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## SELF-CONSISTENT MOLECULAR ORBITAL CALCULATIONS OF NUCLEAR SPIN COUPLING CONSTANTS IN ORGANOSILICON COMPOUNDS; TRIMETHYLSILYL SYSTEMS

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### Summary

Finite perturbation calculations of carbon—silicon nuclear spin coupling constants in trimethylsilyl compounds have been carried out using an INDO scheme extended to the second row. Generally good agreement with experimental values is noted. Correlations between coupling constants and certain parameters related to hybridization and electron distribution are discussed.

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### Introduction

The recent development of Fourier transform procedures has brought renaissance to  $^{13}\text{C}$  NMR and has established other less common nuclei, particularly  $^{29}\text{Si}$ , as useful tools in the study of molecular electronic structure. Investigations of organosilicon compounds by either  $^{29}\text{Si}$  or  $^{13}\text{C}$  NMR have led to the determination of directly-bonded carbon—silicon coupling constants,  $^1J(\text{Si—C})$ , in a variety of molecular systems [1,2]. But only quite recently has substituent influence on  $^1J(\text{Si—C})$  been examined in detail. Harris and Kimber's study [3] of substituent effects in a series of trimethylsilyl compounds remains the most comprehensive investigation of this sort.

The finite perturbation procedure developed by Pople and coworkers [4,5] has been employed widely and with general success in the computation of Fermi contact nuclear spin coupling constants involving first-row atoms. Here we report the extension of this procedure to include second-row atoms and its employment in the calculation of  $^1J(\text{Si—C})$  in compounds of the type  $(\text{CH}_3)_3\text{SiX}$ .

### Experimental

The application of finite perturbation (FP) theory to the calculation of Fermi contact spin coupling constants usually involves the computation of an

unrestricted [6], single-determinant, INDO [7] molecular orbital wavefunction under the influence of the perturbation

$$h_B = (8\pi/3)\mu_B s_B^2(0)$$

due to the presence of a nuclear moment  $\mu_B$ . Then the coupling constant is given by

$$J(A-B) = (4\beta/3)^2 h \gamma_A \gamma_B s_A^2(0) s_B^2(0) [\partial \rho_{s_A s_A}(h_B) / \partial h_B]_{h_B=0}$$

where  $h$  is the Planck constant,  $\beta$  is the Bohr magneton,  $\gamma_A$  is the magnetogyric ratio of the nucleus of atom A,  $s_A^2(0)$  is the valence-shell  $s$ -orbital density of atom A at its nucleus, and  $\rho_{s_A s_A}$  is the diagonal spin density matrix element corresponding to that orbital. The procedure has been described in detail elsewhere [5].

The extension of FP/INDO calculations to the computation of coupling constants involving second-row atoms requires extension of the INDO scheme to the second-row as well as specification of  $s^2(0)$  for each second-row atom of interest.

The extended INDO procedure used here is that suggested by Stevenson and Burkey [8] and employed by them in the investigation of barriers to inversion. If only  $s$  and  $p$  valence-shell basis functions are used for second-row atoms (i.e. no  $d$  orbitals), then the extension involves merely the specification of atomic parameters. The electronegativity ( $-\frac{1}{2}(I + A)$ ) and bonding ( $\beta^0$ ) parameters were taken unchanged from CNDO [9], while the Slater—Condon parameters,  $F^2$  and  $G^1$ , for one-center exchange integrals were those suggested by Stevenson and Burkey, based on extrapolation from corresponding first-row atoms\*.

The  $s^2(0)$  value used for silicon in this study was that calculated from hyperfine coupling constants and reported [11] by Jameson and Gutowsky: 2.06 a.u.<sup>-3</sup>.

Computations were performed using a "standard geometrical model" similar to that described by Pople and Gordon [12]. The specific bond distances em-

TABLE 1  
BOND DISTANCES IN THE STANDARD GEOMETRICAL MODEL<sup>a</sup>

$R(\text{Si}-\text{H}) = 1.48$	$R(\text{Si}-\text{Cl}) = 2.03$
$R(\text{Si}-\text{C}) = 1.86$ (methyl carbon)	$R(\text{C}-\text{H}) = 1.09$ (methyl carbon)
$R(\text{Si}-\text{C}) = 1.84$ (aromatic carbon)	$R(\text{C}-\text{H}) = 1.08$ (aromatic carbon)
$R(\text{Si}-\text{Si}) = 2.32$	$R(\text{C}-\text{C}) = 1.54$ (single bond)
$R(\text{Si}-\text{N}) = 1.78$	$R(\text{C}-\text{C}) = 1.40$ (aromatic bond)
$R(\text{Si}-\text{O}) = 1.63$	$R(\text{C}-\text{O}) = 1.43$
$R(\text{Si}-\text{F}) = 1.57$	$R(\text{N}-\text{H}) = 1.01$

<sup>a</sup> Values in angstroms.

