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INFRARED AND NUCLEAR MAGNETIC RESONANCE STUDIES OF PARASUBSTITUTED PHENYLTIN CHLORIDES

by

GEORGE NG

A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York.

1971

This manuscript has been read and accepted for the University Committee in Chemistry in satisfaction of the dissertation requirements for the degree of Doctor of Philosophy.

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I. Introduction

Despite their similar structures, there are important differences between the alkyl and aryl derivatives of tin. These differences are pointed out in the following ways: (1) In cleavage reactions, aryl groups are cleaved more readily than alkyl groups.[1] (2) In a series of alkyltin hydrides a linear relationship exists between the per cent s character in the Sn-H bond and the $J(^{119}Sn\text{-}H)$ coupling constant. Also in alkyltin hydrides there is a linear relationship between the Sn-H stretching frequencies and the $J(^{119}Sn\text{-}H)$ coupling constant.[2] On the other hand, such linear relationships are not observed in the cases of the phenyltin hydrides.[2] (3) $Ar_2SnClOCOC_6H_5$ and analogous substituted aromatic compounds can be readily synthesized, whereas the same types of compounds cannot be obtained when the organic groups are alkyl radicals.[3] (4) Trimethyltin chloride and dimethyltin dichloride form $(CH_3)_3Sn^+$ and $(CH_3)_2Sn^{++}$ ions, respectively, when dissolved in water.[4] However, formation of the analogous phenyltin ions has not been reported. These differences have been explained in terms of electronegativity, possible $d\pi$-$p\pi$ bonding in the phenyltin systems, or a combination of both effects.

The literature reveals that most of the studies undertaken on organotin compounds to date have been on alkyltin

compounds, particularly methyltin compounds, and relatively few studies of aryltin compounds have been made. This investigation was undertaken to obtain more information on the differences between the bonding in alkyltin and aryltin compounds. A system which parallels an investigation of the reactions of methyltin compounds with various Lewis bases[5] was chosen. For this study the compounds, $(\underline{p}\text{-}XC_6H_4)_nSnCl_{4-n}$, where n = 3 or 4 and X = H-, Cl-, CH_3O- and CH_3-, were dissolved in Lewis bases of various strengths as well as in nondonating solvents such as CCl_4 or $CDCl_3$ and were investigated using infrared and nuclear magnetic resonance spectroscopy. The first objective was to ascertain whether the long range coupling constants arising from the tin atom and the adjacent hydrogen on the aromatic ring could be correlated with the strengths of the Lewis bases and whether $\underline{d}\pi\text{-}\underline{p}\pi$ bonding between the empty $\underline{d}$ orbitals of the tin atom and the pi electrons of the phenyl ring existed. A second objective was to determine whether the substituent X has any effect on the tin phenyl bond.

Another objective was to determine the effects of possible $\underline{d}\pi\text{-}\underline{p}\pi$ bonding on the properties of these organotin compounds. In order to compare them with analogous aliphatic compounds in which there is no $\underline{d}\pi\text{-}\underline{p}\pi$ bonding, it was necessary to devise criteria for determining the structural con-

figuration as well as the bonding of the addition complexes.

As a result of this investigation, it has been demonstrated that the configurations of the addition compounds, in solution, for both the alkyl- and aryltin systems are the same despite differences in the bonding of the two systems.

II. Literature Survey

Although the bonding in alkyltin compounds has been well characterized, the nature of the bonding in aryltin compounds is still not well understood. In a comprehensive survey of cleavage reactions of organotin compounds, Luijten pointed out that aryl groups are easier to cleave than alkyl groups and this behavior was ascribed to the higher electronegativity of the aryl groups.[1]

On the other hand, it has been observed[6] that the $J(^{119}Sn\text{-}H)$ coupling constant for $(CH_3)_3SnH$ is 1744 cps while that of $(C_6H_5)_3SnH$ is 1935.8 cps. If the observed difference were based solely upon electronegativity, a phenyl compound would be expected to have a smaller coupling constant than its methyl analog because the phenyl group exerts a greater electron withdrawing effect and therefore the electron interaction between the tin and hydrogen in the Sn-H bond should be decreased.

On the basis of dipole moment measurements of parasubstituted derivatives of trimethylphenyltin, $(\underline{p}\text{-}XC_6H_4Sn(CH_3)_3)$, Huang and Hui concluded that $\underline{d}\pi\text{-}\underline{p}\pi$ bonding exists between the tin and the aromatic carbon. Strong electron releasing substituents such as $(CH_3)_2N\text{-}$, $CH_3O\text{-}$ and $CH_3\text{-}$ attached para to the $(CH_3)_3Sn\text{-}$ group tend to enhance the pi bonding.[7]

Nagy, studying the ultraviolet spectra of trimethyl-phenyl-M compounds, where M = C, Si, Ge or Sn, observed that λ_{max} was highest for the silicon compound and the values of the dipole moment are lowest for the silicon and germanium compounds. He therefore concluded[8] that, except for carbon, there is conjugation of the d orbitals of the M atoms with the pi orbitals of the aromatic rings.

Further support for $d\pi$ -$p\pi$ interaction between organic substituents and the tin atom is provided by a comparison of the nmr spectra of tetraallyltin and tetravinyltin.[9] It was observed that the protons in tetravinyltin are significantly deshielded compared to tetraallyltin, which can be explained by assuming that the double bond in tetraallyltin cannot donate pi electrons as readily as the double bond in tetravinyltin.

In studying the proton nmr of phenylchlorostannanes, $(C_6H_5)_{4-n}SnCl_n$, with $n \geq 2$, Maire[10] has interpreted the results in accordance with the view that $d\pi$-$p\pi$ interaction occurs between the phenyl ring pi orbitals and the empty tin orbitals. This conclusion was reached because the resonances of both the ortho and meta protons are shifted downfield as n increases. However, the difference of the chemical shift between the ortho and meta protons remains the same when n is equal to 0 or 1 but decreases sharply

when n is equal to 2. Therefore, it is possible that $d\pi$-$p\pi$ bonding may be important in one case but insignificant in another.

