# Chemical shifts for compounds of the group IV elements silicon<sup>1</sup> and tin<sup>2</sup>

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Received August 2, 1967

Chemical shifts for <sup>29</sup>Si in seven series of molecules of the type  $X_n SiY_{4-n}$  have been measured where Y is an alkyl group and X varies widely in electronegativity. A considerable amount of proton and fluorine chemical shift data has been obtained for the same compounds and in one series  $(CH_3)_n SiCl_{4-n}$  the <sup>13</sup>C chemical shifts in the methyl groups have been measured.

the <sup>13</sup>C chemical shifts in the methyl groups have been measured. The gross features of the <sup>29</sup>Si chemical shifts are understood by considering the series (Alkyl)<sub>3</sub>SiX with the electronegativity of X widely varied. The hybridization at silicon is approximately conserved in these series and the theoretically anticipated linear dependence on electronegativity of X is demonstrated. The ligands X = O, N, and F are exceptional and these <sup>29</sup>Si chemical shifts have a high field shift. This additional shielding has been associated with  $(p \rightarrow d)\pi$  bonding. The approximate nature of present chemical shift theories is not likely to provide a measure of the order of  $(p \rightarrow d)\pi$  bonding.

chemical shift theories is not likely to provide a measure of the order of  $(p \rightarrow d)\pi$  bonding. The <sup>29</sup>Si chemical shifts in the series  $X_n SiY_{4-n}$  are discussed and also indicate a net shielding effect with  $(p \rightarrow d)\pi$  bonding. A comparison is always made with corresponding <sup>13</sup>C chemical shifts. A long range proton-proton coupling in molecules Me<sub>3</sub>SnX and Me<sub>2</sub>SnX<sub>2</sub>, *H*—C—Si—C—*H*, is observed when and only when X = O, (N?), F.

and only when X = O, (N?), F. <sup>119</sup>Sn chemical shifts in a series of alkyltin compounds have been measured. The same dependence on the electronegativity of X in the series (Alkyl)<sub>3</sub>SnX is noted, but the variation of X is much more limited. Some shielding due to  $(p \rightarrow d)\pi$  bonding in the series (*n*-Butyl)<sub>n</sub>SnCl<sub>4-n</sub> is suggested. The tin chemical shift has been measured as a function of concentration and solvent for simple methyltin bromides and chlorides. In donor solvents, it has been possible to obtain equilibrium constants for complex formation from tin dilution chemical shifts. The nature of the bonding in complexes suggested previously is consistent with the variations in the coupling constant  $|J_{Sn-C-H}|$  with concentration. The distinction between ionization and complex formation with the solvent for (CH<sub>3</sub>)<sub>2</sub>SnCl<sub>2</sub> can be made on the basis of the concentration dependence of  $|J_{Sn-C-H}|$ .

The spin-lattice relaxation time  $T_1$  for  ${}^{13}C$  and  ${}^{29}Si$  in natural abundance in several pure degassed compounds has been measured. These are not in the case of  ${}^{13}C$  (as has been suggested) of the order several minutes, but are always less than 50 s and in one case as low as 3–4 s. Both  ${}^{29}Si$  and  ${}^{13}C$  T<sub>1</sub> values follow what night be expected on the basis of a dipole-dipole mechanism from the closest protons. The short value of 35 s in CS<sub>2</sub> is probably a result of spin-rotation interaction in the liquid state.

Canadian Journal of Chemistry, 46, 1399 (1968)

#### Introduction

Although <sup>13</sup>C chemical shifts in organic compounds are becoming available at an increasing rate (1, 2), so far only two papers have appeared in which <sup>29</sup>Si and <sup>119</sup>Sn have been studied (3, 4). In both cases the investigators have lacked a systematic set of compounds, but the work on <sup>119</sup>Sn carried out by Lauterbur and Burke with tin compounds was a comprehensive investigation which included solvent effects and predicted a considerable use for tin magnetic resonance in following the nature of tin compounds in solution. Reeves and co-workers recently measured the spin–spin coupling constant for <sup>117</sup>Sn—<sup>119</sup>Sn in hexamethylditin from a study of the <sup>119</sup>Sn

Clearly, there is a need for further data, particularly of a systematic nature, regarding the chemical shifts of Si and Sn in organometallic compounds. It is the aim of this study to fill some of this gap, especially with respect to <sup>29</sup>Si chemical shifts which have not yet been studied systematically.

### Experimental

(a) N.M.R. Measurements

Proton magnetic resonance measurements were made on a Varian HA100 or a Varian A60 spectrometer. With silicon compounds, because of the possibility of near overlap with the tetramethylsilane (TMS) signal, a small amount of benzene was used to provide a lock signal and to serve as an internal reference peak. Subsequently, all proton chemical shift data was referenced to 1% TMS with low field shifts reported with a negative sign in parts per million. The tin compounds were usually measured on a Varian A60 with a 1% TMS internal reference signal included. With suitable care, the chemical shifts of protons are given to  $\pm 0.01$  p.p.m. and coupling constants to  $\pm 0.05$  Hz.

Fluorine n.m.r. spectra were obtained from either Varian HR 60 or HR 100 spectrometers tuned to 56.4 MHz or 94.1 MHz respectively. Monofluorotrichloromethane (FTCM) was added in small amount ( $\sim 2\%$  by volume) to each solution and served as an internal standard for fluorine chemical shift measurements. Spin

<sup>&</sup>lt;sup>1</sup>Presented at the 8th E.N.C. meeting, Pittsburgh, Pa. March (1967).

<sup>&</sup>lt;sup>2</sup>Presented at the 7th E.N.C. meeting, Pittsburgh, Pa. February (1966).

coupling constants to fluorine have a mean square deviation  $\pm 0.1$  Hz, while fluorine chemical shifts are given to  $\pm 0.01$  p.p.m.

<sup>29</sup>Si nuclear magnetic resonance spectra (n.m.r.) were obtained from a spectrometer assembled largely from parts manufactured by Varian Associates. The magnetic field strength was 9.41 kG, and the detecting frequency 7.95 MHz. Field sweep was provided by a V3507 slow sweep unit and signals were recorded on a Varian G10 recorder. The V4311 radiofrequency (r.f.) transmitter and receiver unit was driven by highly regulated power supplies which allow increased stability over those available in a Varian spectrometer. The B+ voltage was supplied from a Lambda Electronics Corporation model 32 power supply and the 12 V d.c. filament source was a Lectronic Research Associates Inc. model T.R. 32-34 0.01% regulated power supply. The silicon signals were all recorded with rapid passage dispersion mode ( $\sim 1~{
m G}/{
m cm}$ min sweep rates) at high r.f. power levels. Relaxation time measurements  $(T_1)$  for <sup>13</sup>C and <sup>29</sup>Si were measured as will be described in the Results section of this paper. The samples were neat liquids in 10 mm o.d. thin wall tubes and immersed in some reference liquid in standard 15 mm o.d. test tubes. The external standard was tetramethoxysilane in almost all cases. Sweep rate calibrations were achieved by using a sample of trimethylsilane. The doublet structure with spacing 184 Hz was measured from the proton spectrum and this corresponds to 23 p.p.m. in the silicon spectrum. The sweep standard was observed with increasing and decreasing magnetic field and the doublet recorded. The external reference and unknown sample were then recorded at exactly the same sweep rates four times in each direction and finally replaced by the sweep standard to assure no drift in sweep rates.

The <sup>119</sup>Sn nuclear magnetic resonance signal was observed with a modified Varian V4310C r.f. unit at 22.3822 MHz in a field 14.1 kG. In this case the signals are somewhat stronger and display through a Varian V3521 base line stabilizer was possible. This latter instrument employs an audio modulation frequency of 1996 Hz in our case, and in most experiments an absorptionmade signal was presented. The modulation frequency provides a calibration for spectra. Heteronuclear double resonance at high power levels at the proton resonance frequency using an NMR Specialties S.D. 60 decoupler causes collapse of the scalar coupling to protons and simplifies the measurement of tin chemical shifts. In many cases, the <sup>119</sup>Sn signal is badly split due to coupling to many non-equivalent protons in the molecule.

#### (b) Sample Preparation

Organosilicon compounds were purchased from several sources (N.M.R. Specialties Co.; Peninsular Chem-Research Corp.; Aldrich Chemical Co.). Several samples were kindly donated by the Dow Corning Corporation. The purchased and donated samples were used without further purification.

