

# Nuclear Quadrupole Coupling in Organotin Halides.

## I. Phenyl- and *n*-Butyltin Chlorides<sup>1</sup>

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The nuclear quadrupole coupling constants of  $\text{Cl}^{35}$  in the mono- and di-*n*-butyltin chlorides and the mono- and diphenyltin chlorides were measured at 77°K. and at 201 and 300°K. where possible. Assuming an electric field gradient asymmetry parameter of zero at the chlorine nuclei, the coupling constants were calculated, from the measured frequencies, to be  $-43.124$ ,  $-34.546$ ,  $-42.332$ , and  $-33.894$  Mc./sec., respectively. The large decrease in the nuclear quadrupole coupling constant on progressive substitution and the lack of a constant nuclear quadrupole coupling constant ratio between analogous carbon and tin compounds suggests a change in the double bond character of the Sn-Cl bond with substitution. The relative values of the coupling constants of analogous aliphatic and aromatic tin chlorides are reversed to those for analogous carbon compounds.

### Introduction

Using the previously determined nuclear quadrupole coupling constant for  $\text{SnCl}_4$ <sup>3</sup> and observed bond lengths, Schawlow<sup>4</sup> has estimated the Sn-Cl bond to contain 22% double, 40% single, and 38% ionic character. Gordy<sup>5</sup> has estimated 9, 49, and 42% for the same contributions. Using the method of Mays and Dailey<sup>6</sup> the same contributions were calculated to be 21, 35, and 44%, respectively. Since the estimation of bond character from nuclear quadrupole coupling constants, in the absence of any knowledge of the electric field gradient (e.f.g.) asymmetry parameter, involves a prior specification of two of the three quantities—fraction s-hybridization, fraction  $\pi$ -bonding, and fraction ionic character—this study is being undertaken to establish more definitely the nature of the Sn-Cl bond.

### Experimental

Commercial samples<sup>7</sup> of *n*-butyltin trichloride [(*n*- $\text{C}_4\text{H}_9$ ) $\text{SnCl}_3$ ], di-*n*-butyltin dichloride [(*n*- $\text{C}_4\text{H}_9$ ) $_2\text{SnCl}_2$ ], phenyltin trichloride [( $\text{C}_6\text{H}_5$ ) $\text{SnCl}_3$ ] and diphenyltin dichloride [( $\text{C}_6\text{H}_5$ ) $_2\text{SnCl}_2$ ] were used without further purification. Samples were sealed in 2-dram vials for insertion into the oscillator coil of the spectrometer.

The resonances were found and measured using an externally quenched Zeeman-modulated super-regenerative spectrometer similar to that described by Graybeal and Cornwell<sup>8</sup> except that it contained some added capacitance in the tank circuit to improve its operation below 20 Mc./sec. The resonances were recorded by

use of a phase-sensitive detector followed by a recording milliammeter. The circuit was operated coherently during the recording and measuring of the absorption lines. The correct identification of the spectral component being absorbed was done by use of an external oscillator as described elsewhere.<sup>8</sup> Frequency measurements were made using a Hewlett-Packard 524D frequency counter and are accurate to 0.1 kc./sec. The observed line widths of 8–10 kc./sec. and the uncertainty associated with setting the spectrometer on an absorption line limits the accuracy of the frequency measurements to  $\pm 2$  kc./sec.

### Results

The observed nuclear quadrupole resonance (n.q.r.) frequencies of the  $\text{Cl}^{35}$  atoms in the compounds studied are listed in Table I. When possible, measurements

Table I. Observed Frequencies and Calculated Nuclear Quadrupole Coupling Constants of  $\text{Cl}^{35}$  in *n*-Butyl- and Phenyltin Chlorides

Compound	—Observed frequency, Mc./sec.—			Calcd.   $e^2Qq_{zz}$  , Mc./sec.
	77°K.	201°K.	300°K.	
( <i>n</i> - $\text{C}_4\text{H}_9$ ) $\text{SnCl}_3$	21.688	(Liquid)	(Liquid)	43.124
	21.436			
( <i>n</i> - $\text{C}_4\text{H}_9$ ) $_2\text{SnCl}_2$	17.273	16.990	16.605	34.546
	( $\text{C}_6\text{H}_5$ ) $\text{SnCl}_2$	21.166	(Not observed)	(Liquid)
( $\text{C}_6\text{H}_5$ ) $_2\text{SnCl}_2$	16.947	16.579	16.317	33.894

