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An Experimental and Theoretical Study of Spin−Spin Coupling in Chlorosilanes

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An experimental and theoretical study of the absolute value of the one-bond spin−spin coupling constant $|^1J(\mathrm{Si,H})|$ in SiH_nCl_{4-n} ($n = 0-4$) dissolved in THF-d_8 is presented. We found $|^1J(\mathrm{Si,H})|$ to increase with an increasing number of chlorine substituents, and the quantitative changes were found to differ from the values previously reported for the same compounds dissolved in cyclohexane-d_{12}. We also report on the variations in $|^1J(\mathrm{Si,H})|$ as a function of temperature, which we found to be linearly temperature dependent for the chlorine-substituted silanes and temperature independent for SiH_4. Furthermore, the temperature dependence of $|^1J(\mathrm{Si,H})|$ varied between the different chlorosilanes. Solvent−solute interactions were studied by quantum chemical DFT calculations. The variations in chloro−silane bond lengths upon adduct formation and the different adduct interaction energies may explain the temperature dependences of the coupling constants.

Introduction

Nuclear magnetic resonance (NMR) spectroscopy may be used to obtain molecular information by measuring the chemical shifts and spin−spin coupling constants, and in the case of chloro-substituted silanes SiH_nCl_{4-n} ($n = 0-4$), both the ^1H and ^{29}Si nuclei can easily be probed. To the best of our knowledge, the number of systematic studies of all the said compounds $n = 0-4$ is limited to the two papers by Ebsworth and Turner, who, in the early 1960s, reported both the coupling constants[1] and the chemical shifts[2] in the nonpolar solvent cyclohexane-d_{12}.

The recent developments within the field of theoretical chemistry have made it possible to calculate various parameters relevant to the NMR observables,[3] but the calculations are mostly concerned with molecules in the gas phase. Various levels of quantum chemical calculations of NMR parameters for SiH_4 in the gas phase have been presented in the literature,[4] but in the case of chloro-substituted derivatives, such calculations have not been reported.

Although experimental data on the SiH_nCl_{4-n} ($n = 0-4$) system have already been presented, we believe further studies of the compounds are merited due to the advances in the NMR instruments and computational possibilities made over the past decades. Furthermore, the presence of a polar NMR solvent, e.g. THF-d_8, may perturb the silanes ($n = 0-4$) to a significant extent, resulting in changes in the one-bond spin−spin coupling constants compared to the values obtained in less polar solvents. Thus, by combining experiments and quantum chemical calculations, the aim of the present work is to present new and reliable data on the absolute value of the one-bond spin−spin coupling constants $|^1J(\mathrm{Si,H})|$ for chlorosilanes in THF-d_8 and to make an attempt at rationalizing the observed experimental data.

Experimental and Computational Methods

General Considerations. All manipulations were performed using standard techniques for handling of air-sensitive compounds, either inside a glovebox or using standard Schlenk techniques. THF-d_8 was dried according to standard procedures prior to use. $SiCl_4$ (Aldrich) and MgH_2 (Alfa Aesar) were used as received.

Sample Preparation. In a typical preparation, MgH_2 (28 mg, 1.1 mmol) and THF-d_8 (0.76 mL) were added to an NMR tube. The mixture was carefully shaken before $SiCl_4$ (75 μL, 0.66 mmol) was added. Finally, the tube was sealed under Ar. The reaction was allowed to take place for 3 days at room temperature, forming a mixture of the various chlorosilanes from which the reported data were obtained.

Instrument. ^1H NMR spectra were measured on a Varian Gemini 2000 using 32 scans and ^{29}Si NMR on a Varian VXR-300S using 5000 scans.

Variable Temperature. The instrument temperature calibration was performed by employing a methanol thermometer in the range 194.3 K $< T <$ room temperature in steps of 10 K.

Computational Details. DFT calculations were carried out using the Spartan 5.1[5] (BP86 functional[6] and DNP basis set[7]) and Gaussian 03[8] (B3LYP functional[9] and aug-cc-pvtz basis set[10]) program packages. For the B3LYP results, counterpoise calculations for estimation of basis set superposition errors (BSSE) were performed using the algorithm built into Gaussian 03.

For each silane−THF adduct, a number of different conformers were investigated to ensure that the global energy minimum was found. From the calculated IR spectra, we could confirm that each stationary state is a true minimum, as witnessed by the absence of imaginary vibrational frequencies.