Several samples were prepared by standard techniques (6) as listed below. Standard vacuum techniques were used where necessary. Samples were usually purified by distillation and purities checked by n.m.r. spectra run on a Varian A -60.

The silanes  $(C_6H_5)_2SiH_2$ ,  $(C_6H_5)SiH_3$ ,  $SiH_4$ ,  $Me_3SiH$ ,

 $Me_2SiH_2$ , and  $MeSiH_3$  were prepared by reduction of the corresponding chlorides with  $LiAIH_4$  under a dry nitrogen environment.

The methyl and phenyl fluorides were prepared from the chlorides using various fluorinating agents as shown below. Silicon tetrafluoride (SiF<sub>4</sub>) was prepared from the reaction of Na<sub>2</sub>SiF<sub>6</sub> and H<sub>2</sub>SO<sub>4</sub> on a silica gel (7). The phenylmethylsilanes were prepared from phenyllithium and the corresponding methylchlorosilanes. Triphenylsilane was prepared from phenylmagnesium bromide and trichlorosilane.

Preparat	ion of fluorosilanes
Compound	Fluorinating agent
Me₃SiF	$AgF/Et_2O$
$Me_2SiF_2$	$PbF_2/reflux$
MeSiF <sub>3</sub>	HF/Et <sub>2</sub> O (low yield)
φ2SiF2	$HF/Et_2O$

The organotin compounds were obtained from Peninsular Chemical Company or graciously supplied by M and T chemical company as research samples through the agency of Dr. Considine. In most cases, the purity of the supplied material was adequately assured from the proton magnetic resonance spectrum, but in a few cases distillation of the materials was made to provide a pure sample.

### Results

## Silicon Compounds

(a) Accuracy of Silicon-29 Chemical Shift Data The error in the <sup>29</sup>Si shift measurements is estimated to be  $\pm 1$  p.p.m. This estimate is based on two facts. First, the standard deviation on a series of seven measurements of the chemical shift in a (MeO)<sub>4</sub>Si/TMS sample was found to be 0.4 p.p.m. Second, many samples give <sup>29</sup>Si spectra which are split into multiplets by direct <sup>29</sup>Si—H coupling. The coupling constants may be measured from the <sup>29</sup>Si spectrum and com-pared with the value obtained from the <sup>1</sup>H spectrum. The values from <sup>29</sup>Si spectra consistently agree to  $\pm 5$  Hz with those obtained from <sup>1</sup>H spectrum. For example,  $J_{2^{9}Si-H}$  in  $\phi_{2}SiMeH$  was found from the <sup>29</sup>Si spectrum to be 190-200 Hz and from the <sup>1</sup>H spectrum to be 196 Hz. In some cases, for example the methylchlorosilanes, the <sup>29</sup>Si spectrum cannot be observed except under very fast sweep and higher than normal power conditions. The errors are consequently somewhat larger, about  $\pm 5$  p.p.m. Also, some signals, particularly tetravinylsilane, are considerably broadened by spin coupling and the error is increased to  $\pm 3$  p.p.m.

While the random error in the <sup>29</sup>Si measurements is  $\pm 1$  p.p.m., there is a systematic error in the measurements which has not been taken into account. Since an external standard is being

used, a correction should be made for differences in bulk susceptibility of the various samples (8). This correction may be applied using the following equation.

$$\delta_{\mathrm{sphere}} = \delta_{\mathrm{obs}} + rac{2\pi}{3} (\chi_{\mathrm{v,ref}} - \chi_{\mathrm{v,sample}}),$$

where  $\delta_{sphere} = spherical$  or true chemical shift,  $\delta_{obs} = observed$  chemical shift,  $\chi_{v,ref} = volume$ susceptibility of reference, and  $\chi_{v,sample} = volume$ susceptibility of sample. The bulk susceptibility correction will be less than 1 p.p.m. and can probably be ignored. As a check, the chemical shift between Me<sub>3</sub>SiH and (MeO)<sub>4</sub>Si was measured from internal and external standards. For the internal standard the shift is 62.6 p.p.m. and for the external standard it is 61.5 p.p.m. It is questionable whether or not this difference is significant. In any case, the small error introduced by failure to apply a bulk susceptibility correction is bound to be preferable to the possibility of larger errors introduced by solvent effects.

## (b) N.M.R. Studies of Silicon Compounds

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The main object has been to collect as complete data as is possible on a series of organosilicon derivatives of related structure. Seven series of the type  $SiX_nY_{4-n}$  have been measured where the ligands X and Y are varied among the following: -OMe, -H, -OEt, -OAc, -Cl,  $-\phi$ , -F, and -Me. An incomplete set of data on the vinyl ligand is also available as well as other miscellaneous silicon chemical shifts which do not fall into regular series. The data is compounded into a series of tables which have adequate legends. In Appendix I, all previously reported silicon chemical shifts are also listed in order to serve as a reference point (2, 3). Whenever there was overlap with this previous data and disagreement in values occurred, our measurements were repeated several times in order to ensure that our reported values were correct. An example of a typical silicon-29 spectrum with calibrated sweep is shown in Fig. 1. In 1A, trimethylsilane with tetramethoxysilane as an external sample was recorded in one sweep. The doublet with 184 Hz, splitting for trimethylsilane is clearly seen. In the lower spectrum 1B at the same sweep rate and in the same field direction, the trimethylsilane is replaced by TMS and the chemical shift of 79.5 p.p.m. is recorded. The average chemical shift reported in the tables is



FIG. 1. <sup>29</sup>Si magnetic resonance spectra in rapid passage dispersion mode. The upper spectrum is used to calibrate the sweep. The sample is tetramethoxylane with trimethylsilane as an external sweep standard. The lower spectrum shows the -79.5 p.p.m. chemical shift change between (CH<sub>3</sub>)<sub>4</sub>Si and (CH<sub>3</sub>O)<sub>4</sub>Si at the same sweep rate.

obtained, of course, from several such sweeps in both increasing and decreasing field direction.

The general features of the data in Tables I to VII inclusive can be summarized as follows. When an oxygen ligand replaces methyl groups on silicon, there is a shift to low field for the first alkoxy group, and for the further addition of alkoxy groups a shift change to high field is observed. This behavior is very similar to that reported by Lauterbur (2) for the methoxy series. There are small differences of up to 10 p.p.m. in the range of chemical shifts for methoxy, ethoxy, and acetoxy groups. The dominant effect, therefore, must be the exchange of carbon for oxygen in the bonding to silicon. Changes in proton chemical shifts of the methyl groups directly bonded to silicon are small and much less characteristic of the ligands on silicon. The value of  $|J_{13C-H}|$  in the silicon methyl increases

	Si <sup>a</sup>	Me <sup>b</sup>	OMe <sup>*</sup>	J <sup>29</sup> SiCH	J 29 <sub>SiOCH</sub>	J <sub>13 CH</sub> <sup>c</sup>
	(p.p.m.)	(p.p.m.)	(p.p.m.)	(c.p.s.)	(c.p.s.)	(c.p.s.)
Me <sub>4</sub> Si Me <sub>3</sub> SiOMe Me <sub>2</sub> Si(OMe) <sub>2</sub> MeSi(OMe) <sub>3</sub> Si(OMe) <sub>4</sub>	79.5 96.5 77 38 0	$-0.0 \\ -0.21 \\ -0.19 \\ -0.12 \\ -0.12$	-3.49 -3.55 -3.58 -3.60	6.62 6.65 7.2 8.35	4.13 3.90 3.82 3.55	118.1 118.0 118.5 119.1

TABLE I N.m.r. data for Me<sub>x</sub>Si(OMe)<sub>4-x</sub>

<sup>a</sup>Silicon-29 chemical shift in p.p.m. from (MeO)<sub>4</sub>Si. <sup>b1</sup>H chemical shift in p.p.m. from TMS. <sup>cJ ia</sup>CH is for a methyl group directly attached to silicon.

with oxygen substitution at silicon, but the effect is much more pronounced with the acetoxy group. The coupling constant  $|J_{Si-C-H}|$  is also enhanced as oxygen ligands are added. While the <sup>13</sup>C satellites of TMS are single sharp lines, in the case of  $Me_3SiX$  and  $Me_2SiX_2$ , where X = O, F, fine structure is resolved. In the Me<sub>3</sub>SiX compounds, the side bands have a septet structure, while for Me<sub>2</sub>SiX<sub>2</sub> compounds, a quadruplet is resolved. For the oxygen and fluorine ligands which are probably bound to silicon by partial  $(p \rightarrow d)\pi$  bonds there is a long range proton coupling between equivalent methyl protons,  $J_{H-C-Si-C-H}$ . The splitting is always J = 0.35 $\pm$  0.1 Hz. We shall consider this feature in the Discussion section.

