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STUDIES ON ORGANOTIN COMPOUNDS USING THE DEL RE METHOD

VIII. MÖSSBAUER SPECTRA OF ORGANOTIN COMPOUNDS

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SUMMARY

A method for calculating the electron density at the nucleus of the tin atom in a tetravalent compound has been developed using the quantities available from the Del Re calculations. The calculated electron densities show a fair correlation with the experimental Mössbauer isomer shifts, and a value of $+3.2\times10^{-4}$ is obtained for $(\Delta R/R)$, in excellent agreement with the value of $+3.30\times10^{-4}$ obtained from an independent method using internal electron conversion measurements. By defining an asymmetry parameter, A, which is a measure of the deviation of the calculated p-electron distribution from the hypothetical spherically-symmetric distribution, in which the p-electrons would be distributed equally between the three p-orbitals, the experimental quadrupole splittings have been correlated and interpreted. Factors governing the magnitude of quadrupole splitting are also discussed.

INTRODUCTION

Mössbauer spectroscopy, using the naturally occurring ^{119}Sn isotope, is being applied increasingly to the study of the nature of the bonds and the coordination number of the tin atom in organotin compounds. Much information on both isomer shifts and quadrupole splittings in organotin compounds is already available, though a satisfactory interpretation of the experimental data is not available in most cases. In some cases, a correlation between the isomer shift and the electronegativity of the substituents bound to the tin atom has been observed[1]. The relationship between the isomer shifts and tin–proton spin–spin coupling constants[2], as well as a number of theoretical approaches to the calculation of the isomer shifts in organotin compounds[3,4], have been also examined. It has been suggested that imbalance in the π-interactions determines whether or not a quadrupole splitting would be observable in an organotin compound[5,6]. This rule is, however, only qualitative, furthermore it fails in many cases[5,7–10]. More recently the imbalance in the tin–ligand σ-bond polarities has been suggested as the dominating factor in determining the quadrupole splittings, and a good correlation between the inductive Taft constant and the quadrupole splittings has been obtained for a number of organotin compounds[11].

However, in spite of the considerable attention given to this topic, no general approach of wide applicability has yet been developed for the interpretation and correlation of the Mössbauer parameters in organotin compounds.

Theoretically the ^{119}Sn isomer shift is linearly related to the total electron density at the tin nucleus[12], which in turn is related to the s- and p-electron populations of the valence shell[3,13]. In the present work we have therefore developed a simple method of calculating the s- and p-electron populations, and hence the electron density at the tin nucleus from the quantities available through the Del Re calculations on organotin compounds. The calculated electron densities show a fair correlation with the experimental Mössbauer isomer shifts, and the value of $(\Delta R/R)$, calculated from the correlation line, is $+3.2\times10^{-4}$, in excellent agreement with the value ($+3.3\times10^{-4}$) obtained from an independent method based on internal electron conversion measurements[14]. Moreover, a method for calculating the asymmetry in the p-electron distribution at the tin atom has been developed, and an asymmetry parameter has been defined. This parameter shows an excellent correlation with the experimental quadrupole splitting.

METHOD, RESULTS AND DISCUSSION

(*A*). *Mössbauer isomer shifts in organotin compounds*

The Mössbauer isomer shift in an organotin compound relative to a standard source is given by eqn. (1)[12,15], where $(\Delta R/R)$ is the fractional change in nuclear charge radius of the tin atom on excitation, C is a constant involving nuclear radius, charge etc., and $\Psi_a^2(o)$ and $\Psi_s^2(o)$ are the overall electron densities at the tin nucleus in the absorber and the source respectively.

$$\delta = C\cdot(\Delta R/R)\cdot[\Psi_a^2(o) - \Psi_s^2(o)] \tag{1}$$

Using relativistic wave functions for the tin atom in various oxidation states and different electronic configurations, Lees and Flinn have shown that $\Psi^2(o)$, in units of a_0^{-3}, is given by eqn. (2), where ρ_0 represents the electron density of the bare core state (Sn^{4+}), and n_s and n_p are the s- and p-electron populations of the valence shell[13]

$$\Psi^2(o) = \rho_0 + \rho \tag{2}$$

where

$$\rho = n_s(57.28 - 3.77\,n_s - 3.30\,n_p) \tag{2a}$$

Combining eqn. (1) and (2) gives eqn. (3) where C' is a constant for a given source.