Infrared studies on tetramethyltin[11,12] have led to the assignment of the symmetric and asymmetric stretching modes of Sn-CH_3 vibrations as being near 500 and 550 cm^{-1}, respectively.

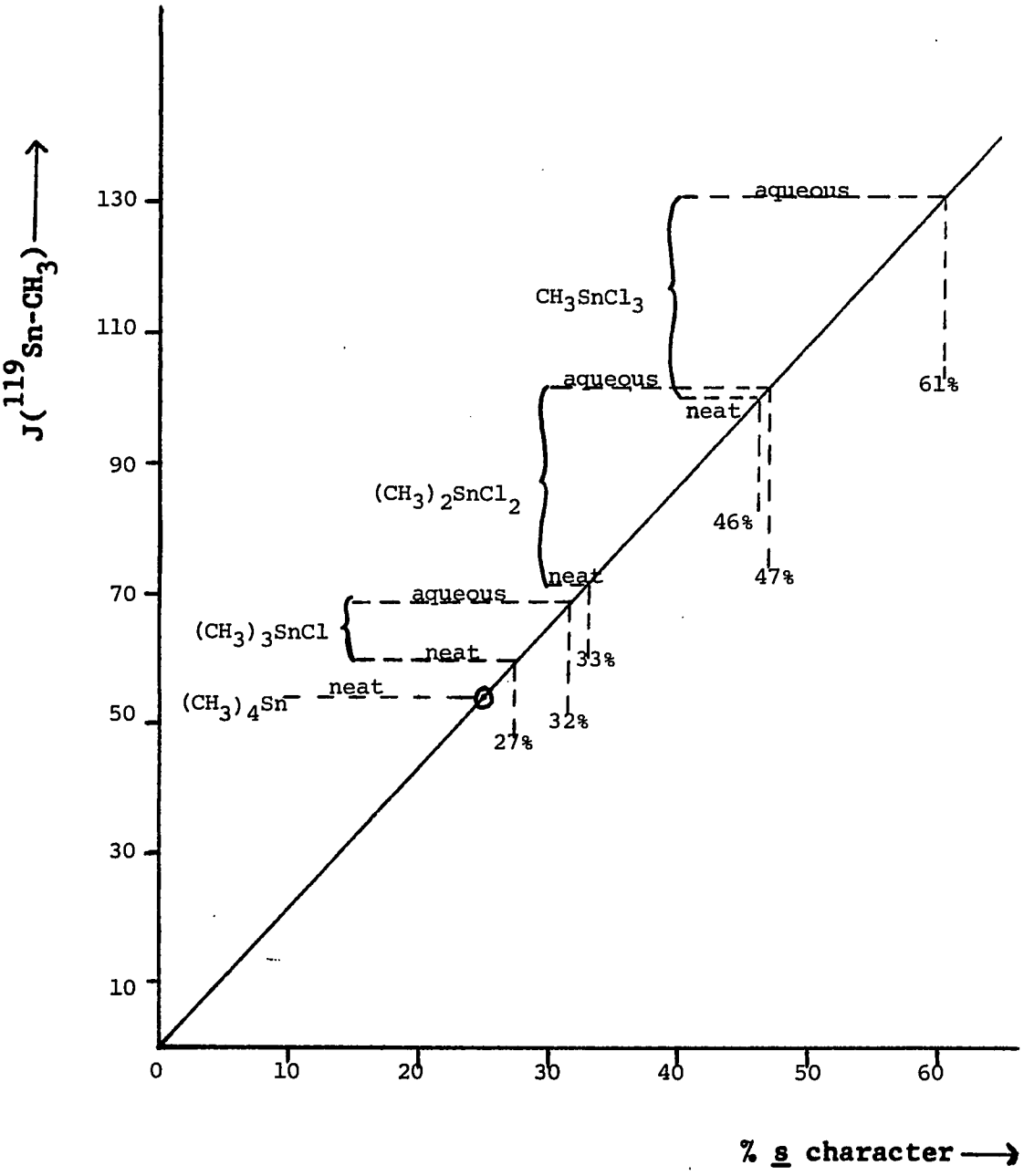
The tin phenyl stretching vibrations can be expected to occur at lower frequencies due to the larger mass of the phenyl group. A simple mass consideration would suggest that the tin phenyl bond may occur in a position similar to that of the Sn-Br vibration, i.e. ~250 cm^{-1}, as is the case with the germanium phenyl and Ge-Br bonds.[13] Comparison of the silicon phenyl asymmetric mode[14] at 485 cm^{-1} and the germanium phenyl asymmetric vibration[13] at 320 cm^{-1} leads to a similar conclusion. Poller[15] has investigated some phenyltin halides in the 667-222 cm^{-1} region and has assigned the tin phenyl asymmetric and symmetric modes at 270 and 240 cm^{-1}, respectively. Tanaka,[16] in studying the stereochemistry of a dimethylsulfoxide complex of tin(IV), $(C_6H_5)_2SnCl_2 \cdot 2DMSO$, has supported these assignments.

Some insight into the nature of bonding in organotin compounds can be obtained from nmr studies. It has been established that the contribution of the Fermi contact term

to the spin-spin coupling constant between two nuclei is directly proportional to the product of the electron densities at both nuclei of the two bonding orbitals.[17] For atoms with hybridized bonding orbitals, the contact contribution is proportional to the per cent s character in the hybridized orbitals used in forming the bond. Thus, the $J(^{13}C\text{-}H)$ coupling constants for a series of saturated and unsaturated hydrocarbons show a linear relationship which depends on the hybridization of the carbon atom.[18]

This idea was extended by Holmes and Kaesz to organotin compounds.[19] By measuring the $J(^{119}Sn\text{-}CH_3)$ coupling constant for tetramethyltin and assuming that the tin methyl bond in this compound contains 25% s character, they plotted a graph of $J(^{119}Sn\text{-}CH_3)$ versus per cent s character, as shown in Figure I, and determined per cent s character from a line drawn from the origin through the point representing J for $(CH_3)_4Sn$ at 25% s character. The validity of this linear relationship was tested by obtaining the per cent s character from the observed $J(^{119}Sn\text{-}CH_3)$ coupling constants both for neat samples and for aqueous solutions of $(CH_3)_3SnCl$, $(CH_3)_2SnCl_2$ and CH_3SnCl_3. This linear relationship between the tin coupling constants and the per cent s character does not apply in the cases of phenyltin compounds.[20]

Figure I. Apparent Per Cent of s Character of Hybrid in the Sn-C Bond.