### Tin Compounds

#### (a) Chemical Shifts

These series of compounds available were not particularly systematic, though some major trends in the effects of substituents can be seen. The chemical shifts measured are listed as miscellaneous tin chemical shifts in Table IX. If the tin compounds are solids, the chemical shifts correspond to measurements in saturated chloroform solutions. The internal or external reference peak is always the <sup>119</sup>Sn shift in tetramethyltin.

The chemical shift range encountered corresponds to  $\sim$  250 p.p.m., which is considerably less than the total range of chemical shifts for tin compounds (2, 4, 8). The present list is restricted to alkyltin compounds, and does not include the tetra- and di-valent halides which have large chemical shifts to high field (8). Tin chemical shifts often exhibit a concentration dependence in polar solvents (4), and this was the object of a quantitative study. In the list of tin chemical shifts, solvent conditions are specified where a study was made.

#### (b) Solvent Dilution Studies

Solvent studies were made on trimethyltin bromide and chloride. The <sup>119</sup>Sn resonance position could be located with good precision  $(\pm 1.0 \text{ p.p.m.})$  to dilutions of approximately 10 mole % in the solvents investigated. These results are plotted for the polar solvents acetone and acetonitrile in Fig. 2. The open circle points are tin chemical shifts relative to the chemical shift equal to zero for tetramethyltin. The right hand scales correspond to this chemical shift in p.p.m. Trimethyltin bromide is a liquid, but trimethyltin chloride is a solid with maximum solubility  $\sim 40$ mole % in acetone and acetonitrile.

Dilution of the two trimethyltin halides in

TABLE II N.m.r. data for MerSi(OEt)4-r

	Si <sup>a</sup> (p.p.m.)	Me <sup>b</sup> (p.p.m.)	J <sup>29</sup> siсн (c.p.s.)	
Me₄Si	-79.5	0.0	6.62	118.1
MeaSiOEt	-93	-0.23	6.67	118.Õ
$Me_2Si(OEt)_2$	-72	-0.20	7.08	118.2
MeSi(OEt) <sub>3</sub>	-34	-0.16	8.35	119.2
Si(OEt) <sub>4</sub>	+4			_

<sup>a</sup>Silicon-29 chemical shift in p.p.m. from (MeO)<sub>4</sub>Si. <sup>b</sup><sup>t</sup>H chemical shift in p.p.m. from TMS.



FIG. 2. Concentration dependence of <sup>119</sup>Sn chemical shifts and spin-spin couplings  $J_{Sn-C-H}$  for trimethyltin halides in donor solvents.

nonpolar solvents, such as chloroform, benzene, and carbon tetrachloride, does not change the chemical shifts of <sup>119</sup>Sn more than 5 p.p.m. from the pure compound value. The extrapolated infinite dilution chemical shifts for trimethyltin bromide are +5, 0, and -5 p.p.m. for carbon tetrachloride, benzene, and chloroform respectively. The corresponding figures for trimethyltin chloride are the same within experimental error. The relatively large extrapolation and small observed change leave an uncertainty of approxi-

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mately  $\pm 2$  p.p.m. in these figures. The lack of large changes in chemical shift with dilution in these solvents is indicative that no complexing occurs between the tin compound and the solvent and, furthermore, no self-association occurs in the trimethyltin halides. On the other hand, it is clear that some complexing between the trimethyltin halides and acetone and acetonitrile does occur. Further studies on dioxane solutions of trimethyltin bromide were made. These, too, indicated a large change in chemical shift ( $\sim 45$ 

TABLE III N.m.r. data for  $Me_xSi(OAc)_{4-x}$ 

	Si <sup>a</sup>	Me <sup>b</sup>	J <sup>29</sup> sicн	J <sup>13</sup> сн
	(p.p.m.)	(p.p.m.)	(c.p.s.)	(c.p.s.)
Me <sub>4</sub> Si Me <sub>3</sub> SiOAc Me <sub>2</sub> Si(OAc) <sub>2</sub> MeSi(OAc) <sub>3</sub> Si(OAc) <sub>4</sub>	-79.5-103-85-35-5	$0 \\ -0.36 \\ -0.53 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ -0.67 \\ $	6.62 7.10 7.77 9.5	118.1 119.5 121.3 123.4

<sup>a</sup>Silicon-29 chemical shift in p.p.m. from  $(MeO)_4Si$ . <sup>b</sup><sup>1</sup>H chemical shift in p.p.m. from TMS.

## TABLE IV

N.m.r. data for  $Me_xSiCl_{4-x}$ 

	Si <sup>a</sup>	C <sup>b</sup>	Me <sup>c</sup>	J <sup>29</sup> SICH	
	(p.p.m.)	(p.p.m.)	(p.p.m.)	(c.p.s.)	(c.p.s.)
Me <sub>4</sub> Si Me <sub>3</sub> SiCl Me <sub>2</sub> SiCl <sub>2</sub> MeSiCl <sub>3</sub> SiCl <sub>4</sub>	-79.5 -115 -120 -96 -63	190 176 190 210	0 -0.39 -0.45 -1.05	6.62 7.00 7.61 9.07	118.1 120.77 123.6 125.5

<sup> $a_{29}$ Si chemical shift in p.p.m. from (MeO)<sub>4</sub>Si. <sup> $b_{13}$ C chemical shift in p.p.m. from CS<sub>2</sub>. <sup> $c_{1}$ </sup>H shift in p.p.m. from TMS.</sup></sup>

TABLE V N.m.r. data for MerSi(C<sub>6</sub>H<sub>5</sub>)<sub>4-r</sub>

	Si <sup>a</sup>	Me <sup>b</sup>	J <sup>29</sup> <sup>51CH</sup>	J <sup>13</sup> сн
	(p.p.m.)	(p.p.m.)	(c.p.s.)	(c.p.s.)
Me <sub>4</sub> Si	-79.5	$0 \\ -0.26 \\ -0.52$	6.62	118.1
Me <sub>3</sub> Si¢	-75		6.60	119.0
Me <sub>2</sub> Si¢ <sub>2</sub>	-72		6.60	120.5
$Me\overline{Si}\phi_3$ $Si\phi_4$	-67 °	0.74	6.64	c 

<sup>429</sup>Si chemical shift relative to (MeO)<sub>4</sub>Si. <sup>b1</sup>H chemical shift relative to Me<sub>4</sub>Si. <sup>c</sup>Too insoluble to be measured.

p.p.m. to high field at infinite dilution) consistent with molecular complexing between dioxane and trimethyltin bromide.

These studies were complemented by a similar study of the changes in chemical shift of the protons with dilution in the same solvents. As expected, the only appreciable change in the proton chemical shift occurred in benzene solutions. The changes in chemical shift of the protons of trimethyltin bromide between the pure compound and infinite dilution are -0.033p.p.m. in CHCl<sub>3</sub>, -0.066 p.p.m. in acetone, -0.1 p.p.m. in CH<sub>3</sub>CN, -0.13 p.p.m. in dioxane, and -0.47 p.p.m. in benzene. These

shifts are characteristic only of the well-known changes in chemical shift that occur with nonpolar solvents (such as cyclohexane) in benzene due to its large molecular diamagnetic anisotropy (8). The proton magnetic environment must be considered virtually insensitive to the complex formation, which is known to involve donation into d orbitals on the central tin atom. These observations are a complete vindication of the promise held out by Burke and Lauterbur (4) regarding the utility of tin magnetic resonance for the study of solution complexes of tin.