$$\delta = C\cdot(\Delta R/R)\rho + C' \tag{3}$$

Eqn. (3) shows that the isomer shifts will be linearly related to ρ, which may be calculated from the s- and p-electron populations of the valence shell by eqn. (2a). In the following paragraphs we therefore develop a simple method of calculating these quantities by Del Re methods.

Consider a tetravalent tin compound. The ith hybridised valence orbital Ψ_i of the tin atom may be written as in eqn. (4), where s, p_x, p_y and p_z represent the respective atomic orbitals of the tin atom. The bonding MO, Φ_i, formed from Ψ_i and the ligand orbital Ψ_X, may be represented by eqn. (5).

$$\Psi_i = a_{is}\cdot s + a_{ix}\cdot p_x + a_{iy}\cdot p_y + a_{iz}\cdot p_z \tag{4}$$

$$\Phi_i = C_i\cdot \Psi_i + C_X\cdot \Psi_X \tag{5}$$

The electron population n_j in the jth atomic orbital ($j = s$, p_x, p_y or p_z) of the tin atom will then be given by eqn. (6)

$$n_j = \sum_i 2C_i^2\cdot a_{ij}^2 \tag{6}$$

Since the Del Re bond charge $Q_{\mathrm{Sn}i}$ for the ith tin–ligand bond is given by eqn. (7), the total electron population N, the s-electron population n_s and the total p-electron population n_p in the valence shell of the tin will be given by eqns. (8), (9) and (10) respectively.

$$Q_{\mathrm{Sn}i} = 1 - 2\,C_i^2 \tag{7}$$

$$N = \sum 2\,C_i^2 = \sum_i (1 - Q_{\mathrm{Sn}i}) = 4 - q_{\mathrm{Sn}} \tag{8}$$

$$n_s = \sum 2\,C_i^2\cdot a_{is}^2 = \sum_i (1 - Q_{\mathrm{Sn}i})\cdot \lambda_{si} \tag{9}$$

$$n_p = N - n_s = 4 - q_{\mathrm{Sn}} - \sum_i (1 - Q_{\mathrm{Sn}i})\cdot \lambda_{si} \tag{10}$$

In these eqns., $q_{\mathrm{Sn}} (= \Sigma_i Q_{\mathrm{Sn}i})$ represents the partial charge on the tin atom, and a_{is}^2 has been replaced by λ_{si}, the s-character of the ith hybridised valence orbital of the tin atom. In a previous communication[16] we have shown that for $\mathrm{Me}_n\mathrm{SnX}_{4-n}$ compounds the s-character λ_s, of the tin orbital used to bond to the methyl group is given by eqn. (11). The constant K in this eqn. can be calculated from the relation between tin–proton spin–spin coupling constants and $\Sigma(\delta_X - \delta_{\mathrm{Sn}})/n$.

$$\lambda_s = 0.25 + K\cdot \sum (\delta_X - \delta_{\mathrm{Sn}})\;/n \tag{11}$$

Using a value of 0.284* for K, calculated from the correlation between J(Sn–C–H) and $\Sigma(\delta_X - \delta_{\mathrm{Sn}})/n$ given in Fig. 4 of that paper[16], eqn. (11) reduces to eqn. (12) for $\mathrm{Me}_n\mathrm{SnX}_{4-n}$ (all X's identical) type compounds. For such compounds eqn. (9) also simplifies to eqn. (13), since the s-character in the Sn–X orbital will be $(1 - n\cdot\lambda_s)/(4-n)$ in this case. All the parameters involved in eqn. (12) and (13) are available