Maddox, Flitcroft and Kaesz[2] found a linear relationship between the $J(^{119}Sn\text{-}H)$ coupling constants and the Sn-H stretching frequencies for a series of alkylstannanes, R_nSnH_{4-n}, where R = CH_3- and C_4H_9-. However, it was observed that the phenyl compounds do not follow such a relationship.

It has been suggested that in phenyltin compounds, $(C_6H_5)_nSnCl_{4-n}$, where n = 1, 2 or 3, the tin-ortho hydrogen coupling constants are determined not only by the quantity of s character in the Sn-C-C-H bond, but also are influenced by the amount of pi electron interaction.[20] This conclusion was based on the reasonable assumption that the d orbitals of the tin atom have a greater contact with the phenyl ring as the tin atom is progressively substituted by chlorine atoms, thereby increasing the contribution of $d\pi$-$p\pi$ orbital overlap to the tin-ortho hydrogen coupling constants, $J(^{119}Sn\text{-}C\text{-}C\text{-}H)$.

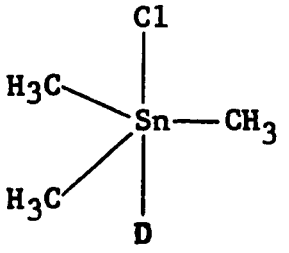
Whereas the methyltin coupling constants for alkyltin compounds are readily obtainable, the phenyltin coupling constants obtained by Verdonck and Van der Kelen[20] are uncertain because the resonance frequencies of the ring protons could not be assigned accurately. These investigators obtained two groups of peaks in the nmr spectra. The downfield group was assigned as the protons

ortho to the tin atom while the highfield group was assigned as the protons meta and para to the tin atom. These workers calculated the ^{119}Sn ortho hydrogen coupling constants, $J(^{119}Sn\text{-}C\text{-}C\text{-}H)$, by assuming that the resonance frequency of the ortho protons is the center of the multiplet of peaks assigned to the ortho protons.

Further insight into the bonding in organotin compounds is provided by a consideration of the geometries of addition complexes. Triorganotin halides, R_3SnX, show a marked tendency to form 1:1 addition compounds with Lewis bases rather than the 1:2 adducts which are formed by both R_2SnX_2 and $RSnX_3$. The most thoroughly investigated example is the 1:1 addition compound of $(CH_3)_3SnCl$ and pyridine, for which Beattie and McQuillan[21] suggested a planar arrangement of the three methyl groups based on the fact that only one $Sn\text{-}CH_3$ stretching frequency, at 560 cm^{-1} was observed. (If the molecule were not planar, two bands due to $Sn\text{-}CH_3$ stretching should be observed). This geometry was later confirmed by an X-ray crystal study.[22]

Drago and co-workers[5,23] have reported that trimethyltin halides also show a marked tendency to form 1:1 addition compounds with Lewis bases, D, in solution as well as in the solid state. It was further proposed that in these adducts, $(CH_3)_3SnCl\cdot D$, a weak donor such as acetone would lead to a

distorted tetrahedral configuration in which the CH_3-Sn-Cl angle is close to 109^{o}, while a strong donor such as dimethyl sulfoxide would induce more rehybridization of the tin atom so that the structure of the addition complex is a trigonal bipyramid.



III. Theory and Calculations

Bonding in Organotin Compounds.

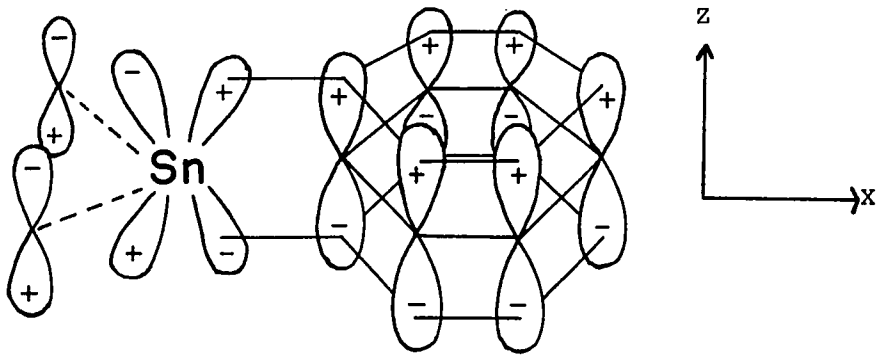
According to valence bond theory, bonding of the tin atom in compounds such as tetramethyltin and trialkyltin halides is by means of sp^3 hybridized orbitals. In these compounds the coordination number of the tin atom is four. However, in compounds in which the tin atom has a coordination number greater than four, the d orbitals of the tin atom are utilized in bonding. The most common examples of molecules containing pentacoordinated tin are the trialkyltin halide adducts such as $(CH_3)_3SnCl \cdot D$, where D is a Lewis base.[24]

Depending upon which d orbital of the tin atom is utilized, two sets of dsp^3 hybridized molecules are possible. If the d_{z^2} orbital is employed, the adduct formed would have a trigonal bipyramidal configuration, whereas if the $d_{x^2-y^2}$ orbital is utilized, a square pyramidal adduct would be obtained.[25] It should be noted here that there are no known pentacoordinated tin compounds which have square pyramidal configurations.

