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Silicon-29 NMR Chemical Shifts of Organosilicons as Studied by the FPT CNDO/2 Method

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The ^{29}Si chemical shifts of silicon hydrides and fluorosilanes were calculated by means of the FPT method within the CNDO/2 framework. It was found that, by a small revision of the formula for the off-diagonal elements of the core Hamiltonian matrix in the CNDO/2 method, the calculated results agree well with the gross trend of the experimental values of the ^{29}Si chemical shifts in the literature. Further, the relationship between the ^{29}Si chemical shift and the electronic structure was discussed.

The widespread interest in ^{13}C NMR has ensured that the chemical shift of this nucleus has received much attention at both the semiempirical MO- and ab initio MO-level approaches, and the comparison of the calculated and experimental ^{13}C chemical shifts has provided useful information on the electronic distribution and molecular structure.[1,2] On the other hand, in spite of the fact that ^{29}Si NMR spectroscopy is widely used for investigating molecular structures and electronic distributions in organosilicon compounds, theoretical investigation has been carried out only by using such a rough approximate theory as the averaged excitation energy (ΔE) method.[3,4] This method has an ambiguity in the estimation of the value of ΔE as parameter in the paramagnetic term by which ^{29}Si chemical shift is predominantly governed. According to our best knowledge, there have been few ^{29}Si chemical-shift calculations using sophisticated methods.

In this work, therefore, we aim to calculate the ^{29}Si chemical shifts of several organic compounds containing a silicon atom by the use of the finite-perturbation theory (FPT)[5] within the CNDO/2 framework, which reproduces well the experimental trend for the ^{13}C chemical-shift values;[6] we will also discuss the relationship between the ^{29}Si chemical shift and the electronic structure through a comparison of the calculated and experimental chemical-shift values.

Theoretical

In the FPT method,[5] the ^{29}Si shielding tensor of a nucleus A, $\sigma_{\alpha\beta}(A)$, is expressed as a sum of the diamagnetic term, $\sigma^{d}_{\alpha\beta}(A)$, and the paramagnetic term, $\sigma^{p}_{\alpha\beta}(A)$ as follows:

$$\sigma_{\alpha\beta}(A) = \sigma^{d}_{\alpha\beta}(A) + \sigma^{p}_{\alpha\beta}(A), \qquad [1]$$

$$\sigma^{d}_{\alpha\beta}(A) = \frac{e^2}{2mc}\sum_{\mu}\sum_{\nu} \boldsymbol{P}_{\mu\nu}(0) < \chi_{\mu} \left| \frac{\delta_{\alpha\beta}\mathbf{r}_{\nu}\cdot\mathbf{r}_{A} - r_{\nu\alpha}r_{A\beta}}{|\mathbf{r}_{A}|^3} \right| \chi_{\nu} >, \qquad [2]$$

$$\sigma^{p}_{\alpha\beta}(A) = -\frac{e\hbar}{mc} i \sum_{\mu}\sum_{\nu} \left(\frac{\partial P_{\mu\nu}(\boldsymbol{H}_{\alpha})}{\partial \boldsymbol{H}_{\alpha}} \right)_{\mathbf{H}=0} < \chi_{\mu} \left| \frac{(\mathbf{r}\times\nabla)_{\beta}}{|\mathbf{r}_{A}|^3} \right| \chi_{\nu} > \quad (\alpha, \beta = x, y, z), \qquad [3]$$

where the gauge origin of the vector potential is set at the position of the nucleus A. The $\mathbf{r}_{\nu}$ and $\mathbf{r}_{A}$ vectors are the position vectors of an electron considered from the point of view of a nucleus of the atom containing the $\mathbf{AO}_{\chi_{\nu}}$ and from that of nucleus A respectively. $\boldsymbol{P}_{\mu\nu}(\boldsymbol{H}_{\alpha})$ and $\boldsymbol{P}_{\mu\nu}(0)$ are the elements of the density matrix with and without the perturbation due to the magnetic field $\boldsymbol{H}$ respectively; they are obtained by solving the Roothaan equation[7] with the Hartree–Fock matrix, $\boldsymbol{F}_{\mu\nu}(\boldsymbol{H}_{\alpha})$, containing the perturbation terms:

$$\boldsymbol{F}_{\mu\nu}(\boldsymbol{H}_{\alpha}) = \boldsymbol{H}^{\mathrm{core}}_{\mu\nu} + \sum_{\lambda}\sum_{\sigma} \boldsymbol{P}_{\mu\nu}(\boldsymbol{H}_{\alpha})\left[(\mu\nu|\lambda\sigma) - \frac{1}{2}(\mu\sigma|\lambda\nu)\right] - i(e\hbar/2mc)\sum_{\alpha} \boldsymbol{H}_{\alpha} < \chi_{\mu}|(\mathbf{r}\times\nabla)_{\alpha}|\chi_{\nu} >, \qquad [4]$$