Results and Discussion

Chlorine Substitution. The absolute value of each one-bond spin−spin coupling constant $|^1J(\mathrm{Si,H})|$ was measured as the separation of the Si-satellites in the ^1H NMR spectra or as the separation between the signals in the various multiplets in the ^{29}Si NMR spectra. As seen from Table 1 and Figure 1, the deviations between the ^1H and ^{29}Si NMR experimentally determined $|^1J(\mathrm{Si,H})|$ values are in the range 0.1−0.8 Hz. Although we note that ^1H NMR systematically provides a slightly lower value, the difference is insignificant.

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TABLE 1: Experimentally Determined ^{1}H and ^{29}Si NMR Data for SiH_nCl_{4-n} ($n = 0-4$)[a]

	^{1}H NMR			^{29}Si NMR	
	this work[b]		literature[c]	this work[d]	
	δ_H	$\lvert ^1J(Si,H)\rvert$	$\lvert ^1J(Si,H)\rvert$	δ_{Si}	$\lvert ^1J(Si,H)\rvert$
$SiCl_4$	–	–	–	−18.55	–
$SiHCl_3$	6.09	377.5	362.9	−9.52	378.0
SiH_2Cl_2	5.32	308.5	288.0	−16.83	308.9
SiH_3Cl	4.48	257.4	238.1	−50.87	258.2
SiH_4	3.14	203.0	202.5	−95.84	203.1

[a] Chemical shifts δ are reported in ppm and the one-bond spin−spin coupling constants $|^1J(Si,H)|$ are reported in Hz. [b] $T = 296$ K, in THF-d_8; the chemical shifts δ_H are relative to residual THF protons at 1.73 ppm. [c] Data from Ebsworth and Turner (ref 1). [d] $T = 296$ K, in THF-d_8; the chemical shifts δ_{Si} are relative to TMS at 0 ppm.

TABLE 2: Calculated Bonding Energies (kcal/mol) between Chlorosilanes and THF Computed at Different Levels of Theory

	E(BP86/ DNP)	E(B3LYP/ aug-cc-pvtz)	E(B3LYP/ aug-cc-pvtz) + BSSE
$SiHCl_3$	0.8	1.6	1.3
SiH_2Cl_2	2.0	2.6	2.4
SiH_3Cl	1.5	3.1	2.9
SiH_4	0.1	0.7	0.6

The observed ^{1}H chemical shifts increase monotonically from 3.14 to 6.09 ppm with increasing chlorine substitution, in line with the trend reported by Ebsworth and Turner.[2,11] For the ^{29}Si chemical shifts, also in line with previous reports,[12] a maximum δ_{Si} value is observed for $SiHCl_3$. Thus, the reliability of the $|^1J(Si,H)|$ values to be discussed in further detail below is supported by the trends in the observed chemical shifts.

From Figure 1, we see that successive substitution of H with Cl results in an approximately linear response in $|^1J(Si,H)|$. The observed increase in $|^1J(Si,H)|$ with increasing Cl substitution agrees well with previous findings.[1] However, a careful inspection of Figure 1 shows that there are significant deviations between the data reported herein and the data previously reported in the literature.[1]

When our $|^1J(Si,H)|$ values at 296 K, obtained by probing the ^{1}H nucleus, are compared to the values reported for chlorosilanes in cyclohexane-d_{12}, it is seen that for SiH_4 the values differ by 0.5 Hz, which is within the range of our experimental variations (vide supra). Thus, although the two chosen solvents have very different polarities, the effect exerted on the measured $|^1J(Si,H)|$ for SiH_4 is insignificant.

For the various chloro-substituted molecules, on the other hand, the data reported previously by Ebsworth and Turner[1] does not compare equally well to the data reported herein. In our experiments, the $|^1J(Si,H)|$ values at 296 K were found to be 14.6−20.9 Hz larger than the earlier values, as reported in Table 1. It is reasonable to ascribe this discrepancy to the stronger interactions between the polar and soft chlorosilanes and the polar THF-d_8 used in the present work compared to the nonpolar cyclohexane-d_{12} used by Ebsworth and Turner.[1,2]

To put this hypothesis on firmer ground, we studied THF−silane interactions by DFT calculations. We found that THF−silane adduct formation may indeed occur by coordination of the O atom to the H-rich side of the silane. Calculated bonding energies between THF and the different silanes are given in Table 2. The good qualitative agreement between the results from different methods is gratifying.

Regardless of the level of theory, the calculated interaction between THF and the silanes is higher for the chloro-substituted silanes compared to SiH_4. In Figure 2 we have illustrated the correlation between the difference in the experimentally determined $|^1J(Si,H)|$ values for the two solvents (THF-d_8 and cyclohexane-d_{12}[1]) and the calculated silane−THF bonding energies. As seen, there is a reasonable qualitative agreement between the data, although we note that for the higher level of theory, there is a slight deviation from the expected trend for the highly Cl-substituted silanes.