were made at liquid nitrogen, Dry Ice, and room temperatures. In order to discuss the data it is necessary to calculate the nuclear quadrupole coupling constants,  $|e^2Qq_{zz}|$ , from the observed frequencies. For initial discussions this has been done by assuming an asymmetry parameter equal to zero and using the usual relation for the spin  $3/2$  case

$$\nu = \frac{|e^2Qq|}{2h} \left[ 1 - \frac{\eta^2}{3} \right]^{1/2}$$

For samples exhibiting multiple resonances due to nonequivalent crystal sites, an average frequency was used. This simplification is justified since the lack of cylindrical symmetry will in general have a proportionally greater effect on the asymmetry parameter than on the coupling constant. This is further justified by work on related compounds<sup>6</sup> which has shown that the only noncylindrical contribution which would be important in a Sn-Cl bond in quadrivalent tin chlorides would be a small amount of double bond character. For a double bond character of 10% this would only introduce a difference of 2.5% in the calculated value of  $|e^2Qq_{zz}|$ . The calculated values of  $|e^2Qq_{zz}|$  are given in Table I also.

- (1) Supported by National Science Foundation Grant G-21048.
- (2) National Science Foundation Graduate Fellow, 1964–1965.
- (3) H. Dehmelt, *J. Chem. Phys.*, **21**, 380 (1953).
- (4) A. L. Schawlow, *ibid.*, **22**, 1211 (1954).
- (5) W. Gordy, *Discussions Faraday Soc.*, **19**, 14 (1955).
- (6) J. M. Mays and B. P. Dailey, *J. Chem. Phys.*, **20**, 1695 (1952).
- (7) Metallomer Laboratories, Inc., Maynard, Mass.
- (8) J. D. Graybeal and C. D. Cornwell, *J. Phys. Chem.*, **62**, 483 (1958).

**Table II.** Nuclear Quadrupole Coupling Constants of Cl<sup>35</sup> in Related Series of Group IV Chlorides<sup>a</sup>

Compound	$ e^2Qq_{zz} $ , Mc./sec.	$ e^2Qq_{zz} $ , Mc./sec.		$\beta^c$ $\times$ 100	Change in $\beta^b$ $\times$ 100
		Absolute change <sup>b</sup>	% change <sup>b</sup>		
A					
CCl <sub>4</sub>	81.9			9.7	
SiCl <sub>4</sub>	40.8	41.1	50	54.8	45.1
GeCl <sub>4</sub>	51.3	30.6	37	43.2	33.5
SnCl <sub>4</sub>	48.2	33.7	41	46.6	36.9
B					
CCl <sub>4</sub>	81.9			9.7	
CH <sub>3</sub> CCl <sub>3</sub>	75.9	6.0	7.2	15.0	5.3
(CH <sub>3</sub> ) <sub>2</sub> CCl <sub>2</sub>	69.8	12.0	15	22.9	13.2
(CH <sub>3</sub> ) <sub>3</sub> CCl	62.1	19.7	24	31.2	21.5
C					
SiCl <sub>4</sub>	40.8			54.8	
CH <sub>3</sub> SiCl <sub>3</sub>	38.1	2.7	6.6	57.8	3.0
(CH <sub>3</sub> ) <sub>2</sub> SiCl <sub>2</sub>	35.5	5.3	13	60.8	6.0
(CH <sub>3</sub> ) <sub>3</sub> SiCl	33.0	7.8	19	63.4	8.6
D					
SnCl <sub>4</sub>	48.2			46.6	
( <i>n</i> -C <sub>4</sub> H <sub>9</sub> )SnCl <sub>3</sub>	43.2	5.0	10	52.3	5.7
( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> SnCl <sub>2</sub>	34.6	13.6	28	61.9	15.3

<sup>a</sup> Data other than those from the present study are from ref. 9. <sup>b</sup> Change relative to first member of each division. <sup>c</sup> Assuming 18% s-hybridization and no  $\pi$ -bonding.

## Discussion

There are three interesting features regarding the observed data: (1) there is a large decrease of the Cl<sup>35</sup> nuclear quadrupole coupling constant upon progressive substitution of organic groups as compared to carbon and silicon compounds; (2) there is a lack of constancy in the ratio of the  $|e^2Qq_{zz}|$  values between the tin compounds and analogous compounds of carbon; and (3) there is a reversal of the effect of aliphatic and aromatic substituents on the value of  $|e^2Qq_{zz}|$  as compared to carbon compounds.