\* The value used for the  $F^2$  integral for Si was 0.11464, rather than the previously reported [8] value, which was in error [10].

ployed are those given in Table 1. All bond angles about tetracoordinate atoms were taken as tetrahedral. Additional bond angle information is given in Table 2. The conformation chosen was in each case the one with the greatest number of staggered atoms.

All calculations were carried out in double precision on a UNIVAC Series 70/46 computer, using a suitably modified version of CNINDO [13].

## Results and discussion

The experimental and computed values of  $^1J(\text{Si}-\text{C})$  along with several calculated charge density-bond order parameters are presented in Table 2. It can be seen that there is generally good agreement between the calculated and experimental coupling constants both in terms of their absolute magnitude and with regard to the sensitivity of the couplings to substituent influence. In fact the overall agreement in this series is substantially better than that obtained in any previous FP/INDO study. Even so, it seems possible to consider some of the deviations which do exist. It will be noted that the larger differences between calculated and experimental  $^1J(\text{Si}-\text{C})$  occur for  $\text{X} = \text{NHSi}(\text{CH}_3)_3$  and  $\text{OSi}(\text{CH}_3)_3$ , where the errors are  $-5.2$  and  $-7.2\%$  respectively. The additional geometrical uncertainties attributable to the sheer bulk of these substituents were initially thought to be responsible. However it was found that the sensitivity of calculated  $^1J(\text{Si}-\text{C})$  in these two compounds to variations in bond angles or dihedral angles is insufficient to support this type of rationalization.

TABLE 2

EXPERIMENTAL AND COMPUTED COUPLING CONSTANTS; CALCULATED CHARGE DENSITY AND BOND ORDER PARAMETERS FOR TRIMETHYLSILYL COMPOUNDS,  $(\text{CH}_3)_3\text{SiX}$ .

X	$^1J(\text{Si}-\text{C})^a$		$P_{\text{Si}^2\text{Si}^2\text{C}}^c$	$P_{\text{Si}}^d$	$P_{\text{C}}^e$
	Exp. <sup>b</sup>	Calcd.			
$\text{Si}(\text{CH}_3)_3$	-43.6	-43.5	0.0570	3.6542	4.0860
H	-50.8	-52.2	0.0653	3.4092	4.1173
$\text{CH}_3$	-51.0	-51.4	0.0628	3.4581	4.1149
$\text{C}_6\text{H}_5$	-52.2	-50.6	0.0626	3.4693	4.1144
$\text{NHSi}(\text{CH}_3)_3^f$	-56.2	-53.3	0.0661	3.2871	4.1497
Cl	-57.7	-55.8	0.0670	3.2408	4.1532
$\text{OC}_2\text{H}_5^g$	-59.0	-57.6	0.0690	3.1271	4.1735
$\text{OSi}(\text{CH}_3)_3^h$	-60.0	-55.7	0.0690	3.1195	4.1797
F	-60.5	-59.5	0.0716	3.0046	4.1901

<sup>a</sup> Values in Hz. <sup>b</sup> Taken from ref. [3]. Negative signs assumed throughout, based on the determination for  $\text{X} = \text{CH}_3$  [14]. <sup>c</sup> Square of the bond order between the silicon 3s orbital and the 2s orbital of the methyl carbon. <sup>d</sup> Total computed valence-shell electron density of silicon. <sup>e</sup> Total computed valence-shell electron density of methyl carbon. <sup>f</sup> The Si-N-Si angle was taken as  $130^\circ$ . <sup>g</sup> The Si-O-C angle was taken as  $109.5^\circ$ . <sup>h</sup> The Si-O-Si angle was taken as  $150^\circ$ .

In light of previous work on these and related compounds [14,15] it seems more reasonable to consider the possibility that for these compounds the wavefunction constructed in the calculation is not fully adequate to describe the bonding between silicon and oxygen or nitrogen. Controversy continues [15-23] on the importance of *d* orbitals in determining the chemical and physical properties of silicon compounds, especially when bonded to potential  $\pi$ -donors such as oxygen, nitrogen, halogens, phenyl rings, and other  $\pi$ -hydrocarbons. The omission of silicon *d* orbitals from basis sets used in these calculations effectively eliminates the possibility of representing ( $p \rightarrow d$ ) $\pi$ -bonding. Inclusion of *d* orbitals in a pure INDO scheme introduces the problem of parametrization of the new one-center exchange integrals and is beyond the scope of the present study. However, if the CNDO [9] approximation is used for second-row atoms (that is, if exchange integrals between atomic orbitals centered on second-row atoms are neglected), then *d* orbitals can readily be included. While the effect of this type of procedure is to degrade the quantitative agreement between calculated and experimental results (the calculated couplings then range from -22.9 to -39.3 Hz.) it is found that the computed values of  $^1J(\text{Si}-\text{C})$  for hexamethyldisiloxane and hexamethyldisilazane decrease algebraically relative to computed  $^1J(\text{Si}-\text{C})$  values for other compounds in the series considered here and hence are more in line with experimental trend. Similar, though less dramatic improvements are noted for  $\text{X} = \text{Cl}$  and  $\text{X} = \text{C}_6\text{H}_5$  as well. We take this as supportive of the argument that were a full INDO computation carried out, with the inclusion of *d* orbitals in the basis sets of second-row atoms, improved wavefunctions for several compounds in the series under investigation, particularly for hexamethyldisiloxane and hexamethyldisilazane, would result, leading to better overall agreement between calculated and experimental coupling constants. Work to this end is currently underway.