where $\boldsymbol{H}^{\mathrm{core}}_{\mu\nu}$, $(\mu\nu|\lambda\sigma)$, and $(\mu\sigma|\lambda\nu)$ are the unperturbed core Hamiltonian, the Coulomb integral, and the exchange integral respectively; these are estimated by means of the parameters in the INDO method. In the present calculation, we shall adopt Pole's parameters[8] except for the off-diagonal element of the core Hamiltonian, which is estimated from this expression:

$$\boldsymbol{H}^{\mathrm{core}}_{\mu\nu} = (\kappa_{\pi}/2)(\beta^{0}_{\mathrm{A}} + \beta^{0}_{\mathrm{B}})S_{\mu\nu} \qquad (\mu \neq \nu), \qquad [5]$$

in which κ_{π} denotes a correction factor for the π–π interaction. κ_{π}=0.85 was used in this work according to the previous proposal.[5] β^{0}_{A} is the bonding parameter for the atom A, and $S_{\mu\nu}$, the overlap integral. The density matrix is allowed to be complex

to accommodate the purely imagniary nature of the perturbation, while $\mathbf{Im}[\boldsymbol{P}_{\mu\nu}(\boldsymbol{H}_\alpha)]$ represents the imaginary part. The derivative in Eq. 3 is evaluated numerically using the finite-difference technique, in which it is approximated by a single difference:

$$(\partial \boldsymbol{P}_{\mu\nu}(\boldsymbol{H}_\alpha)/\partial \boldsymbol{H}_\alpha)_{\mathbf{H}=0} = \mathbf{Im}[\boldsymbol{P}_{\mu\nu}(\boldsymbol{H}_\alpha)]/\boldsymbol{H}_\alpha. \quad [6]$$

In this calculation, the bond lengths and bond angles used were taken from the X-ray-diffraction data[9] and also from the standard values proposed by Pople and Gordon.[10] All the calculations were carried out by means of a HITAC M-280H computer of the Tokyo Institute of Technology and a S-810 computer at the Computer Center of Tokyo University.

Results and Discussion

Since the ^{29}Si chemical shift is considered to be governed predominantly by the paramagnetic term as well as by the ^{13}C chemical shift, we will evaluate mainly the contribution from this terms using the FPT CNDO/2 method. In such a semiempirical MO calculation, we sometimes encounter the question of whether or not, the CNDO parameters proposed by Pople et al.[11] are appropriate to give a satisfactory agreement between the calculated and experimental chemical shifts. Ando et al.[6] and Ellis et al.[12] showed that the MO parameters proposed by Pople et al. did not give a satisfactory agreement between the calculated and experimental ^{13}C chemical-shift values in hydrocarbons. They therefore altered the bonding parameters for carbon and hydrogen atoms to improve their results. For our experiment, we will use a set of Ando's bonding parameters,[6] β_C=−15 eV and β_H=−13 eV, for the carbond and hydrogen atoms respectively contained in organosilicon compounds; these parameters reproduce reasonably well the gross trends of the observed values of the ^{13}C chemical shifts and the shielding tensor. However, as for the Si atom considered here, the optimized value of the bonding parameter, which reproduces reasonably well the experimental values of the ^{29}Si chemical shifts is not known. Therefore, the optimized value of the β parameter for the silicon atom will be examined.

First, we will consider the ^{29}Si chemical shift of silicon hydride derivatives, which consist of silicon, carbon, and hydrogen atoms. As is shown in Table 1, the experimental ^{29}Si chemical-shift data indicate that, as the degree of hydrogen substitution is increased, the chemical shifts are displaced upfield; the range of the chemical-shift displacement is about 90 ppm. In spite of such a simple structural change, the range of the chemical-shift displacement is quite large. This means that silicon–hydride derivatives are excellent for use in a theoretical study of the ^{29}Si chemical shift.

We will now examine the ^{29}Si chemical-shift behaviour of silicon–hydride derivatives calculated by using a set of Pople's bond parameters[11] (β_H=−9 eV, β_C=−21 eV, and β_{Si}=−13.065 eV) for hydrogen, carbon, and silicon atoms respectively. A plot of the experimental chemical shifts versus the calculated values is shown in Fig. 1a. The dashed line is a theoretical line with the slope of 1. This means that the experimental and calculated values agree with each other exactly. As may be seen from Fig. 1a, the data points greatly deviate from the theoretical line, and the calculated chemical-shift range is quite small compared with the experimental data. This means that the set of Pople's bonding parameters are not appropriate in the ^{29}Si chemical-shift calculation.