$$\lambda_s = 0.25 + 0.284(4-n)(\delta_X - \delta_{\mathrm{Sn}})/n \tag{12}$$

$$n_s = n(1 - Q_{\mathrm{SnC}})\cdot\lambda_s + (1 - n\cdot\lambda_s)\cdot(1 - Q_{\mathrm{SnX}}) \tag{13}$$

from the Del Re calculations, so that n_s and hence n_p [eqn. (10)] may be easily obtained. Although the validity of eqn. (12) has been demonstrated in the case of $\mathrm{Me}_n\mathrm{SnX}_{4-n}$ type compounds only[16], we assume that the relation is true for all $\mathrm{R}_n\mathrm{SnX}_{4-n}$ type compounds as long as $\delta_X > \delta_C(\mathrm{R})$. This assumption is justified by the correlations obtained between the calculated parameters and the experimental Mössbauer isomer shifts and quadrupole splitting in a number of organotin compounds.

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* A very different value is obtained for K if one considers the correlation of the ethyl compounds given in Fig. 5 of that paper[16]. Because of considerable discrepancies in the reported values of $J(^{119}\mathrm{Sn{-}C{-}H})$ in the ethyl compounds (values as low as 32.2 Hz and as high as 69.2 Hz have been reported for $\mathrm{Et_4Sn}$) the data appear to be unreliable and are therefore not taken into account in evaluating K.

TABLE 1

CALCULATED VALUES OF THE ELECTRON POPULATION, n_s AND n_p AND THE EXPERIMENTAL MÖSSBAUER ISOMER SHIFTS

Compound	n_s	n_p	ρ in a_0^{-3}	δ (*mm/sec*) *relative to* SnO_2
Me_4Sn	0.840	2.520	38.48	1.22–1.29
Me_3SnCl	0.851	2.442	39.15	1.41–1.44
Me_3SnCF_3	0.829	2.440	38.22	1.31
$Me_3Sn(C_6F_5)$	0.834	2.489	39.30	1.27
Me_3SnPh	0.835	2.495	38.32	1.16
Me_3SnVi	0.835	2.493	38.33	1.30
Me_2SnCl_2	0.859	2.375	39.69	1.52–1.61
$Me_2Sn(C_6F_5)_2$	0.829	2.459	38.18	1.25
$MeSn(C_6F_5)_3$	0.823	2.429	37.99	1.19
Bu_4Sn	0.840	2.520	38.48	1.30–1.35
Bu_3SnCl	0.852	2.444	39.19	1.36, 1.58–1.65
Bu_2SnCl_2	0.861	2.377	39.77	1.50–1.60
$BuSnCl_3$	0.865	2.324	40.10	1.31, 1.70
Ph_4Sn	0.810	2.429	37.43	1.15–1.27
Ph_3SnCl	0.825	2.384	38.19	1.31–1.45
Ph_2SnCl_2	0.839	2.345	38.91	1.31–1.38
$PhSnCl_3$	0.849	2.314	39.43	1.27
$(Neop)_4Sn$[a]	0.840	2.519	38.48	1.34
$(Neop)_3SnCl$[a]	0.851	2.433	39.18	1.41
$(C_6F_5)_4Sn$	0.804	2.412	37.21	1.04
$SnCl_4$	0.788	2.362	36.66	0.7–0.9

[a] Neop = $PhC(Me_2)CH_2$.

The calculated values of n_s, n_p and ρ for a number of tetravalent tin compounds for which the necessary Del Re parameters are available, are given in Table 1 along with the reported isomer shifts[15,17,18]. Fig. 1 shows the correlation between ρ and the isomer shifts. In view of the large discrepancies in the reported isomer shifts no meaningful choice of the data is possible, and the complete range, wherever available is shown in Fig. 1. In a few cases (*e.g.*, $BuSnCl_3$) the discrepancy between the values reported by different workers is so large that these points had to be omitted. It will be seen that the correlation between ρ and the isomer shift is very satisfactory, and except for only two cases out of a total of 21 compounds given in Table 1, the deviation of the experimental data from the correlation line is less than ± 0.05 mm/sec, the reported uncertainty in the isomer shift data being of the order of ± 0.1 mm/sec. This clearly demonstrates the wide applicability, as well as the reliability, of the present method.