While it is not expected that proton chemical shifts should be sensitive to complexing at the tin

TABLE VI N.m.r. data for Me<sub>r</sub>SiF<sub>4-x</sub>

	Si <i>ª</i> (p.p.m.)	Me <sup>b</sup> (p.p.m.)	F <sup>c</sup> (p.p.m.)	J <sup>29</sup> sif (c.p.s.)	J <sup>29</sup> siсн (c.p.s.)	<i>J</i> <sup>13</sup> сн (c.p.s.)	$J_{\rm HCSIF}$ (c.p.s.)
Me <sub>4</sub> Si Me <sub>3</sub> SiF Me <sub>2</sub> SiF <sub>2</sub> MeSiF <sub>3</sub>	-79.5 -110 -84 d	$0 \\ -0.19 \\ -28 \\ +0.2$	158 130 133	276 278	6.62 7.40 7.60 8.8	118.1 120.0	7.23 6.25 4.14
SiF₄	d		161.8	178			—

<sup>429</sup>Si chemical shift relative to (MeO)<sub>4</sub>Si. <sup>b1</sup>H chemical shift from TMS. <sup>c19</sup>F chemical shift from CFCl<sub>3</sub>.

<sup>d</sup>Too volatile to be measured.

Ξ

	Si <sup><i>a</i></sup> (p.p.m.)	Me <sup>b</sup> (p.p.m.)	H <sup>c</sup> (p.p.m.)	$J_{\text{SIH}}$ (c.p.s.)	J <sup>29</sup> sicн (c.p.s.)	J <sup>13</sup> <sub>СН</sub> (c.p.s.)	J <sub>HCSiH</sub> (c.p.s.)
Me <sub>4</sub> Si Me <sub>3</sub> SiH Me <sub>2</sub> SiH <sub>2</sub> MeSiH <sub>3</sub> SiH <sub>4</sub>	79.5 61 38	$\begin{array}{c} 0 \\ -0.20 \\ -0.26 \\ -0.27 \\ -\end{array}$	$-4.20 \\ -4.03 \\ -3.71 \\ c$	183.8 188.5 194.6 202.5	6.62 7.20 7.5 7.9	118.1 119.35 120.8 123.6	3.76 4.15 4.67

TABLE VII N.m.r. data for  $Me_xSiH_{4-x}$ 

<sup>a29</sup>Si chemical shift from (MeO)<sub>4</sub>Si. <sup>b1</sup>H chemical shift from TMS. <sup>c</sup>Too volatile to be measured.

TABLE VIII	
Miscellaneous <sup>29</sup> Si chemical shifts	

Compound	Chemical shift <sup>a</sup>
	(p.p.m.)
ViSi(OEt)3 <sup>b</sup>	-15.5
C <sub>6</sub> H <sub>5</sub> SiH <sub>3</sub>	-18
C <sub>6</sub> H <sub>5</sub> Si(OEt) <sub>3</sub>	-19
(MeO) <sub>6</sub> Si <sub>2</sub>	-27
$(C_6H_5)_2SiH_2$	-45
$(C_6H_5)Si(OEt)_2$	-45
$(C_6H_5)_2^2SiF_2$	-49
Vi <sub>4</sub> Si	-57
Me <sub>6</sub> Si <sub>2</sub>	-59
$Me(C_6H_5)_2SiH$	-60
$[(MeO)_2MeSi]_2$	-72
Et <sub>2</sub> SiF <sub>2</sub>	-80
ClCh <sub>2</sub> SiMe <sub>3</sub>	-81.5
$(Me_3Si)_2O$	-83.5
Me₃SiOϕ <i>t</i> -Bu	-92

<sup>a</sup>Relative to (MeO)<sub>4</sub>Si. <sup>b</sup>Vi = vinyl.

atom, the indirect spin-spin coupling from <sup>119</sup>Sn to the methyl protons is very sensitive to dilution in the same manner as the <sup>119</sup>Sn chemical shifts. Any change in coordination at the tin atom will result in variations in the use of the 's' electron state function for any particular bond to the tin. This must be reflected in changes in coupling constant through the Fermi contact interaction  $|\Psi_{5s}(0)|^2$ . A complementary study of  $J_{119Sn-C-H}$ in the same solvents for the trimethyltin halides has been made.

These studies are summarized with the chemical shift data in Fig. 2. The solid circles on each graph show changes in coupling constant  $J_{Sn-C-H}$  referred to the left hand scales as indicated. The sensitivity of the proton resonance signal allows the detection and measurement of peaks to a limit of about 1 mole % for the <sup>119</sup>Sn side bands. The points for chemical shift and coupling constant are plotted so that the scale on the left and right of each graph corresponds to the same linear distance for changes in these parameters in going from pure compound to infinite dilution.

Dimethyltin dichloride has limited solubility in most solvents (less than 40 mole%). A dilution study from a saturated solution was made for the variation of  $|J_{Sn-C-H}|$  in the following solvents: acetonitrile, acetone, methanol, 50/50 mole % acetone-water, and water. The first three solvents were carefully dried over vacuumbaked anhydrous calcium sulfate. The results of this study are shown in Fig. 3. In nonpolar solvents such as chloroform, benzene, and carbon tetrachloride the variation in  $|J_{Sn-C-H}|$ from the pure compound in very dilute solutions was less than  $\pm 3$  Hz.

The dilution studies of  $|J_{Sn-C-H}|$  shown in Fig. 3 are of two types. In water and water/ acetone, the value of the coupling constant



FIG. 3. Concentration dependence of the spin-spin couplings  $J_{Sn-C-H}$  for dimethyltin dichloride in various solvents.

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Compound	Solvent	(p.p.m.) tetramethyltin $\delta = 0$
(CH <sub>2</sub> =CH) <sub>4</sub> Sn	None	$\pm 165.1$
(CH <sub>2</sub> )SnCl <sub>2</sub>	Acetone <sup>a</sup>	+103.6 to $+151.2$
(CH <sub>3</sub> )SnCl <sub>3</sub>	Water <sup>a</sup>	+474 to $+481$
Triphenyltin	CUCI	115 2
-2 ethylhexoate	CHCl <sub>3</sub>	+115.3
Triphenyltin	Pure CHCI	+113.7
-cyclohexyl $\int$	rule CHCl <sub>3</sub>	+125
$(CH_3)_3Sn - Sn(CH_3)_3$	None	+109.0
Diphenyltin	CHCL	$\pm 106.5$
-dicyclohexyl $\int$	energ	100.5
Phenyltin	CHCl	+102.5
-tricyclohexyl	011013	
Diphenyltin	CHCl <sub>3</sub>	+101.2
Triphopyltip	5	
SS dimethylthiocorbonate	CHCl <sub>3</sub>	+94.5
(CH - CH) Sp(n Butyl)	None	+86.4
Ris-triphenyltin oxide	CHCL	+80.4
( <i>n</i> -Butyl), Sn.	None	+79.5
$(CH_2)_2 Sn(CH=CH_2)_2$	None	79 4
Diphenyltin	21.0110	
-dibutyl	None	+65.9
$(CH_3)_2 Sn\phi_2$	None	+59.8
bis(triphenyltin sulfide)	None	+48.7
Triphenyltin chloride	None	+46.0
Tetraisopropyltin	None	+43.9
Phenyltintributyl	None	+41.7
$(CH_2 = CH)_2 SnCl_2$	None	+40.9
$(CH_3)_3Sn(CH=CH_2)$	None	+35.4
(CH <sub>3</sub> ) <sub>3</sub> Snphenyl	None	+30.3
$(n-\text{Propyl})_4 \text{Sn}$	None	+10.8
$(CH_3CH_2)_4Sn$	None	+0.7
$(CH_3)_3 SII(CH_2 CH_2 CH_3)$	None	+2.9
$(CH_3)_3SH$ Cyclonicxyl	None	-1.7
$(CH_{a})_{a}Sn(n-Butyl)_{a}$	None	-0.4
$(CH_3)_2Sn(CH_2CH_3)$	None	-5.9
$(CH_3)_3Sn(Isopropyl)$	None	9.9
$(CH_3)_3 Sn(t-Butyl)$	None	-17.5
Diphenyltin sulfide	CHCl <sub>3</sub>	-19.5
Tris(Trimethyltin )	None	-24.9
-orthophosphate J	CUCU	20.2
Puriding appropriate	CH <sub>3</sub> CH	-20.2
$-$ pyriaine complex $\int$		-23.4
$(CH_3)_3 SIIOH$	Cyclobevane	-51.8
$(CH_a)_a SnBr_a$	CHCl	-74 3
$(CH_2)_2 SnS$	CS <sub>2</sub>	-125.6
$(CH_3)_3 SnBr$	None	-130.7
(CH <sub>3</sub> ) <sub>3</sub> SnBr	QUQ	140.0
– aniline complex )	CHCl <sub>3</sub>	-149.9
(CH <sub>3</sub> ) <sub>3</sub> SnCl	Cyclohexane <sup>a</sup> ∫	-155.7
	<u>∖</u> to	-158.6
(CH <sub>3</sub> CH <sub>2</sub> ) <sub>3</sub> SnCl	None	-155.9