In the case of triaryltin halide adducts, the possibility of $d\pi$-$p\pi$ interaction between the empty d orbitals of the tin atom and the pi electrons of the phenyl ring must be considered. Assuming that the three phenyl rings are

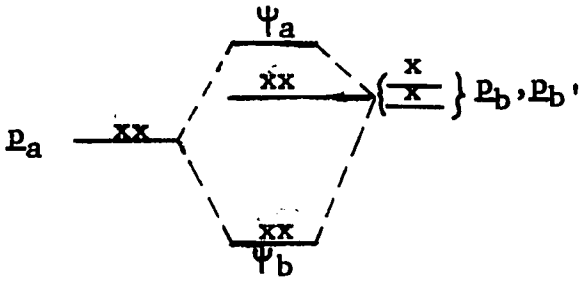
coplanar with the trigonal plane of the molecule, it can be shown by group theory that the $\underline{d}_{xz}$ and $\underline{d}_{yz}$ orbitals have the correct symmetry to overlap the pi orbitals of the phenyl rings. The $\underline{p}_z$ orbital of the tin atom also has the correct symmetry, however it is already involved in bonding with the axial groups. Details of the group theory treatment are given in **Appendix E.**

A schematic diagram showing the $\underline{d}\pi$-$\underline{p}\pi$ interaction between the $\underline{d}_{xz}$ and $\underline{d}_{yz}$ orbitals of the tin atom with the phenyl pi bonding orbital is as follows:



An equivalent configuration is possible for the Y-axis, hence there is a possibility for extensive delocalization of electrons due to pi bonding. Since delocalization would involve a lower energy state, the coplanar configuration would be favored over "propeller" or perpendicular configurations for the three phenyl rings. The σ bonds between the phenyl groups in the equatorial plane and the tin atom will involve sp^2 hybridization of the tin $\underline{s}$, $\underline{p}_x$, and $\underline{p}_y$ orbitals.

The tin atom, in a trigonal bipyramidal structure for the triaryltin halide adducts, will be bonded to the Cl and the donor molecule along the Z-axis by means of hybrid orbitals involving its p_z and d_z2 orbitals. Person[26] has studied the bonding of ions such as ICl_2^-, $BrCl_2^-$ and Br_3^- which have ten bonding electrons similar to the tin adducts being studied in this work. He proposed[26] that in these ions the d orbitals of the central atom do not have a major participation in the bonding. The bonding in these ions can be interpreted in terms of three-centered molecular orbitals based on np atomic orbitals.[27] In the simplest approximation, four of the electrons may be considered to be taking part in the bonding and occupying molecular orbitals formed from linear combinations of three np orbitals, one associated with each atom. An energy level diagram would be the following:



where p_a is the p orbital from atom a, the central atom, and p_b and p_b' are p orbitals from atoms b and b'.

Using this line of reasoning, three-centered molecular

orbitals for the axial bond in the addition compounds, $Ar_3SnCl \cdot D$, would involve the linear combination of the tin $\underline{p}_z$ orbital and one orbital with the proper symmetry from each of the Cl and donor atoms. The following set of three molecular orbitals would then be formed: (1) a bonding orbital involving D, Sn and Cl, but polarized toward Cl; (2) an essentially nonbonding orbital concentrated on D and Cl; and (3) an antibonding orbital. The four electrons involved in the D-Sn-Cl bonding would occupy the bonding and nonbonding orbitals. It should be pointed out that the $\underline{d}_z 2$ orbital has the correct symmetry and does overlap with the axial group, and therefore some contribution to the bonding from this orbital is expected.

Furthermore, if the bonding in the equatorial positions is by means of sp^2 rather than dsp^3 hybridization, the tin phenyl asymmetric stretching frequency of the adduct, $Ar_3SnCl \cdot D$, would be higher than the tin phenyl asymmetric stretching mode in Ar_3SnCl. The correlation of the increase in stretching frequency with the increase in the $\underline{s}$ character for a given bond has been observed for many systems.[28,29] Also the tin phenyl symmetric stretching vibration observed in the uncomplexed molecule having tetrahedral configuration disappears upon adduct formation. Therefore, using these criteria, the bonding as well as the

configuration of the addition compounds can be inferred by infrared spectroscopy.

Further tests for the proposed bonding scheme as well as the structural configuration can be found in the nmr spectra. If the proposed trigonal bipyramidal structure is correct, then only one type of phenyl resonance should be observed in the nmr spectra. Furthermore, if the three phenyl rings are coplanar, then the spectrum would consist of essentially two resonance peaks ascribable to the ortho and meta protons, whereas if the three phenyl groups form "propeller" or perpendicular configurations, then four resonance peaks due to the phenyl group protons are expected in the nmr spectrum.

Additional support for delocalization can be found in the chemical shifts of the ring protons in Ar_3SnCl and $Ar_3SnCl \cdot D$. If, upon adduct formation, conjugation does occur, then the protons on the phenyl ring would be expected to be deshielded due to the shift of electrons from the ring toward the tin atom. Therefore, chemical shifts of both the ortho and meta protons of the adducts would be expected to shift downfield with respect to the uncomplexed compound.

Empirical Rules and Correlations.

The electron density for a given position on the phenyl ring in parasubstituted phenyltin compounds, $(p\text{-}XC_6H_4)_3SnCl$,

is influenced by the inductive and resonance effects of the tin atom as well as the substituent X. The tin atom has been observed to exhibit primarily a +R effect,[10] which would tend to donate electrons into the ring by resonance; thus the protons ortho to the tin atom should be more shielded than the meta protons in XC_6H_5. In fact, protons meta to the tin are shielded to a lesser extent. On the other hand, the substituent X may exert both resonance and inductive effects. The protons ortho to X, meta to the tin atom, are influenced by resonance, inductive and steric effects. The proton meta to X, ortho to the tin atom, is influenced primarily by inductive effects. Hence, the observed chemical shifts of the respective protons, ortho and meta to the tin atom, may be correlated with parameters which measure inductive and resonance effects such as the Brown σ^+ values.[30] It is expected that the protons ortho to tin will be more influenced by the tin atom while the protons meta to the tin atom will be more influenced by the substituent X.

