CHAPTER 1

OBJECTIVE AND INTRODUCTION TO THE THEORY

CHAPTER-1

A. Introduction:

The Organic Chemistry of tin began with the isolation of diethyltin diiodide by E.Frankland in 1849. It took about hundred years to start the real exploration of the subject. Since then many new compounds have been reported in quick succession with increasing trend towards the studies of the structures and bonding, stereochemistry, reaction mechanism and spectroscopy. A vast body of data on both physical and chemical properties of these compounds have already accumulated and comprehensive compilations of these data are now available in chemical literature[1-16]. Industrial uses of these compounds as polymer stabilizer, catalyst, water-repellants, additives for paints, varnishes and fuels, corrosion-inhabitors, insecticides, fungicides etc. have started emerging[1,2].

Despite the phenomenal growth of organotin chemistry during the last two decades, satisfactory theoretical interpretation of many experimental observations is yet to be found. For example, the reactivity sequence observed for the cleavage of the R group by halogen or halogen acids in polar solvents in R'_3SnR is R = Me$>$ Et$>$ Bu$>$ Pr$>$ i-Pr$>$ t-Bu[10-13]. This steric rather than inductive sequence is unexpected and there is no entirely satisfactory explanation for it. Similarly, the polarity of the tin-chlorine bond in R_nSnCl_{4-n} compounds is still a controversial topic[3]. While bond distance[17], stretching frequency[5], nuclear quadrupole coupling constant data[18] indicate a decrease in the tin-chlorine bond polarity with progressiv chlorine substitution, opposite conclusion has been drawn from the study of dipole moments[19,20]. Although the difference in electronegativities of the bonded atoms is a very good guide to the bond polarity, the standard electronegativities are of no use in such cases because the Pauling electronegativity implies that the electronegativity of an element may vary with its molecular environment[21-25]. Since it is not possible to make direct electronegativity measurements, theoretical method for evaluation of these quantities or the bond polarities will be of considerable value in the interpretation of such data.

Mossbauer spectroscopy is being increasingly applied to the study of the nature of bonds and coordination number of the tin atom in organotin compounds[1-3]. Much information on both isomer shift and quadrupole splittings in organotin compounds is already available, though a satisfactory interpretation of the experimental data is not available in most cases and no general approach has yet been developed for the interpretation and correlation of the Mossbauer parameters in organotin compounds[1-3,26-31]. Similarly, despite many discussions on factors influencing chemical shift, tin-proton coupling constants etc. in organotin compounds, no general correlation of these quantities with theoretically significant parameters like partial charges, s-character of the bonding orbitals etc. is available[1-3,7,32-38]. Again, the role and extent of $d_\pi - p_\pi$ interaction between the vacant

5d orbitals of the tin atom and p orbital of carbon, oxygen nitrogen and halogen in organotin compounds is uncertain. These are only some of the instances in organotin chemistry where our understanding of the subject is far from satisfactory. A systematic theoretical study of the properties of organotin compounds is thus desirable. Although a great deal of attention has been recently paid to the interpretation of properties of organosilicon compounds by quantum mechanical methods[39-46], no similar studies on organotin compounds are yet available. The present study was, therefore, undertaken with a view to formulating a simple and systematic approach to the interpretation and correlation of the properties of organotin compounds using approximate quantum mechanical methods.

In order to interprete molecular properties by quantum mechanical methods, two different approaches are usually employed. One is to reproduce the experimental data by means of exact calculations. The other is to replace the empirical rules in chemical sciences by nonempirical or semiempirical correlations. The former approach has been attempted by so many theoretical chemists that todgy we have reached the conviction that quantum mechanics should be the only principle governing the world of atoms and molecules. More and more accurate calculations have proved to shorten the distance between theory and practice. The latter concerns the methodology for promoting progress in chemistry by formulating nonempirical or semiempirical relations for the interpretation and correlation of scattered experimental data[47]. For this purpose, accurate wave functions are usually not necessary, rather crude but effective approximations will facilitate the acquirement of theoretical insights to help the development of chemistry. The simple Huckel treatment of π-system provides a very well known example of the latter approach[48,49]. Since the primary objective of the present study is to develop a simple method for the interpretation and correlation of the properties of organotin compounds we have adopted a similar approach.