As is to be expected from the previous results[6] for the ^{13}C chemical shift, the lowering of the absolute value for β_{Si} leads to a wide expansion of the calculated

Table 1. Calculated ^{29}Si Chemical Shifts of Silicon Hydrides[a]

Compound	d	σ^d	σ^p	σ^T	δ_{calcd} [b]	$\delta_{exp.}$ [c]
1) SiH_4	3.4578	66.78	−321.64	−254.86	−63.87	−92.5
2) SiH_3Me	3.5050	67.43	−336.78	−269.35	−49.38	−65.2
3) SiH_3Ph	3.5236	67.69	−333.55	−265.87	−52.86	−60.0
4) SiH_3Bz	3.5175	67.60	−341.22	−273.62	−45.11	−56.0
5) SiH_2Me_2	3.5376	67.88	−348.38	−280.50	−38.23	−40.0
6) SiH_2MePh	3.5546	68.11	−346.13	−278.02	−40.71	−36.9
7) SiH_2Ph_2	3.5874	68.56	−341.51	−272.95	−45.78	−33.6
8) $SiHMePh_2$	3.6058	68.80	−358.63	−289.82	−28.91	−19.5
9) $SiHPh_3$	3.6286	69.11	−352.99	−283.88	−34.85	−17.8
10) $SiHMe_2Ph$	3.5715	68.34	−367.09	−298.75	−19.98	−17.6
11) $SiHMe_3$	3.5577	68.15	−360.83	−292.67	−26.06	−16.3
12) $SiHPr_3$	3.5918	68.62	−375.43	−306.82	−11.91	−8.5
13) $SiHEt_3$	3.5798	68.45	−372.51	−304.05	−14.68	0.2

a) The bonding parameters used are β_H=−13 eV, βc=−15 eV, and β_{Si}=−12 eV. b) Values given in ppm. Chemical shifts calculated with respect to TMS. The negative sign means an upfield shift from TMS. c) Data taken from Ref. 14. The negative sign means an upfield shift from TMS.

^{29}Si chemical-shift range. Thus, the value of β_{Si} which yields the best agreement between the experimental and calculated values for all chemical shifts was determined. This examination leads to the selection of the value of -12 eV for β_{Si}. As was mentioned above, a set of Ando's β_C and β_H bonding parameters ($\beta_C=-15$ eV and $\beta_H=-13$ eV) for carbon and hydrogen atoms was fixedly used. A plot of the experiment chemical shifts versus the calculated ones is shown in Fig. 1b. It may be seen that data points line on the theoretical line. The fit to the least-squares line has a correlation coefficient of 0.933. This means that the calculation reproduces well the experiment.

The diamagnetic, paramagnetic, and total contributions for the ^{29}Si chemical shift calculated using the "new" value of $\beta_{Si}(=-12$ eV), together with the experimental values, are listed in Table 1. Note that the calculated chemical shift (σ) is a nuclear shielding constant, and so the negative sign means deshielding.