In some of the discussions which follow it has been necessary to use data involving similar but not completely analogous compounds. This has been necessary owing to the lack of  $|e^2Qq_{zz}|$  values for some of the carbon and silicon analogs of the tin compounds studied. A study of the effect of aliphatic chain length on a single terminal chlorine n.q.r. frequency has been studied,<sup>9</sup> and it has been shown that from chain lengths of C<sub>2</sub> through C<sub>10</sub> there is less than 1% variation in the observed n.q.r. frequency. In view of this the comparison by n.q.r. data between compounds such as (C<sub>4</sub>H<sub>9</sub>)SnCl<sub>3</sub> and C<sub>7</sub>H<sub>5</sub>CCl<sub>3</sub> is justified. Table II lists the  $|e^2Qq_{zz}|$  values for a number of analogous solid group IV halides. These values have been calculated from available n.q.r. frequencies using the same method as employed in Table I.

Prior studies of the group IV tetrahalides have established an abnormality in the value of  $|e^2Qq_{zz}|$  for SiCl<sub>4</sub>, it being lower than the value calculated from electronegativity differences alone. This abnormality has been ascribed to partial  $\pi$ -bond character of the Si-Cl bond.<sup>6</sup> Since silicon is the first member of group IV to have d-orbitals available to form  $\pi$ -bonds, this is expected. A comparison of the  $|e^2Qq_{zz}|$  values for analogous compounds in Table II shows that this behavior is true regardless of substituents. If one ignores  $\pi$ -bonding and assumes comparable sp-hybridization of the chlorine atom in combination with different group IV elements, then the apparent fraction

ionic character  $\beta$  can be estimated from the  $|e^2Qq_{zz}|$  values. This is done by assuming 18% s-hybridization of the chlorine-bonding orbital and using the relationship

$$\beta = 1 - \frac{U_p}{1 - s}$$

where  $U_p$  is the ratio  $(e^2Qq_{zz})_{\text{mol}}/2(e^2Qq_{zz})_{\text{at}}$  and  $s$  is the fraction s-character. Values of the apparent ionic character calculated in this manner are exceptionally high compared to those based on Pauling electronegativity differences. Calculated values of  $\beta$  are given in Table II. Since  $\pi$ -bonding and increasing ionic character affect the value of  $|e^2Qq_{zz}|$  in a like manner, this is evidence for the occurrence of  $\pi$ -bonding in the higher group IV halides.

Examination of the data in Table II reveals that the decrease in the coupling constant upon replacement of a chlorine with an organic substituent in SnCl<sub>4</sub> is comparable in absolute value and larger in per cent change than those of carbon compounds and much larger in both cases than those of silicon compounds. Since there is little chance for  $\pi$ -bonding in aliphatic substituted chloromethanes, one can determine the change in ionic character produced by successive substitution of organic groups from the coupling constants of these compounds. This is shown in section B of Table II. The decrease in apparent ionic character with substitution is slightly larger in the case of tin compounds than for carbon compounds. Since it is improbable that the electron-repelling power of an aliphatic group would vary greatly with the substituted atom, this larger decrease is evidence for postulating a change in  $\pi$ -bond character with substitution in tin compounds also.

Table III gives the calculated ratios of the  $|e^2Qq_{zz}|$  values for a number of carbon, silicon, and tin compounds. The constant ratio observed for carbon/silicon compounds is absent for carbon/tin and silicon/tin compounds. If, on progressive substitution of aliphatic groups, the only change in the nature of the

(9) H. O. Hooper and P. J. Bray, *J. Chem. Phys.*, **33**, 334 (1960).

**Table III.** Nuclear Quadrupole Coupling Constant Ratios for Analogous Carbon, Silicon, and Tin Compounds

Type compound <sup>a</sup>	C/Si ratio	C/Sn ratio
MCl <sub>4</sub>	1.99	1.69
RMCl <sub>3</sub>	1.99	1.76
R <sub>2</sub> MCl <sub>2</sub>	1.97	2.02
C <sub>6</sub> H <sub>5</sub> MCl <sub>3</sub>	2.02	1.76

<sup>a</sup> R = CH<sub>3</sub> for M = C and Si; R = C<sub>4</sub>H<sub>9</sub> for M = Sn.

bond to the halogen was to increase its ionic character, then this ratio should be constant as for carbon/silicon. The increase in this ratio with progressive aliphatic substitution on SnCl<sub>4</sub> indicates that there is an additional effect on the Sn-Cl bond. This effect could be due to either a change in the hybrid character of the chlorine bonding  $\sigma$ -orbital or a change in the  $\pi$ -bonding. It is doubtful that the s-character of the chlorine atom

bonds in (*n*-C<sub>4</sub>H<sub>9</sub>)SnCl<sub>3</sub> and (*n*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>SnCl<sub>2</sub> as compared to SnCl<sub>4</sub> would be sufficient to explain the larger change in apparent ionic character.