Although several theoretical approaches are available for the study of σ-systems[47,50-53] we have been guided by the following factors in selecting the procedure adopted in the present study:-

(i) The concept of localized σ-bonds, which has greatly contributed to the development of the chemistry of saturated compounds, should not be obscured.

(ii) The method should be simple enough to be intelligible to the practising chemists and

(iii) numerical computations must be kept to the minimum in order to be able to provide quick answers without the help of a computer.

The Del Re approach nearly satisfies all these conditions[51], though its application was limited so far to the calculation of partial charges and dipole moments only[39-45,51]. Although the approximations involved in the Del Re method are undoubtedly very crude, nevertheless, the extreme mathematical simplicity of the method and its success in reproducing the dipole moments of many molecules with remarkable accuracy makes it very attractive for the study of large molecules. The method has been developed and extended to such a point in the present study that it is now possible to present a unified approach to the interpretation of such diverse properties like dipole moment, heat of atomisation, NMR chemical shift and tin-proton coupling constants, reactivity, Mossbauer chemical shifts and quadrupole splitting etc.[54-61] The success of the present approach is so impressive that the approximations involved in the Del Re method must be regarded as well founded.

In the following sections a brief discussion on the Del Re method and the various parameters needed for the present study will be presented and applications of the method for the interpretation of different properties of organotin compounds will be dealt in the subsequent chapters.

B. <u>The Del Re approximation:</u>

The Del Re approach to σ-system is based on the concept of localized bond orbitals, which are bi-centric and monoelectronic[50]. The form of the σ-bond orbital ψ is

$$\psi = C_\mu \psi_\mu \pm C_\nu \psi_\nu \tag{1-1}$$

where ψ_μ and ψ_ν are the appropriate atomic orbitals. The energies of the σ-molecular orbitals are the solutions of the secular equation:

$$\begin{vmatrix} H_{\mu\mu} - E & H_{\mu\nu} \\ H_{\mu\nu} & H_{\nu\nu} - E \end{vmatrix} = 0 \tag{1-2}$$

The integrals $H_{\mu\mu}$, $H_{\mu\nu}$ etc. appearing in eqn. (1-2) are given by:

$$H_{\mu\mu} = \int \psi_\mu \left(- \frac{h^2}{8\pi^2 m} \nabla^2 - \frac{Z_\mu}{r_\mu} \right) \psi_\mu d\tau - \sum_{\lambda \neq \mu} \frac{Z_\lambda}{r_\lambda} \int \psi_\mu^2 d\tau \tag{1-3}$$

$$H_{\mu\nu} = \int \psi_\mu \left(-\frac{h^2}{8\pi^2 m}\nabla^2 - \frac{Z_\mu}{r_\mu} - \frac{Z_\nu}{r_\nu}\right)\psi_\nu \, d\tau - \sum_{\lambda\neq\nu,\mu}\int \frac{Z_\lambda}{r_\lambda}\psi_\mu\psi_\nu \, d\tau$$

$$= \beta_{\mu\nu} - \sum_{\lambda\neq\nu,\mu}\int \frac{Z_\lambda\cdot\psi_\mu\cdot\psi_\nu}{r_\lambda}\, d\tau \qquad (1-4)$$

where Z_λ' s represent the appropriate effective charges and λ stands for the atoms directly bonded to the atom μ ; the contribution from the atoms not directly bonded to the atom μ being neglected. In eqn. (1-3) the first integral contains terms due to μ only and is a constant for a particular atom which is written as $(\alpha+\delta^{\circ}\beta$), while the second integral is approximated as $\gamma_{\mu(\lambda)}\cdot\delta_\lambda\beta$ where $\gamma_{\mu(\lambda)}$ is the so calle inductive Del Re parameter. Theoretical justification of this procedure has been provided by Del Re in this original paper. With this approximation eqn. (1-3) is rewritten as