TABLE IX <sup>119</sup>Sn chemical shifts

<sup>a</sup>Range of chemical shift noted; dependent on concentration.

always increases with dilution, but in the polar organic solvents between 5 and 8 mole % tin chloride the coupling constant decreases sharply in absolute magnitude to a lower value at infinite dilution. The estimates of the infinite dilution coupling constants are: 107 Hz in water, 103 Hz in water/acetone, 90 Hz in methanol, and 84 Hz in acetonitrile and acetone. The coupling constants and chemical shifts in the pure supercooled halides are estimated from the linear dependence

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of these parameters on the relative mole concentration of halogen in their mixtures. Rapid halogen exchange is occurring in these solutions.

 TABLE X

 Tin chemical shifts in trimethyltin halides as a function of concentration in various solvents

Compound	Solvent	Mole %	In p.p.m. from pure compound
(CH <sub>3</sub> ) <sub>3</sub> SnCl	H <sub>2</sub> O	14.0	+102.0
,,	,,	9.9	+120.5
,,	,,	7.2	+121.4
,,	,,	5.2	+124.4
3/	,,	2.8	+125.0
,,	,,	0	+128.6*
,,	MeOH	21.8	+107.4
,,	,,	18.9	+111.5
,,	,,	14.2	+114 8
**	,,	10.1	+117.9
	,,	0	+124.4*
.,	Acetone-H <sub>2</sub> O	27.6	+1094
		22.8	+118.2
,,,		15.9	+125.7
,,,		10.6	+134.0
(CH <sub>3</sub> ) <sub>3</sub> SnBi	H <sub>2</sub> O	4.7	+90.5
( = = = 5) 5 = = = = =		3.9	+93.0
,,	,,	3.2	+96.8
**	Acetone-H <sub>2</sub> O	34.0	+77.4
,,		24.0	+82.4
,,	,,	14.2	+102.3
**	,,	9.7	+107.5

\*Extrapolated values.

In Table X, the tin chemical shifts related to the pure compound are given for trimethyltin bromide and chloride for various accessible dilutions in water and 50/50 mole % acetone/ water mixtures. In the case of trimethyltin chloride, the data also include solutions in methanol.

## Relaxation Times $T_1$ for Some Silicon and Carbon Compounds

The measurement of spin-lattice relaxation times for  $^{13}$ C usually observed in 1.1% natural abundance of spin 1/2 and  $^{29}$ Si in 4.7% natural abundance, spin 1/2 in liquid samples of their compounds has received no attention in the published literature, although for  $^{13}$ C they are often alluded to as long or worse, quoted as several minutes without measurement. In view of the increasing interest in observing  $^{13}$ C by the direct field/frequency lock techniques and accumulated scans of absorption mode spectra, we felt it worthwhile to measure a few values of  $T_1$ in typical pure compounds of these elements.

The method used is based on the adiabatic

rapid passage method. The conditions  $dH_0/dt$  $\ll |\gamma H_1^2|$  and  $\tau$ , the time spent in resonance,  $\cong H_1/(dH_0/dt) \ll T_1$ ,  $T_2$  were satisfied in all measurements (9). The procedure consisted of increasing power levels on the V4311 r.f. unit to 20 db below 0.5 W, the full output, then sweeping rapidly at  $\sim 1$  G/min through the <sup>13</sup>C or <sup>29</sup>Si signal in natural abundance in the purified vacuum-degassed liquids. Probe balance proved to be the limiting factor on the amount of power that could be produced at the sample. The single adiabatic passage inverts the magnetization to the negative z direction, taking positive z as the  $H_0$  field direction. Subsequently, recovery at a relaxation rate  $1/T_1$  occurs back to the positive z direction. The signal strength at constant gains in the adiabatic passage is proportional to the magnetization M(t) at any time, since it is the act of precession of a macroscopic vector of length M(t)through the xy plane perpendicular to  $H_0$  which induces a proportional signal in the receiver coil (9). If the sample is left in the magnetic field  $H_0$ for a period at least  $10T_1$ , then the first adiabatic passage gives a signal proportional to M(0). A second adiabatic passage a time 't' later performs a precession of the magnetization remaining in the negative z direction back into the positive zdirection. The signal height is proportional to -M(t). The signal width under adiabatic conditions is proportional to the  $H_1$  field which remains constant for all traverses of the resonance. By varying the interval 't', the signal heights can be measured and  $T_1$  determined from the first order recovery law

[1] 
$$\ln\left(1+\frac{I_{\iota}}{I_{0}}\right) = \ln 2 - \frac{t}{T_{1}}.$$

I and  $I_0$  are heights of the signal at times t and t = 0.

The plots of ln  $(1 + I/I_0)$  versus t give a straight line of slope  $1/T_1$  and intercept ln 2. These experimental results are shown for the <sup>13</sup>C resonances in pure benzene, acetone carbonyl carbon, and CS<sub>2</sub> at 7.95 MHz and 7.45 kG, and for the <sup>29</sup>Si resonances in tetramethoysilane, tetramethylsilane, and hexamethyldisiloxane at 7.95 MHz and 9.41 kG (Fig. 4). Table XI contains the list of  $T_1$  values. After this work was completed, Drs. Paul Lauterbur and Ray Ettinger made us aware that they had obtained similar measurements on enriched compounds some years ago (10). There is only one compound

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Compound	Nucleus	$T_1$ (s)	Reference
Benzene	13C	14	
Acetone carbonyl	<sup>13</sup> C	19	а
CS <sub>2</sub>	<sup>13</sup> C	35	a,b,c
$^{*13}$ CO <sub>2</sub> in H <sub>2</sub> O	<sup>13</sup> C	35	b
$^{*13}CO_{2}$ in $D_{2}O$	<sup>13</sup> C	45	Ь
$^{*13}CO_{2}$ in $CS_{2}$	<sup>13</sup> C	24	Ь
*OCS	<sup>13</sup> C	20	Ь
*H <sup>13</sup> CO <sub>3</sub> -	13C	9	Ь
*NH <sub>2</sub> <sup>13</sup> ČOONH₄	13Č	5	b
*(C <sub>2</sub> H <sub>4</sub> O) <sub>2</sub> <sup>13</sup> CO	13C	51	b
*(CH <sub>3</sub> O) <sub>2</sub> <sup>13</sup> CO	<sup>13</sup> C	49	$\tilde{b}$
*(C <sub>2</sub> H <sub>2</sub> O), <sup>13</sup> C	<sup>13</sup> C	47	b
* <sup>13</sup> CH <sub>2</sub> I	<sup>13</sup> C	$\sim 3.5$	c
(CH <sub>2</sub> O) <sub>1</sub> Si	<sup>29</sup> Si	73	a
(CH <sub>4</sub> ),Si	29Si	16	a
[(CH <sub>3</sub> ) <sub>3</sub> Si] <sub>2</sub> O	<sup>29</sup> Ši	40	a

TABLE XI

\*Enriched to 55% <sup>13</sup>C in the appropriate position. (a) Present work. (b) Ettinger and Lauterbur. Private communication. (c) Ettinger and Johnson. Private communication.

which is common to both sets of measurements,  $CS_2$ , and the agreement is excellent. Subsequent to our measurements, Ettinger and Johnson (11) rechecked the value of 35 s for <sup>13</sup>CS<sub>2</sub> and in an enriched sample of  $Me_3I$  found  $T_1$  to be 3-4 s. As far as is known, the results in Table II are the only known values of  $T_1$  for <sup>13</sup>C and <sup>29</sup>Si in liquids.

#### Discussion

### Silicon Chemical Shifts

Chemical shift theories for isotropic liquids have followed the formulation of Ramsey (12, 13), who treated the electron-nucleus interaction in the complete Hamiltonian to second order perturbation. Notable exceptions to this include a variation method calculation of O'Reilly (14).