Several investigators have correlated chemical shifts of paradisubstituted aromatic compounds with special parameters such as the Taft σ_I and σ_R values or the Hammett σ constants. For example, a linear correlation between the ^{19}F chemical shifts of substituted fluorobenzenes with both

the Taft σ_I, σ_R and the Hammett σ values have been observed.[31] It should be noted that both the Taft and Hammett constants were calculated for a reaction center which is not directly on the aromatic ring but on a carbon atom attached to the ring. For example, the Hammett constants were based on the ionization of parasubstituted benzoic acids. In the case of the tin compounds, the ^{119}Sn chemical shifts would have to be obtained in order to correlate them with the Taft or Hammett values.

Brown,[30] on the other hand, has calculated electrophilic substituent constants, σ^+ values, for electrophilic aromatic substitution reactions of monosubstituted benzenes. The σ^+ values were based on the rates of solvolysis of substituted t-cumyl chlorides and these σ^+ values correlated well with the rate of bromination, chlorination and nitration of aromatic derivatives. These σ^+ values are then related to the electron density at the various positions on the aromatic ring. It then seems reasonable to expect a correlation between the chemical shifts of the ortho and meta protons with the Brown σ^+ values.

Wu and Dailey[32] have proposed an empirical linear relationship between the chemical shifts of aromatic protons and the change of pi electron density:

$$\sigma_i = K\Delta P_i \quad (1)$$

where σ_i is the chemical shift of the ith carbon atom, ΔP_i is the change of pi electron density on the ith carbon atom and K is a proportionality constant with an average value of 8.08 ppm/electron. ΔP_i is defined as the difference between the electron density in the sample molecule minus that of the reference molecule, benzene.

$$\Delta P_i = P_i - P_{C_6H_6} \quad (2)$$

By convention, the pi electron density for benzene is taken to be one, thus equation (2) becomes

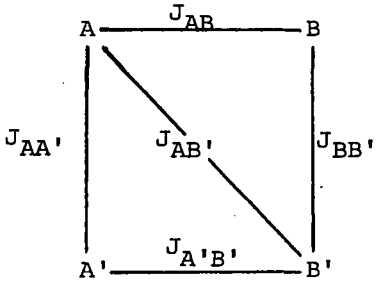
$$\Delta P_i = P_i - 1. \quad (3)$$

Hence, an atom having less pi electron density than benzene would yield a negative σ_i term, while a positive σ_i term would indicate a carbon atom having more pi electron density than benzene. Therefore, this relationship can be used to test whether delocalization occurs in parasubstituted benzene molecules such as the compounds studied in this work. If delocalization occurs, then the ortho and meta protons would be expected to have chemical shifts located downfield from those of the protons in benzene.

Theory of the Analysis of the NMR Spectra.

Neglecting the splitting due to the tin atom, the

compounds $(p\text{-}XC_6H_4)_nSnCl_{4-n}$ studied in this work are classified as belonging to an AA'BB' system.[33] An AA'BB' system is defined as one in which there are two pairs of magnetic nonequivalent nuclei separated from each other by a chemical shift which is of the same order of magnitude as the coupling constants. This system may be represented schematically as



It should be noted that an AA'BB' system contains six parameters: two chemical shifts and four coupling constants. By convention, the protons furthest downfield are labeled as the AA' protons and correspond to the protons that are the least shielded in a given molecule.

AA'BB' systems have been treated extensively in the literature.[34] Explicit transition energies and relative intensities have been calculated and are given in Table I and shown in Figure II. Examination of Table I reveals that the relative intensities of transitions 2, 4, 5, 6, 7 and 8 cannot be expressed explicitly because these six transitions are solutions of a fourth power equation.

Table I. Transition Energies and Relative Intensities for the AA' Part of an AA'BB' Spin System.[35]

Transition	Energy relative to $\frac{1}{2}(\nu_A + \nu_B)$	Relative intensity
1	$\frac{1}{2}N + \frac{1}{2}[(\nu_o J)^2 + N^2]^{\frac{1}{2}}$	$1 - \sin 2\varphi$
2	$-\frac{1}{2}[(\nu_o J)^2 + N^2]^{\frac{1}{2}} - E_1$	
3	$-\frac{1}{2}N + \frac{1}{2}[(\nu_o J)^2 + N^2]^{\frac{1}{2}}$	$1 + \sin 2\varphi$
4	$E_2 - \frac{1}{2}[(\nu_o J)^2 + N^2]^{\frac{1}{2}}$	
5	$\frac{1}{2}[(\nu_o J)^2 + N^2]^{\frac{1}{2}} - E_3$	
6	$E_4 + \frac{1}{2}[(\nu_o J)^2 + N^2]^{\frac{1}{2}}$	
7	$\frac{1}{2}[(\nu_o J)^2 + N^2]^{\frac{1}{2}} - E_4$	
8	$E_3 + \frac{1}{2}[(\nu_o J)^2 + N^2]^{\frac{1}{2}}$	
9	$\frac{1}{2}[(\nu_o J + M)^2 + L^2]^{\frac{1}{2}} + \frac{1}{2}(M^2 + L^2)^{\frac{1}{2}}$	$\sin^2(\theta_a - \psi_+)$
10	$\frac{1}{2}[(\nu_o J - M)^2 + L^2]^{\frac{1}{2}} + \frac{1}{2}(M^2 + L^2)^{\frac{1}{2}}$	$\cos^2(\theta_a + \psi_-)$
11	$\frac{1}{2}[(\nu_o J + M)^2 + L^2]^{\frac{1}{2}} - \frac{1}{2}(M^2 + L^2)^{\frac{1}{2}}$	$\cos^2(\theta_a - \psi_+)$
12	$\frac{1}{2}[(\nu_o J - M)^2 + L^2]^{\frac{1}{2}} - \frac{1}{2}(M^2 + L^2)^{\frac{1}{2}}$	$\sin^2(\theta_a + \psi_-)$

$K = J_{AA'} + J_{BB'}$ $\qquad M = J_{AA'} - J_{BB'}$ $\qquad \nu_o J = \nu_A - \nu_B$