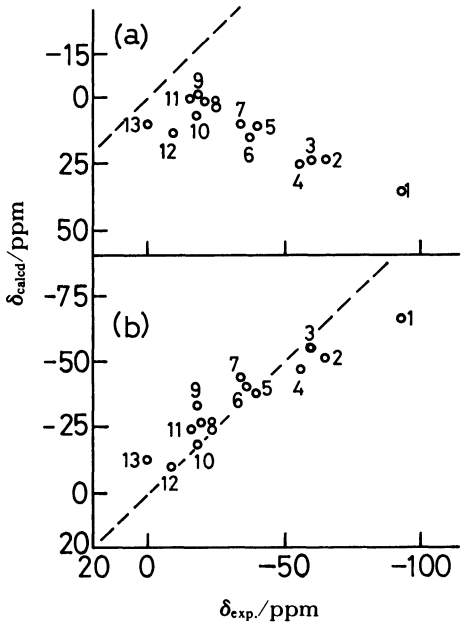

Fig. 1. The plot of the calculated ^{29}Si chemical shifts versus the experimental ones in silicon hydrides.
(a): Pople's β parameters ($\beta_H=-9$ eV, $\beta_c=-21$ eV, and $\beta_{Si}=-13.065$ eV). (b): β parameters proposed in this work ($\beta_H=-13$ eV, $\beta_c=-15$ eV, and $\beta_{Si}=-12$ eV).
The negative sign means upfield shift relative to TMS.
The numbers refer to the following compounds: 1: SiH_4; 2: SiH_3Me; 3: SiH_3Ph; 4: SiH_3Bz; 5: SiH_2Me_2; 6: SiH_2MePh; 7: SiH_2Ph_2; 8: $SiHMePh_2$; 9: $SiHPh_3$; 10: $SiHMe_2Ph$; 11: $SiHMe_3$; 12: $SiHPr_3$; 13: $SiHEt_3$.
The abbreviations used are as follows: Me, methyl; Ph, phenyl; Bz, benzyl; Pr, *n*-propyl; Et, ethyl.
The dashed line is the theoretical one with the slope of 1.0. This means that the experimental and calculated values completely agree with each other.

On the other hand, the negative sign of the experimental chemical shift (δ) means shielding. Therefore, tetramethylsilane was used as the standard reference. As may be seen from Table 1, the diamagnetic term, σ^d, moves upfield by about 2 ppm in going from SiH_4 to $SiHEt_3$. This variation is quite small, and the chemical-shift displacement is in the opposite direction compared with the experimental one. On the other hand, the paramagnetic term, σ^p, moves downfield by about 50—60 ppm. This means that the ^{29}Si chemical shift is predominantly governed by the paramagnetic term.

Next, we will consider the ^{29}Si chemical-shift behavior of organic silicon compounds containing the fluorine atom. The fluorine atom is known to be the most electronegative of all the atoms. This may be attributed to the effect of the higher electron unbalance in the Si–F bond and may lead to a wider range of ^{29}Si chemical shifts compared with the case of silicon–hydride compounds.

In the ^{29}Si chemical-shift calculation, the value of β_{Si} determined above in silicon–hydride compounds was used; also, as the β_F parameter for the fluorine atom, we adopted the value of -20 eV obtained by Ando et al.,[13] by the use of which the ^{19}F chemical-shift calculation reproduces the experiment reasonably well. The diamagnetic, paramagnetic, and total contributions calculated using these β parameters are listed, together with the experimental chemical-shift values, in Table 2. It may be seen that the chemical-shift range is more greatly expanded than in the case of silicon–hydride compounds. It may also be found that the relative chemical shift is

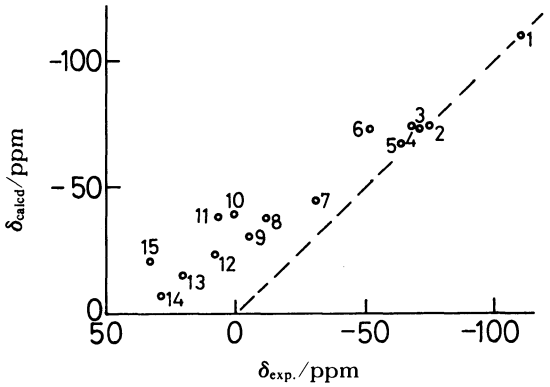

Fig. 2. The plot of the calculated ^{29}Si chemical shifts versus the experimental ones in fluorosilanes.
β bonding parameters ($\beta_H=-13$ eV, $\beta_c=-15$ eV, $\beta_{Si}=-12$ eV, and $\beta_F=-20$ eV). The negative sign means upfield shift relative to TMS.
The numbers refer to the following compounds: 1: SiF_4; 2: SiF_3Ph; 3: SiF_3PhMe; 4: SiF_3PhOMe; 5: SiF_3Bz; 6: SiF_3Me; 7: SiF_2Ph_2; 8: SiF_2MePh; 9: $SiFPh_3$; 10: SiF_2Et_2; 11: SiF_2Me_2; 12: $SiFMePh_2$; 13: $SiFMe_2Ph$; 14: $SiFPr_3$; 15: $SiFMe_3$.

Table 2. Calculated ^{29}Si Chemical Shifts of Fluorosilanes[a)]