Nuclear spin couplings have often been discussed in terms of the "s-character" of the hybrid orbitals participating in the bonding between the coupled nuclei. The theoretical justification for the hybridization arguments has been based largely on valence-bond [24] or molecular orbital [25] developments from Ramsey's [26] second-order perturbation formula for the Fermi contact term, using the average sum over states (or " $\Delta E$ ") approximation. In the molecular orbital development this approach gives rise to the expression

$$J(\text{A}-\text{B}) = (4\beta/3)^2 h \gamma_{\text{A}} \gamma_{\text{B}} (\Delta E)^{-1} s_{\text{A}}^2(0) s_{\text{B}}^2(0) P_{s_{\text{A}}s_{\text{B}}}^2$$

where  $\Delta E$  is a "mean electronic excitation energy" and  $P_{s_{\text{A}}s_{\text{B}}}$  is the element of the first-order density matrix corresponding to the valence *s* orbitals on atoms A and B. It is the assumed constancy of the product  $(\Delta E)^{-1} s_{\text{A}}^2(0) s_{\text{B}}^2(0)$  which has led to interpretations based on the "s-character" concept via the  $P_{s_{\text{A}}s_{\text{B}}}^2$  term. This assumption has been criticized in the case of  $^{13}\text{C}-\text{H}$  couplings [27-30] and alternative views based on the assumed dominance of variations in  $\Delta E$  [29] or in  $s^2(0)$  [30] have been presented for substituted methanes. More recent work however has tended to indicate that variations in the effective nuclear charge are of less significance in the determination of couplings between multielectron atoms than in couplings involving protons [31,32].

While the FP/INDO method makes no explicit use of either  $\Delta E$  or  $P_{s_{\text{A}}s_{\text{B}}}^2$  in

the computation of  $J(A-B)$ , the effective nuclear charge factor,  $s^2(0)$ , is employed in the calculation as a constant atomic parameter (vide supra).  $P_{s_A s_B}^2$  values are nonetheless available as "by-products" of the molecular wavefunction constructed in the computation. It is of interest then to examine the relationship between carbon-silicon coupling constants in the trimethylsilyl system and the hybridizational parameter  $P_{s_{Si} s_C}^2$ . Values of  $P_{s_{Si} s_C}^2$  are given along with the coupling constants in Table 2. Linear least squares analyses of these data establish the relationship (correlation coefficient  $r = 0.98$ )

$${}^1J(\text{Si}-\text{C}) = -1055.4P_{s_{Si} s_C}^2 + 15.9 \text{ Hz}$$

for the computed carbon-silicon coupling constants and the correlation ( $r = 0.96$ )

$${}^1J(\text{Si}-\text{C}) = -1227.7P_{s_{Si} s_C}^2 + 26.0 \text{ Hz}$$

for the experimental couplings. These relationships suggest sensitivities of calculated and experimental  ${}^1J(\text{Si}-\text{C})$  to changes in  $P_{s_{Si} s_C}^2$  generally comparable to the sensitivities of  ${}^1J(\text{C}-\text{C})$  to  $P_{s_C s_C}^2$  found earlier for a series of t-butyl compounds [33]. Thus, for example, it was observed previously that for calculated carbon-carbon coupling constants in the t-butyl system, the relationship ( $r = 0.96$ )

$${}^1J(\text{C}-\text{C}) = 1168.8P_{s_C s_C}^2 - 23.7 \text{ Hz}$$

held\*. However, when consideration is confined to a series of hydrocarbons representing a wide range of formal hybridization states, FP/INDO and other methods [34-36] reveal markedly lower sensitivities of  ${}^1J(\text{C}-\text{C})$  to  $P_{s_C s_C}^2$ , or its valence bond analog, ranging from 556 to 633. Furthermore, Kovacevic and Maksic [37], using the maximum overlap method, have found a similar low sensitivity of  ${}^1J(\text{Si}-\text{C})$  to the valence bond equivalent of  $P_{s_{Si} s_C}^2$  in a series of six compounds containing only silicon, carbon, and hydrogen. It seems likely that the disparities in these data may ultimately be traceable to the assumption of constant  $\Delta E$ . Clearly further study is in order. Meanwhile this evidence should serve as a caveat to those attempting to use experimental coupling constants as a basis for detailed hybridization information, especially in systems containing electronegative substituents.