$L = J_{AB} - J_{AB'}$ $\qquad N = J_{AB} + J_{AB'}$

$\cos 2\theta_s : \sin 2\theta_s : 1 = K : L : (K^2 + L^2)^{\frac{1}{2}}$

$\cos 2\theta_a : \sin 2\theta_a : 1 = M : L : (M^2 + L^2)^{\frac{1}{2}}$

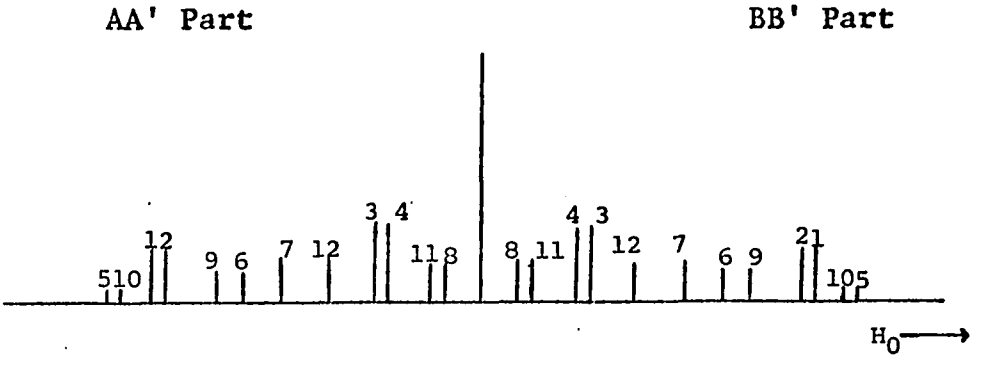
$\cos 2\varphi : \sin 2\varphi : 1 = \nu_o J : N : [(\nu_o J)^2 + N^2]^{\frac{1}{2}}$

$\cos 2\psi_{\pm} : \sin 2\psi_{\pm} : 1 = \nu_o J_{\pm} M : L : [(\nu_o J_{\pm} M)^2 + L^2]^{\frac{1}{2}}$

Only the AA' transitions need to be considered since the BB' part of the spectrum is a mirror image of the AA' part. In each half of the spectrum there are 14 possible transitions, but two of them have such weak intensities that only 12 distinct lines can be observed. The theoretical spectrum is shown in Figure II.[33]

It can be seen from both Table I and Figure II that each part of an AA'BB' spectrum will contain: (1) two strong doublets formed from lines 1, 2, and 3, 4; (2) two sets of quartets (transitions 5, 6, 7, 8, and 9, 10, 11, 12). Both sets of quartets are centered on the resonance frequency of the A nuclei, ν_A.

Figure II. Theoretical Spectrum for AA'BB' Nuclei in an AA'BB' System Where $J_{AB} \gg J_{AB'} > 0$ and $J_{BB'} > J_{AA'} > 0$.



Detailed Analysis of AA'BB' Systems.

In order to analyze the nmr spectra, it is convenient to introduce the following parameters:

$$K = J_{AA'} + J_{BB'} \qquad M = J_{AA'} - J_{BB'} \qquad \nu_0\delta = \nu_A - \nu_B$$

$$L = J_{AB} - J_{AB'} \qquad N = J_{AB} + J_{AB'}$$

Examination of Table I shows that lines 1 and 3 can be used to find the difference between the chemical shifts, $\nu_0\delta$, together with parameter N. Subtraction and addition of ν_1 and ν_3 will give the following equations respectively:

$$N = \nu_1 - \nu_3 \tag{4}$$

$$[(\nu_0\delta)^2 + N^2]^{\frac{1}{2}} = \nu_1 + \nu_3 \tag{5}$$

Lines 9 and 11 can be used to find the parameters M and L.

$$(M^2 + L^2)^{\frac{1}{2}} = \nu_9 - \nu_{11} \tag{6}$$

$$[(\nu_0\delta + M)^2 + L^2]^{\frac{1}{2}} = \nu_9 + \nu_{11} \tag{7}$$

The most difficult aspect of an AA'BB' analysis is to find a suitable value for K. For many molecules K cannot be found directly and a reasonable value is assumed. Values for K used in this work were obtained by employing Garbisch's formula,[36] which assumes that K is related to lines 2, 3, 4, 6 and 8.

$$K = (\nu_4 - \nu_8) + (\nu_2 - \nu_3) + (\nu_4 - \nu_6) \tag{8}$$

Having obtained values for K, L, M, N and $\nu_0\delta$, the coupling

constants for an experimental spectrum can then be calculated.

Assignment of Lines in an AA'BB' Spectrum.

The assignment of the lines in the experimental nmr spectra is a straightforward process. As previously shown, only the lines 1, 2, 3, 4, 6, 8, 9 and 11 need to be assigned. However, in the present study, lines 1, 2, and lines 3, 4 are within $\pm$0.1 cps of each other, respectively. Therefore, lines 1, 2, and 3, 4 could not be resolved. Lines 1 and 3 are intense transitions, therefore, they are fairly easy to assign. Transitions 6 and 8 are assigned with the aid of lines 7 and 5. Examination of Table I indicates that the sum of the transition frequencies 5 and 8 and that of 6 and 7 are both equal to $[(\nu_o J)^2 + N^2]^{\frac{1}{2}}$, a value which is already known. Lines 9 and 11 are assigned by means of a trial and error method. However, in parasubstituted benzenes, line 9 is close to line 1 while line 11 is close to line 3, facts which facilitate the assignment of lines 9 and 11.

Having assigned the key lines in the spectrum, the parameters K, L, M, N and $\nu_o J$ can be calculated using equations 4 through 8. These parameters in turn will yield the trial chemical shifts and coupling constants, which can be used to construct a theoretical spectrum.

A computer program has been written to facilitate the calculation of the trial chemical shifts and coupling constants using equations 4 through 8. The program is given in the Appendix C.

The method for calculating the detailed nmr spectrum for a given set of parameters (chemical shifts and coupling constants) is well established.[33,35] Except for the most simple cases, it is a laborious procedure best done using a computer.[37,38] The computer program, LAOCOON III, was used in this work.[37] The program, which has been modified to fit an IBM 360 Model 40 computer, is also listed in Appendix A.