More recent attempts to use the Ramsey method in more approximate forms, usually with an average excitation energy approximation, have met with some success in explaining the gross features of the chemical shift behavior of heavier nuclei (15-20). The paramagnetic contribution in the Ramsey formulation (12, 13) is considered only for the atom containing the nucleus in question (except in Cornwell's paper (19)). The  $\sigma$  and  $\pi$  systems used in bonding and the ionicity of these bonds are a requirement in computing the matrix elements for the perturbation calculation. Bond orders must be known. If the p and d content of all bonding orbitals remains an invariant factor in a series of molecules, the assumptions lead to the general result that chemical shift is a linear function of p and d



Results for  $T_1$  measurements for <sup>13</sup>C and Fig. 4. <sup>29</sup>Si signals in six compounds.  $I/I_0$  represents the ratio of the peak intensities at arbitrary times t and t = 0; ln  $(1 + I/I_0)$  is plotted versus t.

orbital occupancy, which is often empirically represented by differences in electronegativity. At present, the theory of Saika and Slichter (15) with respect to p orbital occupancy in the F-X bond remains less than satisfactory. Numerous exceptions are found among experimentally measured fluorine chemical shifts (21).

In the compounds of silicon, the participation of  $(p \rightarrow d)$  bonding from a suitable ligand has been a subject of some controversy (22-26). Bond shortening in Si-N, Si-O, and Si-F can be characterized using the criteria of Shomaker and Stevenson (27) and the unusual bond angles of silylamines and silyl ethers are well known (26). It is to be hoped that the chemical shifts, which are also crudely dependent on electronegativity differences, can, when taken in consideration with carbon, point out the peculiarity of certain silicon-X bonds. Previous studies of proton chemical shifts in silicon compounds cannot be expected to show bonding changes at silicon so well.

Gutowsky and Juan (34) have an approximate

expression for the chemical shift based on either valence bond or linear combination atomic orbital – molecular orbital calculations. They consider only the second order paramagnetic term on the bonding orbitals of the atom in question and an equation may be written.

2] 
$$\sigma^2 = -\left(\frac{2e^2\hbar^2}{3\Delta m^2c^2}\right)\left(\left\langle\frac{1}{r_p^3}\right\rangle P_u + \left\langle\frac{1}{r_d^3}\right\rangle D_u\right)$$

 $\Delta$  is a mean ground state to triplet state excitation energy and *e*, *h*, *m*, and *c* are constants.  $\langle 1/r_p^3 \rangle$  and  $\langle 1/r_d^3 \rangle$  are mean inverse cubes for distances electrons to nucleus and  $P_u$  and  $D_u$  may be called the 'electron unbalance' for valence p and d orbitals respectively.

 $P_{\rm u}$  and  $D_{\rm u}$  are dependent on coordination number, hybridization of atomic orbitals in bonding, and ionicity of bonds. In order to extract the dependence on ionicity, one assumes that  $\Delta$ ,  $\langle 1/r_p^3 \rangle$ , and  $\langle 1/r_d^3 \rangle$  can be approximately constant in a series of compounds and, further, that one can arrange a series such that the coordination number and hybridization do not change. For silicon compounds, it is convenient to choose the series  $(CH_3)_3$ Si-X where X varies in electronegativity as widely as possible. In order to avoid any dependence on an n.m.r. scale of electronegativities, the <sup>29</sup>Si chemical shifts of (CH<sub>3</sub>)<sub>3</sub>Si-X compounds have been plotted against the Pauling electronegativity (28) difference between silicon and X in Fig. 5. The lower half of the figure is devoted to <sup>29</sup>Si chemical shifts in  $(CH_3)_3SiX$  compounds and the upper half to previously published data on <sup>13</sup>C chemical shifts in CH<sub>3</sub>X compounds (2). Features which distinguish <sup>13</sup>C chemical shift dependence on electronegativity have been discussed (1, 2). The odd feature in the experimental data is the high field shifts for CH<sub>3</sub>I, CH<sub>3</sub>Br, and CH<sub>3</sub>Cl, which stand out as exceptions to the gross linear dependence on electronegativity. The shifts for the three odd methyl halides depend within themselves linearly on electronegativity, but the line through them is well displaced from zero chemical shift change for the C-C bond, which is arbitrarily set at zero for zero electronegativity difference. This aspect of <sup>13</sup>C chemical shift behavior has received some attention (29, 30). Both diamagnetic anisotropy and intramolecular dispersion forces have been suggested as contributing a shielding effect for these halides.

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The silicon chemical shift data in the lower



FIG. 5. <sup>29</sup>Si chemical shifts in  $(CH_3)_3SiX$  and <sup>13</sup>C chemical shifts in  $CH_3X$  compounds plotted against the electronegativity differences  $(\chi_X - \chi_{Si})$  and  $(\chi_X - \chi_C)$ . The <sup>13</sup>C chemical shifts are given in the figure at the upper right.

half of Fig. 5 show marked contrasts to the <sup>13</sup>C data. In this case a regular linear trend is seen for the elements Si, C, I, Br, and Cl, with the expected zero relative shift with Si = X in (CH<sub>3</sub>)<sub>3</sub>Si-Si(CH<sub>3</sub>)<sub>3</sub> being on the line. With X = N, O, and F, an additional shielding effectbecomes operative. The shift with X = H seems in both <sup>13</sup>Ĉ and <sup>29</sup>Si shifts to be a little displaced to high field from what might be expected for the electronegativity of hydrogen. Bonds to hydrogen are known to be exceptional even with regard to bond length, e.g. Si-H bonds are longer than calculated from electronegativities and covalent radii (27). Gutowsky and Larmann (31) computed chemical shifts for tervalent phosphorous compounds where no appreciable  $(p \rightarrow d)\pi$  back donation of charge occurs. In tetravalent phosphorous compounds, calculations have been extended to include arbitrary

 $(p \rightarrow d)\pi$  donation (32). In this paper, the use of an experimental shielding in conjunction with a crude theoretical estimate of a  $\sigma$  bond contribution to the chemical shift to determine the quantitative amount of  $(p \rightarrow d)\pi$  bonding must be subject to large uncertainties. The more qualitative dependence on electronegativity for silicon chemical shifts is, however, established here and the role of  $(p \rightarrow d)\pi$  bonds in shielding the silicon is similar to the behavior of tetrahedral phosphorous derivatives.

The tables of silicon chemical shifts 1-8 for the series  $SiX_{4-n}Y_n$  do show the 'sagging' behavior characteristic of phosphorous compounds as the value of n is changed (32). The empirical rule of Letcher and Van Wazer, who find that deviations from linearity of changes in chemical shift with 'n' are constant for <sup>31</sup>P chemical shifts do not apply to silicon chemical shifts. The compounds  $M(CH_3)_n(OR)_{4-n}$  give opposite trends for the M chemical shift. If M = carbon, the addition of -OR groups is strongly deshielding, while for M = silicon the effect is strongly shielding after the first (OR) group. Similar behavior is also noted for nitrogen and fluorine ligands. On the assumption that appreciable  $(p \rightarrow d)\pi$  bonding causes a shielding effect, whereas the increasing polarity of the sp<sup>5</sup> hybrid orbitals causes deshielding (one assumes as a first approximation orthogonality of the sp<sup>3</sup>- $\sigma$  orbitals and (p  $\rightarrow$  d) $\pi$  bonds), it follows that the net shielding effect of the  $\pi$  bonds is greater and results in a net high field shift after the first (OR), -F, or  $-N(Me)_2$  group.

An interesting observation is the behavior of the chloromethylsilanes, which have a chemical shift at lowest field for Me<sub>2</sub>SiCl<sub>2</sub>. Jaffé (25) has tabulations which enable crude estimates of  $(p \rightarrow d)\pi$  overlap to be made for Si—O, Si—F, and Si—Cl bonds. The overlap integrals are 0.2, 0.2, and 0.15 respectively. For the larger halogens overlap will be even smaller because of the large mean radius of the valence shell. The  $(p \rightarrow d)\pi$ donation will be less effective for chlorine and the  $(p \rightarrow d)\pi$  bond order smaller. This is in agreement with the regular behavior of the trimethylsilyl chloride in Fig. 5 and lack of a strong shielding effect in the series Me<sub>4-n</sub>SiCl<sub>n</sub> as n is increased (see Table IV).