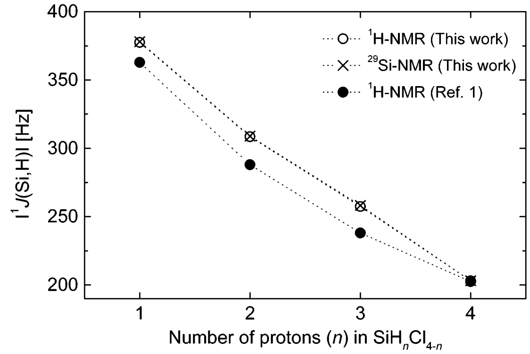

Figure 1. Experimentally observed one-bond spin−spin coupling $|^1J(Si,H)|$ in SiH_nCl_{4-n} ($n = 0-4$) dissolved in THF-d_8 (this work) and cyclohexane-d_{12} (ref 1).

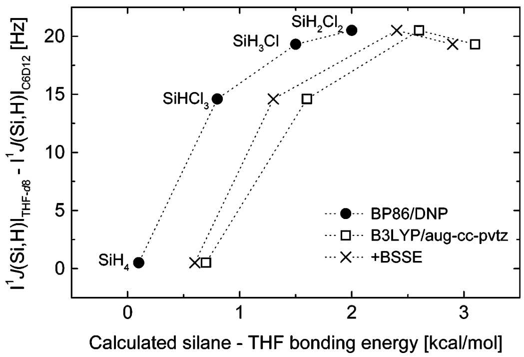

Figure 2. The correlation between the difference in the $|^1J(Si,H)|$ values measured in THF-d_8 (this work) and cyclohexane-d_{12} (ref 1) and the theoretically calculated silane−THF bonding energies.

Due to the weak solvent−SiH_4 interactions in THF-d_8, a comparison between the calculated gas phase and experimentally determined coupling constants should be of value. However, we note that, depending on the chosen method, SCF, CAS, DFT, SOPPA, or SOPPA(CCSD), theoretically derived $^1J(Si,H)$ values in the range from −186.10 to −243.74 Hz have been reported for SiH_4.[13,14] Among these data, we find the calculated value of −202.541 Hz reported by Sauer et al.[14] to show the best numerical agreement with our measured $|^1J(Si,H)|$ values for SiH_4. This is reasonable, as their calculations were performed at a higher level of theory (CCSD) than the others. A certain amount of fortuity may not be ruled out, however, as the calculations model a gas-phase molecule rather than a molecule in solution, and the SOPPA approximation may introduce errors as well. For chlorine-substituted silanes, theoretically calculated values are currently not available from the literature.

Our measured $|^1J(Si,H)|$ values in THF-d_8 are systematically larger than the results reported for cyclohexane-d_{12}. Further DFT calculations serve to elucidate the factors, giving raise to this difference: Coordination of THF-d_8 perturbs the geometry of the silane, and although the changes in the Si−H bond lengths (Figures 3−6) are rather subtle, the coupling constant is known to depend strongly on atomic distances.[15] The change in the calculated average Si−H bond length upon THF coordination is in the range 0.1−0.4%, whereas the concomitant change in

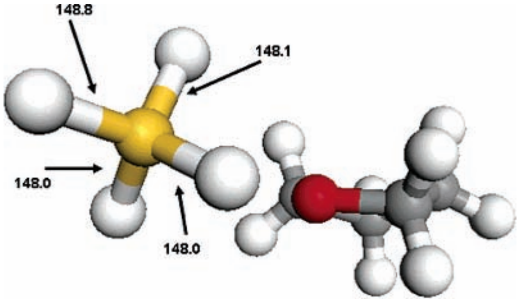

Figure 3. THF−SiH_4 complex. Si−H Bonding distances in picometers. Si−H distance for unperturbed SiH_4 is 148.3 pm.

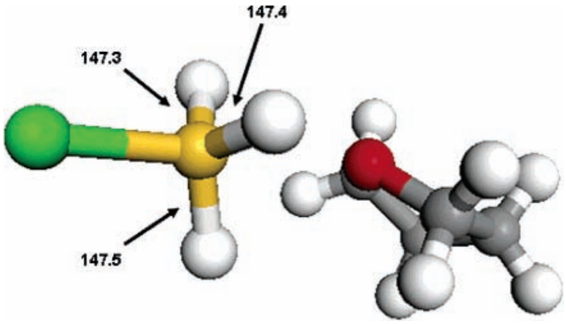

Figure 4. THF−SiH_3Cl complex. Bonding distances in picometers. Si−H distance for unperturbed SiH_3Cl is 147.8 pm.

