{AB} weighting factor depends only on the nature of the constituent atoms A and B in order to keep the number of empirical parameters at minimum. In other words, we shall employ only five weighting factors $k_{C\text{–}H}$, $k_{C\text{–}C}$, $k_{C\text{–}Si}$, $k_{Si\text{–}Si}$, and $k_{Si\text{–}H}$ for silanes. The first two constants are taken from the earlier work on hydrocarbons[8] and they are $k_{C\text{–}C} = 121$ and $k_{C\text{–}H} = 136$ kcal/mol. The weighting factor $k_{C\text{–}Si} = 130.4$ kcal/mol was discussed in a previous paper concerned with the calculation of J(C–Si) spin–spin coupling constants.[9] The remaining factors $k_{Si\text{–}Si}$ and $k_{Si\text{–}H}$ are estimated by using heats of formation of silane and disilane which are 7.3[10] and 19.2 kcal/mol[11] respectively. The ΔH_f values are converted to heats of atomization of these two compounds which correspond to bonding energies. By using the proportionality relationship between bond energies and bond overlap integrals $E_{AB} = k_{AB}S_{AB}$, one obtains $k_{AB} = E^\circ_{AB}/S^\circ_{AB}$ where the degree sign stands for the standard bond AB° used for calibration. By employing Clementi double-ζ atomic functions[12] and assuming sp^3 hybridization in disilane it is easily deduced that $k_{Si\text{–}Si} = 65.9$ and $k_{Si\text{–}H} = 105.9$ (in kcal/mol). In this procedure we use implicitly the concept of average bond energies which is open to criticism. Namely, any breakdown of the heat of atomization to particular bond contributions in polyatomic molecules is arbitrary especially if bonds of different kind are involved. If we deal with a molecule of the type AB_n, where all A–B bonds are equivalent, the average bond energy is defined as $1/n$ times the heat of atomization into A + nB atoms in their ground states. This energy is sometimes quite different from the energy required for the rupture of the first A–B bond.[13] It would be advantageous to use instantaneous bond energies which do not involve the relaxation energies of the forming radicals.[14] Unfortunately, they are not available for organosilanes and we are forced to rely on average energies. It is gratifying that the final hybridization parameters are not highly sensitive to the accuracy of the weighting factors. In acyclic parts of the molecular skeleton the hybrid orbitals are assumed to follow bond directions. However, in cyclic structures the direction of hybrids may deviate from the straight lines passing through bonded atoms thus forming bent bonds introduced first by Coulson and Moffitt[15] and thoroughly discussed in ref 16. The optimization of expression 2 is based on the simplex algorithm.[17]

Results and Discussion

Hybridization. The calculated optimal hybrid orbitals and bond overlap integrals for some silanes and the corresponding hydrocarbons are given in Table I.

The hybridization parameters $n = (1 - a^2)/a^2$ for carbon and silicon atoms are close to 3 but the deviations from this canonical value are significant and very instructive. Increase in the parameter n of one hybrid causes decrease in the hybridization parameters of the remaining hybrids residing on the same atom. It is interesting to observe that the sum of all four hybridization parameters for an atom is conserved if the deviations from the sp^3 hybridization state are small. This is easily checked by the following simple algebra. Since the hybrid orbitals placed on the same nucleus A are orthogonal, the relationship

$$\sum_{i=1}^{4} a_{Ai}^2 = 1 \qquad (6)$$

is a consequence of the fact that exactly one ns orbital is used for the construction of four hybrids. Taking a total differential of the eq 6 one obtains

$$2(a_{A1}\Delta a_{A1} + a_{A2}\Delta a_{A2} + a_{A3}\Delta a_{A3} + a_{A4}\Delta a_{A4} = 0 \qquad (7)$$

where Δa_{Ai} ($i = 1, ..., 4$) are small changes in s character. The coefficients a_{Ai} ($i = 1, ..., 4$) corresponding to the sp^3 state are all equal to 0.5. Therefore the conservation of the s character directly follows from