As a further test of the reliability we have calculated the values of $(\Delta R/R)$ from the slope of the correlation line. The constant C in eqn. (1) is given by $\frac{4}{5}\pi \cdot e^2 \cdot Z \cdot R^2$, where R is the equivalent nuclear radius in the uniformly charged sphere approximation, Z is the atomic number of the Mössbauer nucleus and e, the electronic charge. Expressing the isomer shift in mm/sec, and using the value of R for tin given by Anderson *et al.*[19], this constant is calculated to be 0.85×10^{-22} for the 23.8 keV Mössbauer transition of tin. Using this value, $(\Delta R/R)$ is found to be $+3.2 \times 10^{-4}$. This value, though in excellent agreement with the value of $+3.3 \times 10^{-4}$ obtained from an independent method based on internal electron conversion[14], differs by a

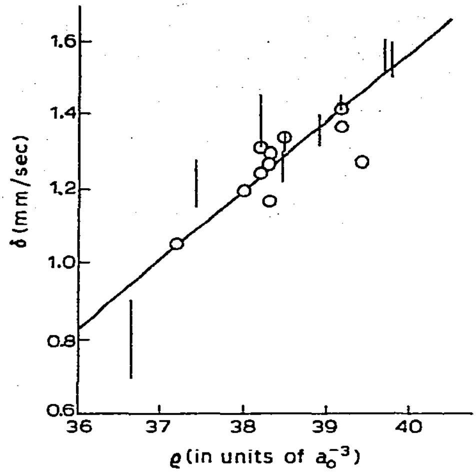

Fig. 1. Correlation between the calculated electron density ρ and the experimental isomer shift, δ.

factor of about 3 from that obtained by Lees and Flinn[13]. We consider the present calculations, though apparently crude in nature, to be more reliable because: (*i*) the reliability of the Del Re calculations and the various parameters involved in the present calculations have been already demonstrated by the very successful interpretation of many other properties of organotin compounds[16,20-25], (*ii*) no assumption of doubtful validity is involved in the calculation of electron density, as is the case with most other methods*, and (*iii*) the calculated asymmetry in the electron distribution at the tin atom, to be discussed in the following section, shows a good quantitative correlation with the experimental quadrupole splittings. The excellent agreement between our value and that obtained by the direct method[14] further supports our contention.

(*B*). *Quadrupole splittings in organotin compounds*

The Mössbauer quadrupole splitting in a chemical compound depends on the magnitude of the electric field gradient at the nucleus of the absorber. In a tetravalent tin compound the electric field gradient can be due to (*i*), asymmetry in the distribution of the *p*-electrons between the three *p*-orbitals, and/or (*ii*), asymmetric distribution of the charges of the ligand atoms. The existence of a good linear relation between the inductive Taft constant and quadrupole splittings in a number of organotin compounds[11] indicates the asymmetry in the distribution of the *p*-electrons to be the dominating factor. In order to obtain a quantitative correlation between the asymmetry in the *p*-electron distribution and the quadrupole splittings we will first develop a method for calculating the electron population in the different *p*-orbitals of the tin atom and then define an asymmetry parameter capable of providing a quantitative measure of the deviation of the calculated electron distribution from spherical symmetry.

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* For example, Lees and Flinn considered the bonding in $[SnF_6]^{2-}$ to be purely ionic, with an ideal Sn^{4+} central ion, which is very doubtful since the possibility of considerable covalent character can not be excluded. Similarly, the calculation of the isomer shift for ideal $5s^2$ configuration by extrapolation to zero quadrupole splitting may be in error, in view of our discussion on quadrupole splitting and asymmetry. Consideration of these effects leads to an increase in the calculated values.