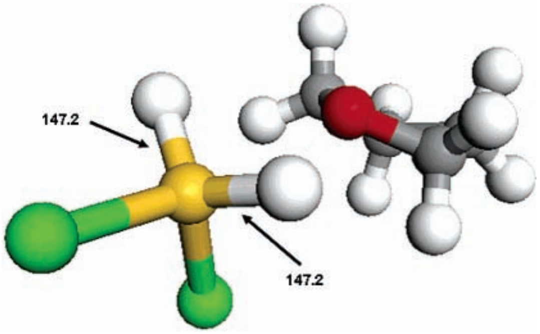

Figure 5. THF−SiH_2Cl_2 complex. Bonding distances in picometers. Si−H distance for unperturbed SiH_2Cl_2 is 147.3 pm.

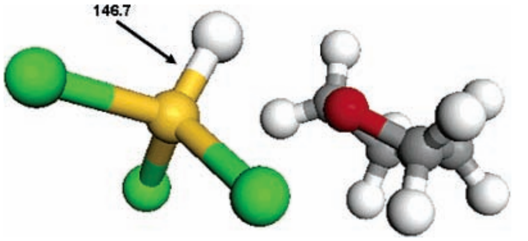

Figure 6. THF−$SiHCl_3$ complex. Bonding distances in picometers. Si−H distance for unperturbed $SiHCl_3$ is 146.7 pm.

$|^1J(\mathrm{Si,H})|$ is in the range 4−8%. For SiH_4, Sauer et al.[14] calculated the coupling constant's dependence on geometry deformations by computing the former for a large number of different geometries. Further, they parametrized the results, allowing us to estimate the effect of the perturbation. If we enter the silane geometry from our geometry optimizations on the silane−THF complex into the expression from Sauer et al., we arrive at a coupling constant change of 10.8 Hz due to geometry changes. This is on the same order of magnitude as the discrepancies observed between the chlorinated silanes in the two different solvents. The lack of discrepancy in the case of SiH_4 may be ascribed to the weak bonding and concomitant short lifetime of the SiH_4−THF adduct.

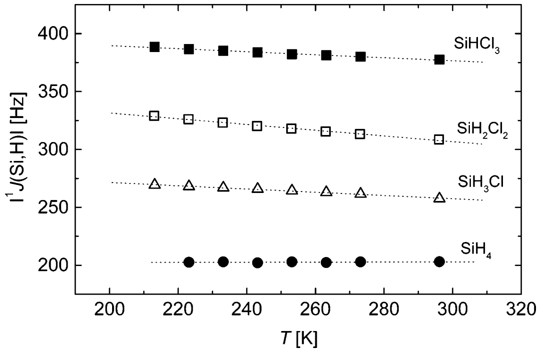

Figure 7. Experimentally observed one-bond spin−spin coupling $|^1J(\mathrm{Si,H})|$ at various temperatures in silane and the various chlorosilanes dissolved in THF-d_8.

TABLE 3: Estimated Slopes (*a*) and $|^1J(\mathrm{Si,H})|$ at 0 K (J_0) Obtained by Fitting $J_T = aT + J_0$ to the Experimentally Determined $|^1J(\mathrm{Si,H})|$ Values at Various Temperatures[a]

	a	J_0		*a*	J_0
$SiHCl_3$	−0.131	415.8	SiH_3Cl	−0.140	299.5
SiH_2Cl_2	−0.247	380.9	SiH_4	0.006	201.3

[a] The temperature dependence of $|^1J(\mathrm{Si,H})|$ is shown in Figure 7. *a* is reported in Hz/K, whereas J_0 is reported in Hz.

Figures 3−6 depict the silane−THF adducts, with the Si−H bond lengths given in picometers. The calculations suggest that the Si−H distance, except for one of the two pseudo-symmetrically independent Si−H bonds in SiH_4, is shortened upon THF coordination to the silane. All of these changes agree qualitatively with the experimental observations of a stronger spin−spin Si−H coupling for chlorosilanes dissolved in THF-d_8 compared to the values measured in cyclohexane-d_{12}. Furthermore, we see that for SiH_4, THF coordination causes one of the Si−H bonds to shorten, whereas the other is elongated. Thus, according to the calculations, on average, the influence of the solvent (THF-d_8 vs cyclohexane-d_{12}) should be lower for SiH_4 than for any of the chloro-substituted silanes. It is gratifying that this is in accordance with the experimental observations.