The overlap between silicon d orbitals and molecular  $\pi$  electrons in the vinyl and phenyl groups will be smaller because of the larger size

of the silicon d orbitals compared with the  $2p-\pi$  carbon orbitals. An electronegativity effect is almost entirely absent in series such as  $(Vinyl)_{4-n}$ -Si $(CH_3)_n$  and  $(Phenyl)_{4-n}Si(CH_3)_n$ , since all bonds are Si—C at silicon. In both cases, there is a linear shielding effect as the number of vinyl and phenyl groups is increased. The shielding effect is 4 p.p.m. per phenyl group and 5.6 p.p.m. per vinyl group. In series (Alkyl or Aryl)\_4SiH\_{4-n}, the hydrogen leads to increased shielding as n increases, but this effect is small and difficult to interpret. Chemical shifts in the molecules MeSiH<sub>3</sub> and SiH<sub>4</sub> proved too difficult to measure because of volatility and explosion hazards in preparation.

## Spin-Couplings in Silicon Compounds

A new feature of spin-coupling constants in silicon compounds is the appearance of a long range interaction H—C—Si—C—H when the silicon is bound to oxygen or fluorine. There are similar long range couplings known, for instance the 0.4 Hz coupling in acetone H-C-C-C-H and in mercury dimethyl H—C—Hg—C—H(33). The fact that this coupling constant in silicon compounds can be observed only when a  $(p \rightarrow d)\pi$ donor such as fluorine and oxygen is bonded to silicon suggests that the use of silicon d orbitals to transmit coupling via the electronic system is facilitated by partial occupancy. Otherwise, silicon proton, carbon, and silicon fluorine couplings are quite regular in behavior and they have been discussed at length by other workers (34).

Recently, the small long range couplings in dimethyl sulfide H—C—S—C—H (35), disilyl sulfide H—Si—S—Si—H (36), and germyl methyl sulfide H—Ge—S—C—H (37) have been reported. The availability of low lying unoccupied or partly occupied p or d orbitals appears to be a prerequisite for such couplings.

#### Tin Chemical Shifts

The chemical shift range encountered in tin compounds is much larger than silicon or carbon because of the increased magnitude of  $\langle 1/r^3 \rangle$ for valence p and d electrons in eq. [2] as indicated by spin-orbit interactions (20). The values of  $\langle a_0^3/r^3 \rangle_{np}$  in atomic units for carbon silicon and tin are 1.7, 2.5, and 8.0 (38) approximately. It has been suggested (20) that the contracted chemical shift range encountered in silicon compounds is the result of a shielding effect due to  $(p \rightarrow d)\pi$  bonds with the ligands oxygen and

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fluorine. The results here support this suggestion. These ligands would otherwise give strong low field chemical shifts for the bonded silicon.  $(p \rightarrow d)\pi$  bonding in tin compounds should occur with larger ligands, such as chlorine and bromine, where overlap is more favorable, but the  $(p \rightarrow d)\pi$  bonding order is expected to be lower than in silicon compounds because the  $\sigma$ bonding will not be as ionic with these more electropositive ligands (23). A chemical shift range of 1900 p.p.m. in tin compounds compared with 316 p.p.m. in carbon reflects the same order of change in  $\langle 1/r^3 \rangle_{np}$ . The chemical shifts measured in this work are only a small fraction of this range,  $\sim 500$  p.p.m., and consist mainly of alkyltin (X) compounds or tin ions in aqueous media.



FIG. 6. <sup>119</sup>Sn chemical shifts in (Alkyl)<sub>3</sub>SnX compounds as a function of  $(\chi_X - \chi_{Sn})$ .

There are several similarities between silicon and tin chemical shifts with respect to molecular structure. The *n*-butyltin chlorides give the same 'sagging' dependence on the number of chlorine atoms that is reported earlier in this paper for silicon bonded to oxygen and fluorine. The first chlorine atom produces a deshielding effect, but all subsequent chlorine atoms to  $SnCl_4$  are shielding. The figures for these results are a combination of the data of Lauterbur (4) and our present work. The shifts are:  $(n-Bu)_4$ Sn +12 p.p.m. (4);  $(n-Bu)_3$ SnCl -143 p.p.m. (4), -139 p.p.m. (present work);  $(n-Bu)_2$ SnCl<sub>2</sub> -71 p.p.m. in acetone solution (4), -56 p.p.m. (present work); (n-Bu)SnCl<sub>3</sub> +3 p.p.m. (4); SnCl<sub>4</sub> +150 p.p.m. (4, present work).

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The results for vinyltin compounds are similar to the silicon vinyls. Apart from  $Sn(C_2H_3)_3CH_3$ , which was not available, the increase in tin shielding per vinyl group is constant at 40 p.p.m. per vinyl added. This shielding effect is almost an order of magnitude larger than for silicon vinyl derivatives and reflects the increased overall sensitivity of tin chemical shifts to molecular structure.

The general form of the dependence of tin chemical shifts on Pauling electronegativity difference in (Alkyl)<sub>3</sub>SnX compounds follows the same form as those for silicon in the lower half of Fig. 4. The number of chemical shifts available is disappointingly small and limited by the formation of solid polymeric substances with the very electronegative elements. A gross linear dependence can be noted for the elements -Sn, -C, -Br, and -Cl. The availability<sup>3</sup> of  $(CH_3)_3SnMn(Co)_5$  enabled us to get a <sup>119</sup>Sn chemical shift of -66.3 p.p.m. It is plotted as a  $(CH_3)_3$ Sn—X compound in Fig. 5. The chemical shift is quite irregular. The much larger slope of the chemical shift versus electronegativity in tin compounds is again a manifestation of the use of (5p) valence electrons for bonding rather than (3p) in silicon. The hybridization of bonding orbitals will be approximately the same.

## The Changes in <sup>119</sup>Sn Chemical Shifts with Solvent and Concentration

It is known that nonaqueous donor molecules complex with tetrahedral tin compounds to form penta- and hexa-coordinated tin complexes (39– 41). Some equilibrium constants have been measured from infrared intensity data (42). Burke and Lauterbur (4) concluded that these tin complexes are formed with large accompanying changes in tin chemical shifts. No quantitative study has followed these earlier observations.

The dissolution of trimethyltin chloride and bromide in donor organic solvents such as acetone, acetonitrile, and dioxane proceeds to a 1:1 complex formation.

<sup>3</sup>We thank Professor H. C. Clark for providing this sample.

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We can write

 $(CH_3)_3SnX + :D \rightleftharpoons (CH_3)_3SnX:D 1:1$  complex.

If we assume there is 1 mole of halide plus donor and C moles of halide and  $\alpha C$  moles of complex are formed at equilibrium, then the equilibrium constant in mole fraction units for the above reaction is given by

[3] 
$$K = \frac{\alpha(1-C\alpha)}{(1-\alpha)(1-C-C\alpha)}$$

The tin chemical shift observed is the time weighted average of the complexed and free forms. If the chemical shifts are referenced to zero for pure trimethyltin halide then

$$[4] \qquad \qquad \delta_0 = \alpha \delta_c.$$

 $\delta_0$  = observed tin chemical shift in a solution of arbitrary concentration,  $\delta_c$  = chemical shift in the complex, and K is given by

$$[5] \quad K = \frac{\delta_0(\delta_c - C\delta_0)}{\delta_c^2(1-C) + C\delta_0^2 - \delta_0\delta_c}.$$

A simple computer program was devised to choose trial values of K and  $\delta_c$  and compute the dilution chemical shift curves shown in Fig. 2. The dotted curve on each graph is the computed dilution chemical shift dependence in each case for the values of K recorded on the top right hand side of each plot, and for an infinite dilution chemical shift  $\delta_c$  recorded on the right. The figures are: Me<sub>3</sub>SnBr in acetone  $\delta_c = -67.2$  p.p.m. with respect to tetramethyltin, K = 3.00; Me<sub>3</sub>-SnBr in CH<sub>3</sub>CH  $\delta_c = -106.6$ , K = -106.6; Me<sub>3</sub>SnCl in CH<sub>3</sub>CN  $\delta_c = -86.5$ , K = 2.7.