$$H_{\mu\mu} = \alpha + \delta^{\circ}\beta + \sum_{\lambda\neq\mu}\gamma_{\mu(\lambda)}\delta_\lambda\cdot\beta = \alpha + \delta_\mu\cdot\beta \qquad (1-5)$$

and ,

$$\delta_\mu = \delta^{\circ}_\mu + \sum_{\lambda\neq\mu}\gamma_{\mu(\lambda)}\cdot\delta_\lambda \qquad (1-6)$$

where α and β are two empirical parameters representing the standard Coulomb integral and standard resonance integral respectively. The second integral in eqn. (1-4) is neglected in the Del Re approximation on the ground that it involves the product of two small terms, $S_{\mu\nu}$ the overlap integral and Z_λ the effective charge on the atom λ and the first integral is expressed in terms of β as in eqn. (1-7)

$$H_{\mu\nu} = \beta_{\mu\nu} = \varepsilon_{\mu\nu}\cdot\beta \tag{1-7}$$

The parameter $\varepsilon_{\mu\nu}$, which may be called Del Re resonance integral parameter, is taken to be constant for a given bond $\mu - \nu$.

Like the Huckel method, numerical values of the parameters α and β are not usually necessary in actual practice. The parameter δ°_{μ}, which may be termed as the standard Coulomb integral parameter is a measure of Coulomb integral of the atom μ related to a standard atom, conventionally taken to be the hydrogen atom. These parameters are therefore estimated from the electronegativities using the relation

$$\delta^{\circ}_{\mu} = K(x_{\mu} - x_{H})/x_{H} \tag{1-8}$$

where x_μ and x_H are the electronegativities of the atom μ and hydrogen respectively; K is a proportionality constant usually assigned a value of 0.57. $\varepsilon_{\mu\nu}$'s are taken to be proportional to the bond energies, though the final values for both $\varepsilon_{\mu\nu}$ and δ°_{μ} are adjusted to give good fit with some chosen experimental properties, usually the dipole moments. Although the parameters $\gamma_{\mu(\nu)}$'s are regarded as inductive parameters, these are in fact some complicated function of the effective charges and bond distance etc., as is evident from comparison of eqs. (1-3) and (1-5); and as such no standard method is available for their evaluation. These parameters are therefore obtained by trial.

The Del Re method is, thus, essentially a semiempirical quantum mechanical method in which the interaction between the different bond orbitals and the interelectronic repulsions are not explicitly introduced. However, the interaction between the different bond orbitals is taken in to account through the empirical inductive parameters which determine the bond orbital in a given environment, while the interelectronic repulsion is taken into account empirically by the resonance parameter $\varepsilon_{\mu\nu}$. In this respect the approximations involved in the Del Re method are similar to those involved in the simple Huckel LCAO MO treatment of π-system.

Once the necessary parameters are evaluated, the σ-bond orbitals and their energies can be easily obtained by solving the 2 x 2 secular eqn. (1-2). In actual practice, however, this is rarely done. Instead the bond polarity $Q_{\mu\nu}$ of the bond $\mu\nu$ is computed from eqn. (1-9).

$$Q_{\mu\nu} = C_\nu^2 - C_\mu^2 = (\delta_\nu - \delta_\mu)/2\varepsilon_{\mu\nu} \qquad (1\text{-}9)$$

The partial charge on the μth atom, q_μ, is then obtained by summing all the bond charges $Q_{\mu\nu}$ about the atom μ as in eqn. (1-10)

$$q_\mu = \sum_\nu Q_{\mu\nu} \qquad (1\text{-}10)$$

Eqn. (1-9) is only an approximate one and noticeable discrepancy between the values calculated from eqn. (1-9) and those obtained by solving the secular eqn. (1-2) may occur in some cases, particularly when $\delta_\mu - \delta_\nu$ is large. However, irrespective of the actual values of δ_μ and δ_ν, eqn. (1-9) is uniformly used in all Del Re calculations[39-45,51]. In fact this approximate relation has become a part of the method itself and the various Del Re parameters are determined by the use of this equation.