In a tin compound of the type Y_3SnX belonging to the point group C_{3v}, the Z-axis will be conventionally chosen along the C_3 axis (along the Sn–X bond direction). With this choice of axis, and using the normalization condition, the coefficients a_{iz}'s of the different hybrid orbitals [eqn. (4)] will be as follows:

For the hybrid orbital Ψ_1, directed along the Z axis, *i.e.*, along the Sn–X bond, $a_{1x}=a_{1y}=0$; so that a_{1z} will be given by eqn. (14). Because of the symmetry the remaining p_z-character will be equally distributed between the three remaining hybrid

$$a_{1z}=(1-a_{1s}^2)^{\frac{1}{2}} \tag{14}$$

orbitals so that:

$$a_{2z}^2=a_{3z}^2=a_{4z}^2=a_{1s}^2/3 \tag{15}$$

Using these values along with eqn. (6) and (7), it is easy to show that n_z will be given by eqn. (16), where a_{1s}^2 has been replaced by λ_{sX}, the s-character of the hybrid orbital used to bond X. Since λ_{sX} can be calculated by eqn. (12), and all other quantities

$$n_z=1+\lambda_{sX}(Q_{SnX}-Q_{SnY})-Q_{SnX} \tag{16}$$

in this eqn. are available from the Del Re calculations, n_Z can be easily obtained. Further, because of the axial symmetry in Y_3SnX molecules, the population of the p_x and p_y orbitals will be equal, and may thus be readily calculated from eqn. (17).

$$n_x=n_y=(n_p-n_z)/2 \tag{17}$$

For molecules of the type Y_2SnX_2 belonging to the point group C_{2v}, the Z-axis may be chosen along the C_2 axis, and the X- and Y-axes are chosen along the mutually perpendicular SnX_2 and SnY_2 planes, respectively, as shown in Fig. 2. With this choice of axes, and using the normalization and the orthogonality conditions, the four hybridised valence orbital of the tin atom may be written as in eqns. (18a–d), where the superscripts refer to the plane in which the orbitals are located. Substituting the values of the appropriate coefficients from eqns. (18a–d) in eqn. (6) and using eqn. (7), it is easy to show that the population of the different p-orbitals will be given by eqns. (19)–(21)

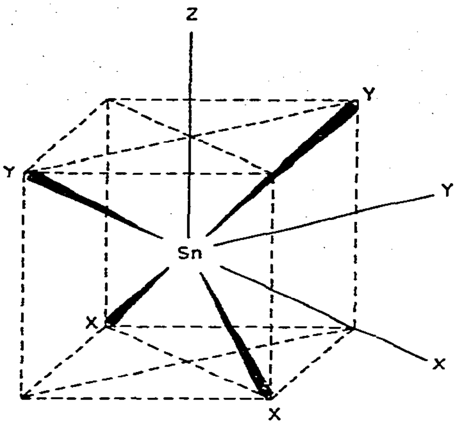
$$\Psi_1^{xz}=a\cdot s+(\tfrac{1}{2})^{\frac{1}{2}}\cdot p_x+(\tfrac{1}{2}-a^2)^{\frac{1}{2}}\cdot p_z \tag{18a}$$
$$\Psi_2^{xz}=a\cdot s-(\tfrac{1}{2})^{\frac{1}{2}}\cdot p_x+(\tfrac{1}{2}-a^2)^{\frac{1}{2}}\cdot p_z \tag{18b}$$
$$\Psi_3^{yz}=(\tfrac{1}{2}-a^2)^{\frac{1}{2}}\cdot s+(\tfrac{1}{2})^{\frac{1}{2}}\cdot p_y-a\cdot p_z \tag{18c}$$
$$\Psi_4^{yz}=(\tfrac{1}{2}-a^2)^{\frac{1}{2}}\cdot s-(\tfrac{1}{2})^{\frac{1}{2}}\cdot p_y-a\cdot p_z \tag{18d}$$

where a^2 has been replaced by λ_{sX}, the s-character in the tin hybrid orbitals along the Sn–X bond. Thus, the p-electron distributions in all organotin compounds of the type

$$n_x=(1-Q_{SnX}) \tag{19}$$
$$n_y=(1-Q_{SnY}) \tag{20}$$
$$n_z=1+2\lambda_{sX}\cdot(Q_{SnX}-Q_{SnY})-Q_{SnX} \tag{21}$$

R_nSnX_{4-n} may be calculated.