$$\sum_{i=1}^{4} \Delta a_{Ai} = 0 \qquad (8)$$

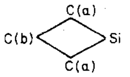
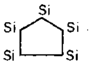
By using the relation $n_{Ai} = (1 - a_{Ai}^2)/a_{Ai}^2$ one easily obtains the conservation rule for p characters

$$\sum_{i=1}^{4} \Delta n_{Ai} = 0 \qquad (9)$$

In other words, the total sum of the hybridization parameters is invariant for small deviations. By an obvious extension of the argument one concludes that the conservation rules hold for the small deviations from the canonical sp^2 and sp states. A survey of the results summarized in Table I shows that the rule for sp^3 state holds with fair accuracy. The p characters are not conserved for large deviations. An excellent example is provided by cyclopropane where the C–C and C–H bonds are described by $sp^{3.86}$ and $sp^{2.40}$, respectively.[8] The total sum of p characters is 12.5 which is larger by 0.5 than the corresponding sum for the sp^3 canonical state.

It is interesting to observe the increase in s character of the hybrid orbitals describing C–Si bonds at the expense of the s content of hybrids participating in C–H and Si–H bonds. This feature is a consequence of the large difference in size of the carbon and silicon atomic orbitals. The 3p Si orbital is much more diffuse than the 2p orbital of the carbon atom so that their σ overlap is poor. The unfavorable overlapping of these orbitals in C–Si bonds is remedied by the increase in s character which is roughly 0.1 for the silicon atoms in a series: CH_3SiH_3, $(CH_3)_2SiH_2$, $(CH_3)_3SiH$, and $(CH_3)_4Si$. The relatively high p character (3.0) in the last molecule is determined by the symmetry. On the contrary, the low p character of 2.66 of the Si atom in methylsilane is very unusual for an unstrained bond between the two four-coordinated atoms. The p characters of the Si–H bonds are considerably larger than 3.0, the highest value being 3.37 which is found in $(CH_3)_3SiH$. It is interesting to mention that the C–H[18] and Si–H[19] bond dissociation energies correlate very well with the reaction yields for the abstraction of hydrogens by the energetic tritium atoms. The higher yields correspond to lower bond dissociation energies. Measurements of this type[19] have led to the conclusion that the Si–H bond strength diminishes along the series SiH_4, CH_3SiH_3, $(CH_3)_2SiH_2$, and $(CH_3)_3SiH$, which is consistent with our finding that the p character of the corresponding hybrids increases in this series. The S(Si–C) overlap integrals show a small but significant decrease in a proper direction. The electronic structure of methylsilane deserves some more comments. Zeeman study[20] of this molecule favors the $^+CH_3$–SiH_3^- charge distribution contrary to the relative electronegativities of C and Si atoms. This is supported by the ab initio calculations of Liskow and Schaefer.[21] Of course one should not use atomic electronegativities as an argument for a discussion of electronic charge distribution in molecules since it is well documented by now that electronegativity is not an invariant property of atoms. However, if one takes into account group electronegativities of CH_3 and SiH_3 groups as calculated by Huheey,[22] who employed the method of Clifford,[23] it turns out that they are 2.28 and 2.22, respectively. It seems at the first sight that the CH_3 group should be still slightly more electronegative than the SiH_3 one. It must be stressed, however, that the group electronegativities of Huheey[22] were obtained assuming sp^3 hybridization of C and Si atoms. While this is a reasonable assumption for carbon, it is not justified for Si because the corresponding hybrid is of $sp^{2.66}$ type (Table I). Since the orbital electronegativity is proportional to s character of the hybrid orbital in question,[6,24] the $sp^{2.66}$ hybrid directed from silicon to carbon in CH_3SiH_3 makes the SiH_3 group more electronegative. Thus, our results are concomitant with the experimental finding of Shoemaker and Flygare[20] and ab initio calculations[21] and provide their additional justification. The hybrids of the carbon atoms in silanes exhibit a characteristic shift of the s character from C–H to C–Si bonds but this transfer is less pronounced than for silicon. The characteristic structural groups have fairly constant hybridizations in different molecules. Therefore, one can easily construct the hybrid orbitals for higher alkanes and silanes by using their transferability.