Recent Mossbauer studies<sup>11</sup> on phenyltin chlorides indicate that the change in ionic character in going from SnCl<sub>4</sub> through (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>SnCl<sub>2</sub> is less than 5%. This is much lower than the 15% indicated by the present study assuming no change in  $\pi$ -bond character. This tends to support the contention, based on the large apparent fraction ionic character, the large decrease in the coupling constants and apparent fraction ionic character with progressive substitution, and the lack of constancy of the coupling constant ratios of carbon to tin in analogous compounds, that there is appreciable  $\pi$ -bond character in the Sn-Cl bond and that there is an increase in the  $\pi$ -bond character of the Sn-Cl bond with substitution. The determination of the exact amount of  $\pi$ -bonding could be made, were the e.f.g. asymmetry parameter known.

**Table IV.** Substituent Effects on Nuclear Quadrupole Coupling Constants

Compound	[e <sup>2</sup> Qq <sub>zz</sub> ], Mc./ sec.	Compound	[e <sup>2</sup> Qq <sub>zz</sub> ], Mc./ sec.
( <i>n</i> -C <sub>4</sub> H <sub>9</sub> )SnCl <sub>3</sub>	43.2	CH <sub>3</sub> COCH <sub>2</sub> Cl	70.6
(C <sub>6</sub> H <sub>5</sub> )SnCl <sub>3</sub>	42.4	2,4-(CH <sub>3</sub> ) <sub>2</sub> C <sub>6</sub> H <sub>3</sub> COCH <sub>2</sub> Cl	71.2
( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> SnCl <sub>2</sub>	34.6	CH <sub>2</sub> CH <sub>2</sub> Cl	63.4
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> SnCl <sub>2</sub>	33.8	(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> Cl	67.2
CH <sub>2</sub> CH <sub>2</sub> Cl	65.2	( <i>n</i> -C <sub>4</sub> H <sub>9</sub> )CH <sub>2</sub> Cl	66.2
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> Cl	67.2	(C <sub>6</sub> H <sub>5</sub> )CH <sub>2</sub> Cl	67.2
(CH <sub>3</sub> )CCl <sub>2</sub>	75.9	CH <sub>3</sub> SiCl <sub>3</sub>	38.1
(C <sub>6</sub> H <sub>5</sub> )CCl <sub>2</sub>	77.4	(C <sub>6</sub> H <sub>5</sub> )SiCl <sub>3</sub>	38.3

<sup>a</sup> Data other than that from the present study taken from ref. 9.

would be affected, particularly in that an increase would be necessary to explain the observed effect. An increase in the  $\pi$ -bond character would account for the difference. Such an increase, however, is not in agreement with the observed<sup>10</sup> increase in the Sn-Cl bond length in going from SnCl<sub>4</sub> to (CH<sub>3</sub>)<sub>2</sub>SnCl<sub>2</sub>. A comparison of coupling constants of the substituted tin(IV) chlorides, as calculated from those of analogous carbon compounds by use of a constant ratio and as determined experimentally, shows that an increase of 2 and 8% in the double bond character of the Sn-Cl

(10) H. A. Skinner and L. E. Sutton, *Trans. Faraday Soc.*, **36**, 1209 (1940).

Examination of Table IV shows a definite reversal in order for the quadrupole coupling constants of aliphatic- and aromatic-substituted compounds of tin as compared to carbon. The relative order of the coupling constants for the substituted tin(IV) chlorides is that predicted on the basis of the electropositive character of aliphatic and aromatic groups as they affect the ionic character of a halogen as reflected in the ease of hydrolysis of alkyl and aryl chlorides. Study of a larger number of tin compounds will be necessary before any definite conclusions can be drawn regarding this phenomenon.

(11) R. H. Herber, *Chem. Eng. News*, **42**, 66 (July 13, 1964).