As noted earlier, the spin-coupling constant  $J_{Sn-C-H}$  is modulated in the same way by the same exchange process. By assuming that the coupling constant  $J_{Sn-C-H}$  in the complex takes arbitrary values and knowing the coupling constant in the pure halide, then the dotted curve obtained from best computed results also represents the variation of coupling constant with dilution. The infinite dilution values of coupling constants in the complexed form are: Me<sub>3</sub>SnBr:acetone  $J_c = 66.0$  Hz; Me<sub>3</sub>SnBr:acetonitrile  $J_c = 65.1$  Hz; Me<sub>3</sub>SnCl:acetonitrile  $J_c = 66.7$  Hz.

The dimethyltin dihalides are known to be better acceptors and with the same donor molecules complexing takes place in two steps (43).

$$(CH_3)_2SnCl_2 + :D \rightleftharpoons [(CH_3)_2SnCl_2:D]$$

 $(CH_3)_2SnCl_2:D + :D \rightleftharpoons [(CH_3)_2SnCl_2:2D]$ 

In aqueous or mixed aqueous/organic solvents, both the trimethyltin halides and dimethyltin dihalides ionize. In the case of the dihalides, ionization proceeds in two steps to give in dilute solutions the dimethyl stannic ion (44). For dimethyltin dichloride, the equilibrium constants are known (44).

$$(CH_3)_2 SnCl_2 \rightleftharpoons (CH_3)_2 SnCl^+ + Cl^-$$
$$(CH_3)_2 SnCl^+ \rightleftharpoons (CH_3)_2 Sn^{2+} + Cl^-$$
$$K_2$$

 $K_1 = 3.48$  moles  $l^{-1}$  in water and  $K_2 = 0.417$  moles  $l^{-1}$  in water.

The study of dimethyltin dichloride in various solvents is summarized in Fig. 3. In methanol, acetone, and acetonitrile the values of  $J_{Sn-C-H}$ can be interpreted in terms of the formation of a penta-coordinated tin complex in concentrated solutions followed in dilute solution by the predominant formation of a hexa-coordinated tin complex with two donor molecules. The value of  $J_{13C-H}$  in the methyl group changes by less than 1-2 Hz in all solutions and this locates the center of the complexing reaction as being at the tin atom. The approximate proportionality between  $J_{Sn-C-H}$  and the s electron character used in bonding at the tin to the carbon has been established (45). It appears, therefore, that the 's' character used in bonding increases in going from (CH<sub>3</sub>)<sub>2</sub>SnCl<sub>2</sub> to [(CH<sub>3</sub>)<sub>2</sub>SnCl<sub>2</sub>:D] and decreases in proceeding to  $[(CH_3)_2SnCl_2:2D]$ . If the bonding changes at tin can be approximately described as  $(sp^3) \rightarrow (sp^2)dp \rightarrow (dsp^2)(dp)$ , then the Sn—C bond at the tin has 1/4, 1/3, and 1/4 's' electron character respectively. This accounts, at least qualitatively, for the shape of the observed dilution curves. There is support for this bonding scheme in the known bond lengths. The donor molecules occur as axial ligands with longer bonds (41). Extrapolated values of  $J_{Sn-C-H}$  from the concentrated regions of the solution are 90 to 96 Hz, depending on the solvent, compared with 71 Hz in the pure dihalide. The approximate ratio of 4/3 is satisfactory. The infinite dilution values of the coupling are less certain because the extrapolation is difficult to make in view of the rapid decrease of J and decreasing signal to noise.

Ionization in water and acetone/water mixtures is accompanied by an increasing value of J

 $Si^{29}$  chemical shifts (2-3)

to infinite dilution values 107 Hz and 103 Hz respectively. The linear (CH<sub>3</sub>)<sub>2</sub>Sn<sup>2+</sup> ion has a tin-proton coupling constant which is sensitive to solvation, therefore. Addition of excess sodium chloride to the water solutions does not change the coupling, hence water/acetone competition in the solvation process must occur.

Tin chemical shifts in aqueous media are given at a series of dilutions for (CH<sub>3</sub>)<sub>3</sub>SnCl and  $(CH_3)_3$ SnBr in Table X. The latter compound does not dissolve an appreciable amount of water, but is solubilized by addition of acetone. A considerable high field displacement of chemical shifts occurs with ionization. The infinite dilution chemical shift of (CH<sub>3</sub>)<sub>3</sub>SnCl is sensitive to the solvent mixture, indicating some role played by the second solvent component in the solvation process.

### Acknowledgments

The support of the National Research Council of Canada is gratefully acknowledged. We are also indebted to Mrs. Cyr for making some tin chemical shift measurements.

### Appendix

$Si^{29}$ chemical shifts (2, 3)	
5 ( ) /	Chemical shift
Compound	(p.p.m.)
[(CH <sub>3</sub> ) <sub>3</sub> SiO]₄Si	81.5
SiBr <sub>4</sub>	68
Sodium silicate solution	64
$(C_2H_5O)_4Si$	59.5
[(CH <sub>3</sub> ) <sub>3</sub> SiO] <sub>3</sub> SiCH <sub>3</sub>	42.5
$C_6H_5SiH_3$	39
$(C_2H_5O)_3SiH$	21.5
$C_6H_5(CH_3)SiH_2$	14.8
(CH <sub>3</sub> SiHO) <sub>5</sub>	13.1
(CH <sub>3</sub> SiHO) <sub>4</sub>	12
$(C_6H_5)_2SiH_2$	11.8
$[(CH_3)_2SiO]_x$	0
$[(CH_3)_2SiO]_4$	-2.2
$[C_2H_5(CH_3)SiO]_4$	-2.3
$C_6H_5(CH_3)_2SiH$	-4.5
SiCl <sub>4</sub>	-6
$[(CH_3)_2SiO]_2O(C_6H_6 \text{ solution})$	-12.1
[(CH <sub>3</sub> ) <sub>3</sub> SiCH==CH <sub>2</sub> ]	-15.1
$[(CH_3)_2SiH]_2O$	-17.2
$(CH_3)_3SiC_6H_5$	-17.8
$(C_6H_5)_2CH_3SiOC_2H_5$	-18.2
$[(CH_3)_2SiNH]_3$	-18.7

St chemical shifts (2, 5)	
	Chemical shift
Compound	(p.p.m.)
[(CH <sub>3</sub> ) <sub>3</sub> Si] <sub>2</sub> NH	-19.8
(CH <sub>3</sub> ) <sub>3</sub> SiCH <sub>2</sub> OH	-21.8
(CH <sub>3</sub> ) <sub>4</sub> Si	-22.0
[(CH <sub>3</sub> ) <sub>3</sub> Si] <sub>2</sub> CH <sub>2</sub>	-22.5
(CH <sub>3</sub> ) <sub>3</sub> SiCH <sub>2</sub> NH <sub>2</sub>	-23.2
$(CH_3)_3SiCH_2C_6H_5$	-23.4
$(CH_3)_3Si(CH_2)_3CH_3$	-23.8
(CH <sub>3</sub> ) <sub>3</sub> SiCH <sub>2</sub> Cl	-25.5
(CH <sub>3</sub> ) <sub>3</sub> SiCH <sub>2</sub> NCS	-28.2
$[(CH_3)_3Si]_2O$	-28.7
$(CH_3)_3SiOC_2H_5$	-29.4
[(CH <sub>3</sub> ) <sub>3</sub> SiO] <sub>3</sub> SiCH <sub>3</sub>	-29.4
CH <sub>3</sub> SiCl <sub>3</sub>	-30
[(CH <sub>3</sub> ) <sub>3</sub> SiO] <sub>4</sub> Si	-30.4
(CH <sub>3</sub> ) <sub>3</sub> SiI	-30.6
(CH <sub>3</sub> ) <sub>2</sub> Si(CH <sub>2</sub> Si)CHCl <sub>2</sub>	-31.2
[(CH <sub>3</sub> ) <sub>3</sub> SiO] <sub>3</sub> PO	-35
(CH <sub>3</sub> ) <sub>3</sub> SiBr	48.4
(CH <sub>3</sub> ) <sub>3</sub> SiCl	51
(CH <sub>3</sub> ) <sub>3</sub> SiF	-53.1
$(CH_3)_2SiCl_2$	—54
(CH <sub>3</sub> ) <sub>3</sub> SiOSO <sub>3</sub> H	-57.6

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