Table II. Comparison between the Calculated MOA Bond Angles and the Corresponding MINDO/3 and Experimental Values (in deg)

Molecule	Angle	MOA	MINDO/3	Exptl
SiH_4	HSiH	109.5		109.5[a]
Si_2H_6	HSiSi	109.4	112.7	110.3[b]
	HSiH	109.5		108.6
$H_3Si(p)$–$Si(s)H_2$–$Si(p)H_3$	Si(p)Si(s)Si(p)	109.7	118.4	
	HSi(p)Si(s)	109.5	112.7	
	HSi(p)Si(s)	109.5	108.8	
CH_3SiH_3	HSiH	108.6	108.4	108.2[c]
	HCH	109.8	107.4	102.2
	HCSi	109.1		
	HSiC	110.3		
$(CH_3)_2SiH_2$	CSiC	111.0	117.8	110.6[c]
	HSiH	107.9	104.6	107.5
	HCSi	109.2	116.0	109.5
	HCH	109.8		108.0
$(CH_3)_3SiH$	HSiC	108.7	113.0	110.0[c]
	HCSi	109.2	116.1	109.0
	CSiC	110.2		110.1
	HCH	109.8		107.6
$(CH_3)_4Si$	HCSi	109.1	115.5	109.0
	CSiC	109.5		
	HCH	109.9		109.5
$(CH_3)_6Si_2$	CSiC	110.3		110.5[d]
	HCSi	108.9		108.7
	CSiSi	108.6		108.4
	HCH	110.0		110.3
	HSiC(s)	110.2	112.1	
	HC(s)Si	109.7	112.9	
$C(p)H_3C(s)H_2SiH_3$	HC(p)C(s)	109.1		
	HSiH	108.8		
	HC(s)C(p)	109.2		
	HC(p)H	109.9		
	C(a)SiC(a)	79.8	78.5	80.0[e]
	SiC(a)C(b)	90.4		
	C(a)C(b)C(a)	99.4	107.0	109.0
	HSiH	111.2	102.7	100.0
	SiSiSi	108		
	HSiSi	109.5		
	HSiH	109.4		

[a] G. Herzberg, "Molecular Spectra and Molecular Structure", Vol. 1, 2nd ed, Van Nostrand, New York, N.Y., 1950. [b] B. Beagley, A. R. Conrad, J. M. Freemen, J. J. Monaghan, and B. G. Norton, *J. Mol. Struct.*, 11, 371 (1972). [c] L. E. Sutton, *Chem. Soc., Spec. Publ.*, No. 11 (1958). [d] B. Beagley, J. J. Monaghan, and T. G. Hewitt, *J. Mol. Struct.*, 8, 401 (1971). [e] L. V. Vilkov, V. S. Mastryukov, J. V. Baurova, V. M. Volorin, and P. L. Grinberg, *Dokl. Akad. Nauk SSSR*, 177, 1084 (1967).

Bond Angles. The bond angles are coupled with the hybridization parameters through the orthogonality conditions (2). Optimization of the hybridization parameters by using the maximum overlap criterion gives theoretical bond angles which are compared with available MINDO/3 results and experimental values (Table II). Our bond angles are in a good agreement with the experimental ones. The exceptions are the HSiH and CCC angles in silacyclobutane where the calculated values are off by 10°. This discrepancy indicates the limitation of the MOA method in treating the four-membered rings encountered earlier in cyclobutane.[25] Namely, the maximum overlap method minimizes only the angular type of the strain energy. Therefore the most stable conformation for four rings is a planar one. The opposing force which prefers a puckered conformation is the tendency of CH_2 groups to adopt staggered positions. It is this effect which determines the dihedral angle in silacyclobutane[26] of 36°. The reason for this failure of the MOA method is the high insensitivity of the total overlap against the dihedral angle.[25] Thus a small repulsion between CH_2 groups can lead to considerably puckered rings. Since the puckering decreases the bond angles in the rings, it makes our CCC value even worse as compared with experiment. All other bond angles are close to tetrahedral values and are better reproduced by the MOA method than by MINDO/3 approach. Transferability of the hybrid orbitals describing similar chemical environments is reflected in the transferability of the structural parameters characterizing molecular fragments. For example, a very good agreement was obtained between the evaluated and observed moments of inertia for ethylmethylsilane by using only slightly adjusted structural parameters of the related $(CH_3)_2SiH_2$ and $CH_3CH_2SiH_3$ molecules.[27] The calculated bond angles CSiC = 111° (111°) and HSiH = 107.9° (107.8°) around the silicon atom are in good agreement with the experimental values which are given in parentheses.