The LAOCOON III program is divided into two stages. In the first stage, transition energies (line positions) and intensities are calculated based on an assumed set of coupling constants and chemical shifts (which were obtained from the values of K, L, M, N, and $\nu_o J$). This calculated spectrum is then compared with the experimental spectrum, and when a suitable rough fit has been obtained (when the theoretical assignments are within ± 0.8 cps of the lines in the experimental spectrum) the second stage of the program refines the fit using a least square analysis. This refinement will then give the best values for the chemical shifts as well as the coupling constants.

The procedure used in analyzing an AA'BB' spectrum is summarized as follows:

Step 1 — Work with either the AA' or BB' part of the spectrum.

Step 2 — Assign as many lines in the experimental spectrum as possible.

Step 3 — Calculate values for K, L, M, N and $\nu_o J$ using equations 4 through 8.

Step 4 — Compute the theoretical spectrum, based on trial chemical shifts and coupling constants which were obtained from K, L, M, N and $\nu_o J$ using Stage I of the LAOCOON III program.

Step 5 — Compare the theoretical spectrum with the experimental one.

Step 6 — If the lines in the theoretical spectrum are more different than ± 0.8 cps from those in the experimental one, repeat steps 2 through 5. This will necessitate reassigning uncertain lines in step 2.

Step 7 — After the experimental and theoretical

spectra are "matched", the second stage of LAOCOON III is used to fit the experimental lines with those of the theoretical spectrum, employing a least square analysis.

As an illustration, the proton nmr analysis of tris-parachlorophenyltin chloride in acetone is given. The ^1H nmr spectrum is given in Figure III.

The assignments of the various bands to the transition frequencies are achieved by comparing the experimental spectrum with the theoretical AA'BB' spectrum shown in Figure II.

Based on the assignments given in Figure III for the AA' part of the spectrum one can calculate values for the various parameters of the system. For example,

$$N = \nu_1 - \nu_3 = 8.40 \text{ cps} \tag{9}$$

$$[(\nu_o J)^2 + N^2]^{\frac{1}{2}} = \nu_1 + \nu_3 = 36.24 \text{ cps} \tag{10}$$

$$\text{therefore, } \nu_o J = 35.25 \text{ cps} \tag{11}$$

$$(M^2 + L^2)^{\frac{1}{2}} = \nu_9 - \nu_{11} = 7.44 \text{ cps} \tag{12}$$

$$[(\nu_o J + M)^2 + L^2]^{\frac{1}{2}} = \nu_9 + \nu_{11} = 35.28 \text{ cps} \tag{13}$$

$$\text{thus } M = -0.76 \text{ cps and } L = 7.40 \text{ cps} \tag{14}$$

$$K = (\nu_3 - \nu_8) + (\nu_1 - \nu_3) + (\nu_3 - \nu_6) = 3.88 \text{ cps} \tag{15}$$

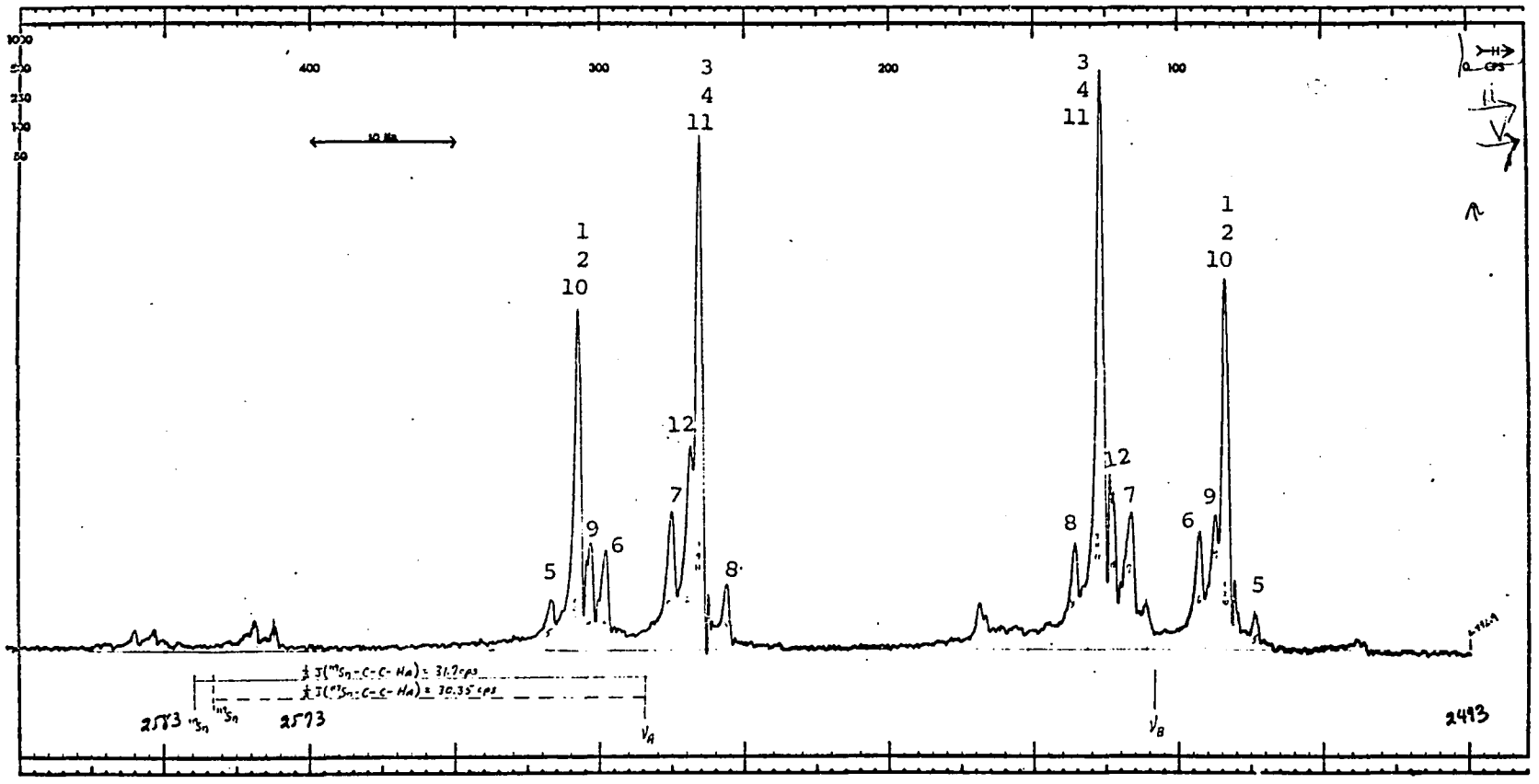


Figure III. The ^{1}H Resonance Spectrum at 100 Mc sec^{-1} of Tris-parachlorophenyltin Chloride in Acetone. Line Assignments are Indicated on the Respective Peaks.