Despite these crude approximations, the Del Re method is very attractive because of (i) its extreme mathematical simplicity, (ii) the retention of the concept of localized bonds and (iii) because of its success in reproducing experimental dipole moments in a large number of cases[39-45,51].

C. Evaluation of the Del Re parameters for tin-carbon, tin-Chlorine and tin-hydrogen bonds:

The method of evaluating the Del Re parameters has been discussed in the preceding section. The Coulomb parameter δ° for tin may be obtained from the electronegativities of tin and hydrogen using eqn. (1-8). Because of serious discrepancies in the reported values for the electronegativity of tin, unique choice is not possible. Use of Pauling's data gives a rough value of about -0.08, which was finally adjusted to -0.1 by variational procedure.

The inductive parameters and the resonance parameters were determined from a consideration of the dipole moments of Me_3SnCl Me_2SnCl_2, $MeSnCl_3$ and $MeSnH_3$ and also the bond energies of tin-chlorine tin-carbon and tin-hydrogen bonds. Many other properties, such as tin-chlorine stretching frequencies, proton chemical shifts etc. were also taken in to account in selecting the values given in Table

(1-1). For all other bonds the parameters given by Del Re have been used and these data are also included in Table (1-1). Recently Nagy et al have used a different value for the inductive parameter $\gamma_{C(H)}$ with a view to improving the calculated dipole moment of some organosilicon compounds and also to obtain linear correlation between proton chemical shifts and calculated partial charges on the hydrogen atom in several organic and organosilicon compounds[45]. In the present work the original parameter has been retained due to the following reasons.

(i) In general the chemical shift data are not reliable indication of electron density around the nucleus being measured since the partial charge on an atom determines the local diamagnetic shielding only. The observed chemical shift data, on the other hand, very often include significant contribution from neighbour anisotropy and other effects[37,38,62], and in general the magnitude of this effect cannot be determined with certainty[63]. Hence, the correlation between the calculated partial charges on hydrogen and the observed chemical shifts in compounds having different central atoms should not be overemphasized.

(ii) The reactivities of organotin compounds are consistent with the original set of parameters. In fact, a reverse order of reactivity would be predicted from the bond polarisability index calculated from the modified set of Nagy et al.

(iii) Minor improvements in the calculated dipole moments in a few cases has no real significance as the dipole moment data are considerably influenced by experimental conditions.

(iv) The C-H bond polarities, calculated with the original set of parameters, are closer to the values obtained by the well known LCAO MO treatment of σ-systems by Fukui[47].

Table (1-1)

Del Re parameters

Bond	$\gamma_{A(B)}$	$\gamma_{B(A)}$	ε_{AB}	δ°_{A}	δ°_{B}
Sn-C	0.10	0.10	0.50	-0.10	0.07(sp^3) 0.12(sp^2)*
Sn-Cl	0.20	0.40	0.45	-0.10	0.35
Sn-H	0.50	-0.40	0.40	-0.10	0.00
C-H	0.30	0.40	1.00	0.07(sp^3) 0.12(sp^2)*	0.00
C-C	0.10	0.10	1.00	0.07(sp^3) 0.12(sp^2)*	0.07(sp^3) 0.12(sp^2)*
C-Cl	0.20	0.40	0.65	0.07(sp^3) 0.12(sp^2)*	0.35
C-F	0.10	0.10	0.85	0.07(sp^3) 0.12(sp^2)*	0.57

*Taken from ref. 45

It is not clear how the parameters $\gamma_{A(B)}$, $\gamma_{B(A)}$ and ε_{AB} have been evaluated.

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