Temperature Dependence. We studied $|^1J(\mathrm{Si,H})|$ in the temperature range 213 K < T < 273 K, and the plots are shown in Figure 7. In a separate experiment we measured $|^1J(\mathrm{Si,H})|$ at 296 K. As seen from Figure 7, the $|^1J(\mathrm{Si,H})|$ measured at 296 K agrees very well with the estimated value obtained by extrapolation of the temperature series and we obtained the same numerical values for $|^1J(\mathrm{Si,H})|$, regardless of whether we probed the ^1H or the ^{29}Si nuclei at 296 K (Table 1).

It is interesting to note that $|^1J(\mathrm{Si,H})|$ is temperature independent for SiH_4, whereas for the chloro-substituted silanes, significant temperature dependences are observed. Over the temperature range studied, each set of $|^1J(\mathrm{Si,H})|$ data may be fitted by a linear equation given as $J_T = aT + J_0$, where T is the absolute temperature, J_T and J_0 are $|^1J(\mathrm{Si,H})|$ at any T and $T = 0$ K, respectively, and a is an empirical constant. In Table 3 we list the results of the linear fits.

For all of the chloro-substituted compounds, $|^1J(\mathrm{Si,H})|$ decreases with an increase in the temperature. The J_0 values presented in Table 3 are obtained under the assumption that $J(T)$ remains linear down to 0 K, which should be kept in mind when the numerical values are interpreted. However, given the large deviations between the estimated J_0 values, we find it reasonable to postulate that J_0 will increase with increasing chlorine substitution on the species also at 0 K.

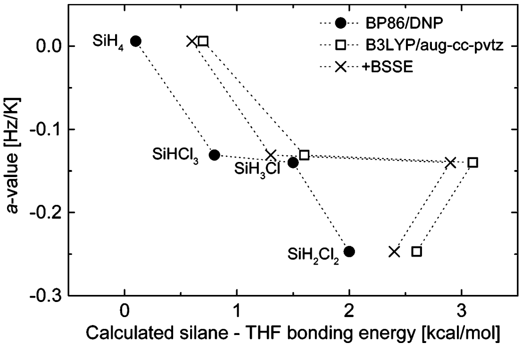

Figure 8. The correlation between the slope of the linear fit to the observed temperature dependence of $|^1J(\mathrm{Si,H})|$, i.e., *a* value from Table 3, and the calculated silane−THF bonding energy.

The temperature dependence of $|^1J(\mathrm{Si,H})|$ is significantly more pronounced for the C_{2v}-symmetric SiH_2Cl_2 than for the C_{3v}-symmetric $SiHCl_3$ and SiH_3Cl, as seen from the slope of the linear fits in Figure 7 and Table 3. Although SiH_3Cl has the highest electrical dipole moment μ of the three chloro-substituted silanes, it does not show the most pronounced temperature dependence. Thus, the slopes *a* reported in Table 3 and shown graphically in Figure 7 cannot be related to μ alone.

The calculated silane−THF bonding energies, given in Table 2, are of a magnitude that makes the adduct lifetimes strongly temperature dependent at and around room temperature ($RT \approx$ 2.3 kJ/mol). The tendency in bonding energies compare well with the tendency in temperature dependence of the coupling constants, as illustrated in Figure 8. While we do not wish to draw any firm conclusions based on these results, they may illustrate a possible cause of the measured temperature dependences, as the time-averaged atomic distances in the adducts will vary as a function of the adduct lifetimes.

Conclusions

Under the given experimental conditions, we found that the observed absolute value of the one-bond spin−spin coupling constant $|^1J(\mathrm{Si,H})|$ increases with an increasing number of chlorine substituents in the chlorosilane SiH_nCl_{4-n} ($n = 0-4$). The quantitative changes observed in THF-d_8 studied herein were found to differ from the values previously reported for the same compounds in cyclohexane-d_{12}. The variations in $|^1J(\mathrm{Si,H})|$ with temperature were found to be linearly temperature dependent for all the chlorine-substituted silanes, and the temperature dependence of $|^1J(\mathrm{Si,H})|$ varies between the different chlorosilanes, being most pronounced for the C_{2v} symmetric SiH_2Cl_2. $|^1J(\mathrm{Si,H})|$ in SiH_4 was found to be temperature independent. Quantum chemical DFT calculations indicate that solute/solvent adduct formation changes the Si−H distances to an extent that may explain the dependence of $|^1J(\mathrm{Si,H})|$ upon the choice of solvent. Further, the calculated adduct formation energies correlate well with the temperature dependence of the coupling constants.

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