Harris and Kimber [3], in their discussion of experimental coupling constants in the trimethylsilyl series, noted a correlation between the absolute magnitude of  ${}^1J(\text{Si}-\text{C})$  and the "electronegativity" of the substituent atom directly bonded to the silicon. This type of relationship has been noted before in numerous other systems [32,33,38] and has been taken as indicative of the dominance of the Fermi contact term in determining the coupling constant. The basis for this argument has been Bent's general rule [39] that "the s-character of an atom tends to concentrate in orbitals that are directed toward electropositive groups". Thus an electronegative substituent on silicon tends to concentrate silicon "s-character" in hybrid orbitals directed toward the methyl carbons. This enhanced s-character in the Si-C bond is then considered to increase the absolute

\* The sign reversals in this expression are attributable to the difference in sign of the magnetic moments of silicon and carbon.

magnitude of  $^1J(\text{Si}-\text{C})$  via the Fermi contact mechanism according to hybridization arguments already discussed above.

These types of considerations led Bartuska and Maciel, in their studies of ethyl [40] and isopropenyl [41] compounds, to search for relationships between carbon-carbon coupling constants and calculated electron-density patterns reflective of electronegative substitution on these hydrocarbon substrates. In a similar manner, we have studied the relationship between  $^1J(\text{Si}-\text{C})$  and two parameters derived from the atomic charge densities obtained in the INDO calculations. Table 2 includes values of  $P_{\text{C}}$  and  $P_{\text{Si}}$ , the valence-shell electron densities on carbon and silicon, respectively. The parameter  $\Delta \equiv 8 - P_{\text{C}} - P_{\text{Si}}$  reflects the net electron deficiency of the C-Si fragment since each atom, if neutral, would carry four valence electrons. Hence, for each compound considered,  $\Delta$  may be taken as one possible measure of the electron-withdrawing capacity (electronegativity) of the substituent involved. The following relationships ( $r = 0.97$  in each case) were noted in linear least squares analyses:

$$^1J(\text{Si}-\text{C}) = -26.4 \Delta - 38.8 \text{ Hz}$$

for calculated couplings, and for experimental couplings

$$^1J(\text{Si}-\text{C}) = -31.4 \Delta - 37.3 \text{ Hz.}$$

Another important parameter  $\Pi \equiv P_{\text{C}} - P_{\text{Si}}$  relates to the degree to which the C-Si bond is polarized in the sense of silicon being more positive than carbon. These correlations were found:

$$^1J(\text{Si}-\text{C}) = -18.6 \Pi - 37.8 \text{ Hz}$$

with  $r = 0.96$  for calculated coupling and, with  $r = 0.97$ , for experimental couplings

$$^1J(\text{Si}-\text{C}) = -22.3 \Pi - 36.0 \text{ Hz.}$$

Together these relationships between  $^1J(\text{Si}-\text{C})$  and the charge density parameters  $\Delta$  and  $\Pi$  are consistent with the view in which the absolute magnitude of the carbon-silicon coupling constant increases with increased  $-I^+$  character of the substituent. The  $-I^+$  notation, developed by Pople and Gordon [12], refers to substituents that withdraw electron density from a moiety while polarizing that moiety in the sense that tends to increase the positive character of the atom  $\alpha$  to the substituent (here, the silicon) relative to the atom  $\beta$  to the substituent (here the carbon).

## Conclusion

Values of carbon-silicon coupling constants computed by the finite perturbation method are in good agreement with experimental values for trimethylsilyl compounds. Some minor improvements are to be expected in individual cases if  $d$  orbitals are included in the basis sets for second-row atoms. Good correlation is noted between values of  $^1J(\text{Si}-\text{C})$  and hybridizational parameters related to the "s-character" of the C-Si bond, but caution should be exercised in attempts to derive detailed hybridizational information from experimental

coupling constants. Linear relationships are noted between  $^1J(\text{Si}-\text{C})$  values and charge density parameters reflecting electron deficiency of the C-Si moiety and polarization of that moiety in the sense ( $\text{Si}^+-\text{C}$ ). These latter relationships are consistent with the view that the absolute magnitude of  $^1J(\text{Si}-\text{C})$  in trimethylsilyl systems increases with increasing  $-I^+$  character of the substituent.

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