Since the electrical field gradient is determined by the deviation from spherical symmetry, it is now necessary to define a parameter capable of expressing this



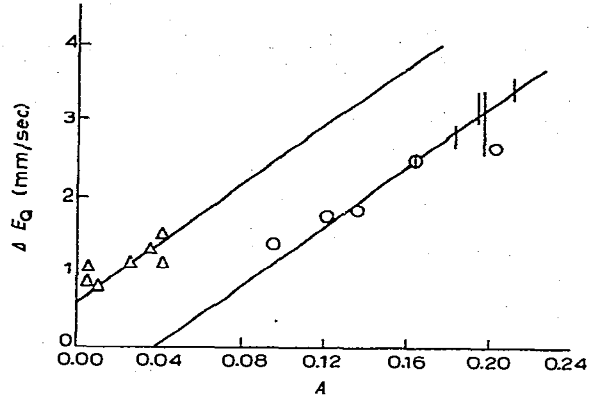


Fig. 2. Choice of coordinates in Y_2SnX_2 type compounds.

Fig. 3. Correlation between the calculated asymmetry parameter A and the experimental quadrupole splitting, ΔE_Q

deviation quantitatively. For spherical symmetry each of the three p-orbitals should have equal number of electrons, and therefore the deviation from the spherical symmetry may be quantitatively defined as the root mean square deviation of the actual electron population from the hypothetical spherically symmetric distribution, in which each of the orbitals would have $n_p/3$ electrons, as shown in eqn. (22), where n_p is the total number of electrons in the valence shell of the tin atom. We will refer to the parameter A as the asymmetric parameter, which should not be confused

$$A = [n_p/3 - n_x)^2 + (n_p/3 - n_y)^2 + (n_p/3 - n_z)^2]^{\frac{1}{2}} \qquad (22)$$

with conventional asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$. If the asymmetry due to the charge distributions of the ligands is very small or constant in a group of organotin compounds, then a correlation between the parameter A and the quadrupole splittings should be expected.

The calculated electron populations n_x, n_y, n_z, and the asymmetry parameters A, in a number of organotin compounds of the type R_nSnX_{4-n} are given in Table 2 along with the reported quadrupole splittings[11,17,18]. Fig. 3 shows that the compounds given in Table 2 fall into two groups. All compounds for which $X = Cl$ or CF_3 fall on one straight line, and those for which X is C_6F_5 or C_6Cl_5 fall on another such line. The linearity of the relation between A and the quadrupole splitting, and the presence of intercepts, indicate that the asymmetry due to the ligand charge distributions around the central tin atom exert a nearly constant influence on the electrical field gradient in a given series. Both the lines shown in Fig. 3, have the same slope, suggesting that the main difference between the two groups of compounds is the magnitude of the asymmetry arising from the substituents. In the case of R_nSnX_{4-n} compounds with $X = C_6F_5$ or C_6Cl_5 and R = alkyl, Ph or p-tolyl, Fig. 3 shows that an appreciable contribution to the total quadrupole splitting comes from the asymmetry in the charge distributions on the substituent X, and when X is Cl or CF_3, this contribution is very small and the correlation line meets the X-axis, representing the asymmetry parameter, at about 0.04. It is noteworthy that all R_nSnX_{4-n} compounds (where R = alkyl, Ph, Vi

TABLE 2

CALCULATED VALUES OF THE ELECTRON POPULATION OF THE p_x, p_y AND p_z ORBITALS OF TIN, THE ASYMMETRY PARAMETER, *A*, AND THE EXPERIMENTAL QUADRUPOLE SPLITTINGS