Heats of Formation. Organosilicon chemistry lacks a large body of reliable and systematic thermochemical data. This is, undoubtedly, due to difficulties encountered in the application of conventional calorimetric techniques. The early thermochemical measurements for alkylsilanes are in error up to ±30 kcal/mol.[28] Potzinger and Lampe[29] combined the bond interaction scheme of Allen[30] with their electron impact results on silane and a number of methylsilanes. Thus, a set of internally consistent heats of formation of alkylsilanes is obtained. It was shown that bond overlap integrals can be successfully correlated with heats of formation of hydrocarbons[31] if it is assumed that the bond energies are linearly dependent on the corresponding overlaps

$$\Delta H_f = \sum_{A-B} (k_{AB} S_{AB} + l_{AB}) \tag{10}$$

Extending this approach to organosilicon compounds one obtains by using the least-square-fit method the following values for constants k_{AB} and l_{AB}: $k_{SiSi} = 289.6$, $k_{SiC} = 146.6$, $k_{SiH} = -226.2$, $l_{SiSi} = -187.4$, $l_{SiC} = -90.3$, $l_{SiH} = 165.0$ (in kcal/mol). The constants related to C–C and C–H bonds were taken from earlier work on hydrocarbons.[31] The correlated and experimental values are compared in Table III. The quality of the correlation is fairly good, the standard deviation being 2.1 kcal/mol. The results exhibit several interesting features. The insertion of an SiH_2 group into silanes increases the heat of formation. This increase is proportional to the number of Si atoms in a chain: $\Delta H_f(Si_3H_8) - \Delta H_f(Si_2H_6) = 10$, $\Delta H_f(Si_4H_{10}) - \Delta H_f(Si_3H_8) = 12.3$, $\Delta H_f(Si_5H_{12}) - \Delta H_f(Si_4H_{10}) = 15.8$ (in kcal/mol). Thus, our calculated heats of formation are concomitant with the experimental findings that higher silanes are very reactive. They are highly explosive with very small amounts of oxygen and they decompose in sunlight. The longer chains Si_nH_{2n+2} ($n > 7$) were not isolated so far despite numerous attempts.[32] The substitution of hydrogen by CH_3 groups in silane stabilizes the system by 24.4 kcal/mol, in good agreement with the observed value (23.5 kcal/mol). Consecutive replacement of CH_3 groups decreases the heat of formation by roughly 11 kcal/mol which is compatible with experimental results (Table III). Our calculations reproduce rather nicely the experimental fact that

$$\Delta H_f[(C_2H_5)_nSiH_{4-n}] < \Delta H_f[(CH_3)_nSiH_{4-n}] \tag{11}$$

where $n = 1$–4. In other words, the ethyl substituent is energetically much more favorable than the methyl one. The differences in heats of formation (eq 11) are 6.2, 8.8, 13.5, and 16.6 kcal/mol for $n = 1, 2, 3,$ and 4, respectively.

Table III. Comparison between the Calculated Heats of Formation for Some Silanes by the MOA Method and the Corresponding MINDO/3 and Experimental Values (in kcal/mol)