Compound	d	σ^d	σ^p	σ^T	δ_{calcd} [b)]	$\delta_{exp.}$ [c)]
1) SiF_4	2.1098	45.17	−254.38	−209.20	−109.53	−111.0
2) SiF_3Ph	2.5888	53.50	−296.91	−243.41	−75.32	−73.7
3) SiF_3PhMe	2.5952	53.61	−297.43	−243.83	−74.90	−72.0
4) SiF_3PhOMe	2.5892	53.50	−297.29	−243.78	−74.95	−71.4
5) SiF_3Bz	2.5805	53.36	−303.18	−249.82	−68.91	−64.2
6) SiF_3Me	2.5345	52.59	−296.31	−243.72	−75.01	−51.8
7) SiF_2Ph_2	2.9720	59.64	−331.09	−271.45	−47.28	−30.5
8) SiF_2MePh	2.9314	59.01	−337.96	−278.95	−39.78	−12.4
9) $SiFPh_3$	3.3213	64.85	−351.88	−287.03	−31.70	−4.7
10) SiF_2Et_2	2.9258	58.93	−335.45	−276.52	−42.21	0.5
11) SiF_2Me_2	2.9006	58.53	−336.55	−278.02	−40.71	6.2
12) $SiFMePh_2$	3.2980	64.51	−358.52	−294.01	−24.72	7.7
13) $SiFMe_2Ph$	3.2633	64.01	−367.00	−302.99	−15.74	19.8
14) $SiFPr_3$	3.2819	64.28	−375.19	−310.91	−7.82	28.8
15) $SiFMe_3$	3.2426	63.71	−359.88	−296.17	−22.56	31.9

a) The bonding parameters used are $\beta_H = -13$ eV, $\beta_C = -15$ eV, $\beta_{Si} = -12$ eV, and $\beta_F = -20$ eV. b) Values given in ppm. Chemical shifts calculated with respect to TMS. The negative sign means an upfield shift from TMS. c) Data taken from Ref. 14. The negative sign means an upfield shift from TMS.

predominantly governed by the paramagnetic term, although the diamagnetic term is more greatly varied by the degree of fluorine substitution than in the case of silicon-hydride compounds. A plot of the experimental chemical shifts versus the calculated ones is shown in Fig. 2. It may be seen that data points deviate slightly from the theoretical line with the slope of 1.0, but the overall trend of the experimental data is reproduced by the calculation. In particular, it can be said that it has been established that the ^{29}Si chemical shift in SiR_nF_{4-n} (R means the substitution group, and n, the substitution number) moves upfield as the degree of fluorine substitution is increased. (It is noticeable that the upfield shift with an increase in the degree of fluorine substitution is opposite to the case of the ^{13}C chemical shift in CR_nF_{4-n}.)

Finally, we will consider the relationship between the ^{29}Si chemical shift and the electron density. It has been reported that the ^{13}C chemical shift is closely related to the electron density on the carbon atom. The larger electron density on the carbon leads to the upfield shift. The calculated electron densities on the silicon atoms considered here are listed in Tables 1 and 2. It may be seen that the electron densities on silicon atoms in silicon-hydride compounds decrease as the degree of hydrogen substitution is increased, while those in SiR_nF_{4-n} decrease as the degree of electronegative fluorine substitution is increased. From Tables 1 and 2 it may also be seen that σ^d moves linearly upfield with an increase in the electron density on the silicon atom, as is to be expected from Eq. 2. The direction of such a shift is opposite to that of the experimental chemial shift. On the other hand, σ^P and σ^T move downfield, with a great scatter, with an increase in the electron density. Further, a plot of the experimental chemical shift versus the electron density on the silicon atom is shown in Fig. 3. The experimental chemical shifts move downfield, with a great scatter, with an increase in the electron density. The direction of such a shift is opposite to the general consideration that an increase in the electron density leads to an upfield shift. Therefore, it seems that it is difficult to explain the ^{29}Si chemical shift obtained experimentally only in terms of the electron density.

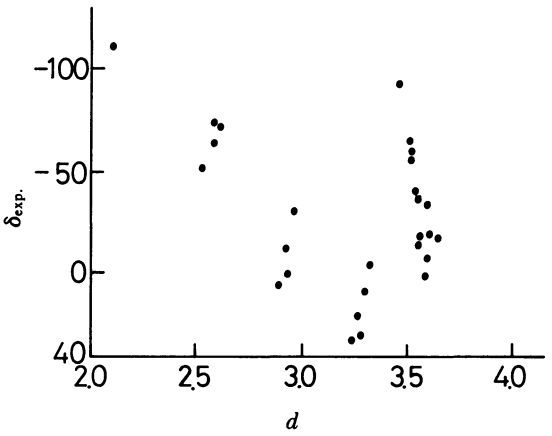

Fig. 3. The plot of the experimental ^{29}Si chemical shift $\delta_{exp.}$ against the calculated electron density d in organosilicon compounds.

From the above-mentioned results, it can be concluded that the experimental overall trend of ^{29}Si chemical shifts in sililcon hydrides and fluorine-containing organic compounds can be fairly reproduced by the FPT CNDO/2 method, with a small improvement of the β-bonding parameter.

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