Compound	n_x	n_y	n_z	*A*	ΔE_Q *(mm/sec)*
Me_3SnCl	0.893	0.893	0.656	0.1935	3.01–3.41
Me_2SnCl_2	0.955	0.662	0.758	0.2114	3.33–3.55
Bu_3SnCl	0.895	0.895	0.655	0.1955	2.78–3.40
$BuSnCl_3$	0.719	0.719	0.886	0.1364	1.83
Ph_3SnCl	0.862	0.862	0.660	0.1649	2.45–2.56
Ph_2SnCl_2	0.923	0.669	0.753	0.1831	2.66–2.90
$PhSnCl_3$	0.723	0.723	0.869	0.1196	1.80–1.84
Me_3SnCF_3	0.853	0.853	0.735	0.0959	1.38
$(Neop)_3SnCl$[a]	0.894	0.894	0.645	0.2033	2.63
$MeSn(C_6F_5)_3$	0.799	0.799	0.832	0.0274	1.14
$Me_2Sn(C_6F_5)_2$	0.850	0.794	0.815	0.0405	1.48–1.56
$Me_3Sn(C_6F_5)$	0.845	0.845	0.799	0.0376	1.31
$PhSn(C_6F_5)_3$	0.803	0.803	0.809	0.0049	0.92
$Ph_2Sn(C_6F_5)_2$	0.811	0.802	0.805	0.0063	1.11
$Ph_3Sn(C_6F_5)$	0.811	0.811	0.803	0.0061	0.90–0.98
$Me_3Sn(C_6Cl_5)$	0.846	0.846	0.794	0.0421	1.09
$Ph_3Sn(C_6Cl_5)$	0.811	0.811	0.798	0.0106	0.84
$(C_6F_5)_3Sn(C_6H_4Me\text{-}p)$	0.803	0.803	0.809	0.0049	1.02
$(C_6F_5)_2Sn(C_6H_4Me\text{-}p)_2$	0.811	0.802	0.805	0.0063	1.18

[a] Neop = $PhC(Me)_2CH_2$.

TABLE 3

CALCULATED ELECTRON POPULATION OF THE p_x, p_y AND p_z ORBITALS AND THE ASYMMETRY PARAMETER, *A*, FOR SOME ORGANOTIN COMPOUNDS SHOWING NO QUADRUPOLE SPLITTING

Compound	n_x	n_y	n_z	*A*
Me_3SnVi	0.844	0.844	0.805	0.0318
Me_3SnPh	0.845	0.845	0.805	0.0327
$Me_3Sn(C_6H_4F\text{-}p)$	0.845	0.845	0.805	0.0327
Ph_3SnVi	0.810	0.810	0.809	0.0014
$PhSnVi_3$	0.809	0.809	0.810	0.0010

and X = Vi, Ph or *p*-substituted phenyl group) for which *A* is less than 0.04 do not show any quadrupole splitting (Table 3). This seems to be a general rule, the only exception being compounds having *o*-substituted phenyl groups. In this case, however, the quadrupole splitting is mainly due to the asymmetric charge distribution associated with such substituents, as is demonstrated by the relatively large intercept in the correlation line. As a further test of the validity of the correlation we have made some preliminary calculations on $R_3SnC{\equiv}CX$ type compounds which show quadrupole splitting. However, the Del Re parameters for the *sp* carbon atom have not so far been evaluated, but since the inductive parameters do not change from sp^3 to sp^2

carbon, we have used the same inductive parameters for the *sp*-carbon atom also. On the basis of δ^0 values for sp^3 and sp^2 carbon atoms, the *sp*-carbon atom may be assigned a δ^0 value of 0.22. With these values, calculations show that for $R_3SnC{\equiv}CX$ (R = Me or Et; X = H, Me, Et, Ph and Cl) type compounds the asymmetry parameters, *A*, fall in the range 0.09–0.10 and the reported quadrupole splittings lie close to the correlation line. Although the parameters used are only approximate, and need to be refined, the asymmetry parameter *A*, will in any case be appreciably greater than 0.04, thus showing that 0.04 represents the approximate limit of the asymmetry parameter, *A*, below which quadrupole splitting will not be observed. Though no satisfactory explanation can be offered for this surprising result, it confirms and quantifies the qualitative observation of Parish and Platt[11] that a large difference in the polarities of R–Sn and Sn–X bond is necessary for quadrupole splittings, since the larger the difference in the bond polarities, the larger will be the asymmetry parameter, *A*.