Molecule	ΔH_f-(MOA)	ΔH_f-(MINDO/3)[a]	Exptl	Δ[b]	Ref
SiH_4	3.0	8.7	7.3	−4.3	*c*
Si_2H_6	19.1	19.0	19.2	−0.1	*d*
Si_3H_8	29.0	30.2	28.9	0.1	*d*
Si_4H_{10}	41.3	41.7			
Si_5H_{12}	57.1	53.9			
CH_3SiH_3	−5.3	−11.8	−4.3	−1.0	*e*
$(CH_3)_2SiH_2$	−16.4	−29.8	−16.8	0.4	*e*
$(CH_3)_3SiH$	−27.4	−44.5	−29.6	2.2	*e*
$(CH_3)_4Si$	−42.0	−55.5	−42.4	0.4	*e*
$(CH_3)_6Si_2$	−60.1		−60.1	0.0	*e*
$C_2H_5SiH_3$	−11.5	−16.3	−15.0	3.5	*f*
$(C_2H_5)_2SiH_2$	−25.2		−23.5	−1.7	*e*
$(C_2H_5)_3SiH$	−40.9		−39.5	−1.4	*e*
$(C_2H_5)_4Si$	−58.6		−56.9	−1.7	*e*
$(CH_3)_3SiC_2H_5$	−45.8		−45.7	−0.1	*e*
$(CH_3)_3CSiH_3$	−20.2		−24.0	3.8	*g*

[a] MINDO/3 results were taken from the ref 3. [b] Difference between the MOA value and the experimental one: $\Delta = H_f(\text{MOA}) - H_f(\text{exptl})$. [c] P. Potzinger and F. W. Lampe, *J. Phys. Chem.*, **74**, 719 (1970). [d] D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, *Natl. Bur. Stand. (U.S.), Tech. Note,* No. 270-3 (1968). [e] P. Potzinger, A. Ritter, and J. Krause, *Z. Naturforsch. A*, **30**, 347 (1975). [f] W. C. Steele, L. D. Nichols, and F. G. A. Stone, *J. Am. Chem. Soc.*, **84**, 4441 (1962). [g] S. Tannenbaum, *ibid.*, **76**, 1027 (1954).

***J*(Si–H) Spin–Spin Coupling Constants.** The spin–spin coupling constants of the directly bonded carbon and hydrogen nuclei were independently related to bonding parameters by several investigators[33-35] as early as 1959. It was found that the Fermi contact term and the hybridization parameters are the principal factors determining the magnitude of the spin–spin coupling constants. This point of view was later supported by the extensive maximum overlap calculations performed on hydrocarbons.[36] The Si–H coupling constants in substituted silanes were discussed by Juan and Gutowsky within the VB approach.[37] It was established that the coupling constants exhibit large, systematic deviations from the simple additivity rules operating in substituted methanes. These deviations were explained in terms of changes in Si–H bond ionicity which depends on the nature of a substituent. Since carbon, silicon, and hydrogen atoms have similar electron-withdrawing powers, we shall neglect the effect of bond polarity and consider only the dependence of the spin–spin coupling constants on the bond hybridization. It is well documented by now that the simple proportionality between the C–H coupling constant and the s character $J(\text{C–H}) = 500a_{CH}^2$ recommended by Muller and Pritchard[34] does not hold if the deviations of the hybridization from the ideal sp^2 and sp values in ethylene, acetylene, and strained cyclic hydrocarbons are taken into account.[36] Therefore we employed two types of correlation formulas

$$J(\text{Si-H}) = k_1 a_{\text{Si-H}}^2 + l_1 \quad (\text{Hz}) \tag{12}$$

$$J(\text{Si-H}) = k_2 a_{\text{Si-H}}^2/(1 + S_{\text{Si-H}}^2) + l_2 \quad (\text{Hz}) \tag{13}$$

where the overlap integral appearing in the normalization constant of the two-center wave function is explicitly included.

Table IV. Comparison between the Calculated and Experimental J(Si-H) Spin-Spin Coupling Constants (in Hz)

Molecule[a]	% s character	Eq 12	Eq 13	Exptl	Δ_1[b]	Δ_2[b]
Si_2H_6	25.05	197.5	197.7	198.2[c]	−0.7	−0.5
$SiH_3SiH_2Si^*H_3$	25.01	197.2	196.6	199.0[c]	−1.8	−2.4
$SiH_3Si^*H_2SiH_3$	24.83	195.9	196.1	193.1[c]	2.8	3.0
Si_5H_{10}	24.94	196.7	196.9	195.0[d]	1.7	1.9
CH_3SiH_3	24.22	191.5	191.4	194.2[e]	−2.7	−2.8
$(CH_3)_2SiH_2$	23.60	186.9	186.8	188.6	−1.7	−1.8
$(CH_3)_3SiH$	22.89	181.8	182.1	184.0	−2.2	−1.9
$(CH_3CH_2)_3SiH$	23.17	183.9	183.7	179.2	4.7	4.5

[a] The Si nucleus in question is denoted by an asterisk. [b] Differences between the calculated values obtained by eq 12 and 13 and the observed values are denoted by Δ_1 and Δ_2, respectively. [c] E. A. V. Ebsworth and J. J. Turner, *Trans Faraday Soc.*, **60**, 256 (1964). [d] E. Hengge and G. Bauer, *Angew. Chem.*, 85, 304 (1973). [e] M. A. Jensen, *J. Organomet. Chem.*, **11**, 423 (1968).

A comparison between the correlated and observed values is given in the Table IV. The correlation constants k_i and l_i ($i = 1, 2$) were obtained by the least-squares method. They are $k_1 = 725$, $l_1 = 15.9$, $k_2 = 1123.2$, and $l_2 = 12.7$. The standard deviations for the correlations (12) and (13) are 2.7 and 2.8 Hz, respectively. The range of the experimental values is rather small because the compounds involving silicon atoms in sp^2 and sp have not been synthetized as yet.

Conclusion

The hybrid orbitals obtained by the maximum overlap approximation method provide a useful basis for the discussion of various physical and chemical properties of silanes. The calculated s characters predict the bond angles and J(C–Si)[9] and J(Si–H) coupling constants with a good acurracy. A number of other properties are related to hybridization parameters but the experimental data are unfortunately scarce. For example, the β-CH_2 antisymmetric stretching frequency in silacyclobutane[38] is 2990 cm^{-1}. It can be compared with our prediction of 2953 cm^{-1} which is obtained by using the linear relationship between $\nu(C-H)_{as}$ and the s character of the hybrid orbital in question.[39] The overlap integrals between the bonded hybrids are linearly related to the heats of formation of silanes. The quality of our correlation (10) is such that we can evaluate the experimental data which are frequently in contradiction. Dimethylsilane provides a very good illustrative example. We agree with Dewar et al.[3] that the earlier measurement[40] of its $\Delta H_f^\circ = -48.0$ kcal/mol is in error by 20–30 kcal/mol and that the result of Potzinger et al.[29] is much more reliable. Finally, it should be pointed out that fresh and accurate thermochemical data in organosilicon chemistry are highly desirable.

Acknowledgment. We thank a referee for several useful suggestions which improved the presentation of the material.

Registry No. SiH_4, 7803-62-5; CH_4, 74-82-8; SiH_3SiH_3, 1590-87-0; CH_3CH_3, 74-84-0; $SiH_3SiH_2SiH_3$, 7783-26-8; $CH_3CH_2CH_3$, 74-98-6; CH_3SiH_3, 992-94-9; $CH_3SiH_2CH_3$, 1111-74-6; $(CH_3)_3SiH$, 993-07-7; $(CH_3)_3CH$, 75-28-5; $(CH_3)_4Si$, 75-76-3; $(CH_3)_4C$, 463-82-1; $(CH_3)_3SiSi(CH_3)_3$, 1450-14-2; $(CH_3)_3CC(CH_3)_3$, 594-82-1; $(CH_3)_3CSiH_3$, 18165-85-0; $(CH_3CH_2)_4Si$, 631-36-7; $(CH_3CH_2)_4C$, 1067-20-5; $(CH_2)_3SiH_2$, 287-29-6; $(CH_2)_4$, 287-23-0; $(SiH_2)_5$, 289-22-5; $(CH_2)_5$, 287-92-3; $(CH_3CH_2)_3SiH$, 617-86-7; $CH_3CH_2SiH_3$, 2814-79-1; Si_4H_{10}, 7783-29-1; Si_5H_{12}, 14868-53-2; $(C_2H_5)_2SiH_2$, 542-91-6; $(CH_3)_3SiC_2H_5$, 3439-38-1.

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