Our conclusions are (*i*), that the Mössbauer isomer shifts in tetravalent organotin compounds can be interpreted in terms of the calculated electron density at the tin nucleus, (*ii*) that the magnitude of quadrupole splitting is primarily determined by the asymmetry in the *p*-electron distribution at the tin atom, and (*iii*) that, in a majority of cases, the asymmetry in the charge distributions of the ligands exerts only a minor effect on the electrical field gradient.

REFERENCES

1 R. V. Parish and P. J. Rowbotham, *Chem. Phys. Lett.*, 11 (1971) 137.
2 L. May and J. J. Spijkerman, *J. Chem. Phys.*, 46 (1967) 3272.
3 V. I. Goldanskii, E. F. Makarov and R. A. Stukan, *J. Chem. Phys.*, 47 (1967) 4048.
4 N. N. Greenwood, P. G. Perkins and D. H. Wall, *Symp. Faraday Soc.*, 1 (1967) 51, [*Chem. Abstr.*, 69 (1968) 101526].
5 T. C. Gibb and N. N. Greenwood, *J. Chem. Soc. A*, (1966) 43.
6 R. H. Herber and G. I. Parisi, *Inorg. Chem.*, 5 (1966) 769.
7 A. Yu. Aleksandrov, V. I. Bregadze, V. I. Goldanskii, L. I. Sakharkin, O. Yu. Okhlobystin and V. V. Khrapov, *Dokl. Akad. Nauk SSSR*, 165 (1965) 593.
8 R. V. Parish and R. H. Platt, *Chem. Commun.*, (1968) 1118.
9 J. Philip, M. A. Mullins and C. Curran, *Inorg. Chem.*, 7 (1968) 1895.
10 H. A. Stoeckler and H. Sano, *Trans. Faraday Soc.*, 64 (1968) 577.
11 R. V. Parish and R. H. Platt, *J. Chem. Soc. A*, (1969) 2145.
12 G. K. Wertheim, *Mössbauer effect Principles and Applications*, Academic Press, New York, 1964.
13 J. K. Lees and P. A. Flinn, *J. Chem. Phys.*, 48 (1968) 882.
14 J. P. Bocquet, Y. Y. Chu, O. C. Kistner, M. L. Perlman and G. T. Emery, *Phys. Rev. Lett.*, 17 (1966) 809.
15 J. J. Zuckerman, *J. Inorg. Nucl. Chem.*, 29 (1967) 2191.
16 R. Gupta and B. Majee, *J. Organometal. Chem.*, 40 (1972) 97.
17 R. C. Poller, *The Chemistry of Organotin Compounds*, Logos Press, London, 1970, p. 249.
18 W. P. Neumann, *The Organic Chemistry of tin*, Wiley, New York, 1970, p. 228.
19 H. L. Anderson, C. S. Johnson and E. P. Hincks, *Phys. Rev.*, 130 (1963) 2468.
20 R. Gupta and B. Majee, *J. Organometal. Chem.*, 29 (1971) 419.
21 R. Gupta and B. Majee, *J. Organometal. Chem.*, 33 (1971) 169.
22 R. Gupta and B. Majee, *J. Organometal. Chem.*, 36 (1972) 71.
23 R. Gupta and B. Majee, *J. Organometal. Chem.*, 40 (1972) 107.
24 R. Gupta and B. Majee, *J. Organometal. Chem.*, 49 (1973) 191.
25 R. Gupta and B. Majee, *J. Organometal. Chem.*, 49 (1973) 197.