By use of the foregoing information a complete set of coupling constants and chemical shifts is obtained for the experimental spectrum as follows:

$J_{AA'} = 1.56$ cps $\quad J_{AB} = 7.90$ cps $\quad J_{A'B} = -0.50$ cps

$J_{AB'} = -0.50$ cps $\quad J_{A'B'} = 7.90$ cps $\quad J_{BB'} = 2.32$ cps

$\nu_o J = 35.25$ cps

In Table II is listed the theoretical spectrum which was calculated using the above parameters. Also given in Table II are the experimental line frequencies. A comparison of the calculated spectrum with the experimental spectrum shows that both the line frequencies and relative intensities are within ± 0.2 units.

Splitting Resulting From the Tin Atom.

In the above discussion only the splitting of the ring protons by others has been considered. In addition, splitting is expected resulting from the magnetic isotopes ^{117}Sn and ^{119}Sn (each with nuclear spin $I = \frac{1}{2}$; relative abundances 7.67 and 8.68% respectively).

Assuming first order splitting, the tin atom will split the ortho hydrogen, H_A, on the ring into a doublet and this doublet is further split into a quartet by the

Table II. Observed and Calculated ^{1}H Spectrum of Tris-parachlorophenyltin Chloride in Acetone at 100 Hz.

LINE[a]	EXP	FREQ	CALC FREQ	INTEN[c]	ERROR	CALC[d]	OBS[e]	ERROR
45	5[b]	93.080	93.146	0.385	-0.066	0.063	0.071	0.008
55	1	95.100	95.061	1.534	0.039			
51	2	95.100	95.119	1.539	-0.019	0.620	0.717	0.097
26			95.186	0.696				
34	9	95.780	95.940	0.884	-0.160	0.145	0.261	0.116
19	6	96.980	97.001	1.231	-0.021	0.203	0.232	0.029
37	7	101.580	101.601	1.583	-0.021	0.260	0.266	0.006
24	12	102.820	102.851	1.304	-0.031	0.215	0.340	0.125
1			103.540	2.466				
42	3	103.740	103.604	1.116	0.136	1.000	1.122	0.122
5	4	103.740	103.661	2.497	0.079			
21	8	105.520	105.455	0.764	0.065	0.126	0.204	0.078
47	8	129.620	129.569	0.764	0.051	0.126	0.127	0.001
29			131.362	2.497				
36	4	131.540	131.419	1.116	0.121	1.000	1.000	0.000
53	3	131.540	131.484	2.466	0.056			
14	12	132.180	132.173	1.304	0.007	0.215	0.397	0.182
7	7	133.420	133.423	1.583	-0.003	0.268	0.266	0.006
39	6	137.980	138.023	1.231	-0.043	0.203	0.221	0.018
44	9	138.980	139.084	0.884	-0.104	0.145	0.207	0.062
12			139.838	0.696				
22	2	139.940	139.905	1.539	0.035	0.620	0.660	0.040
3	1	139.940	139.962	1.534	-0.022			
9	5	141.780	141.878	0.385	-0.098	0.063	0.096	0.033

---

a Line numbers as generated by the computer program.

b Relabeled according to Pople (Ref. 33).

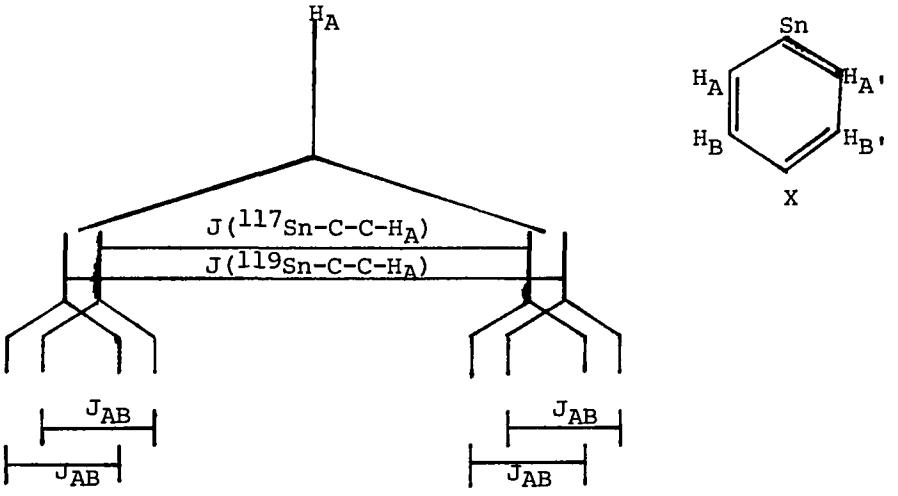
c Line intensities as generated by the computer program.

d All calculated frequencies which are within $\pm$ 0.8 cps are grouped as one frequency and the intensities are grouped as one intensity and normalized.

e Normalized to same intensity as calculated values.

meta hydrogens, H_B. This is illustrated in Figure IV. It is also expected that a similar quartet will result from the splitting of the meta protons. However, in the case of the meta protons the coupling is smaller than the width of the meta proton resonance in molecules containing non-magnetic tin isotopes, therefore, the tin meta hydrogen coupling constants will not be observable.

Figure IV. A Schematic Illustration of Sn-C-C-H_A Splitting in Tris-parasubstituted Phenyltin Chlorides.



Calculation of the Sn-H_A Coupling Constants.

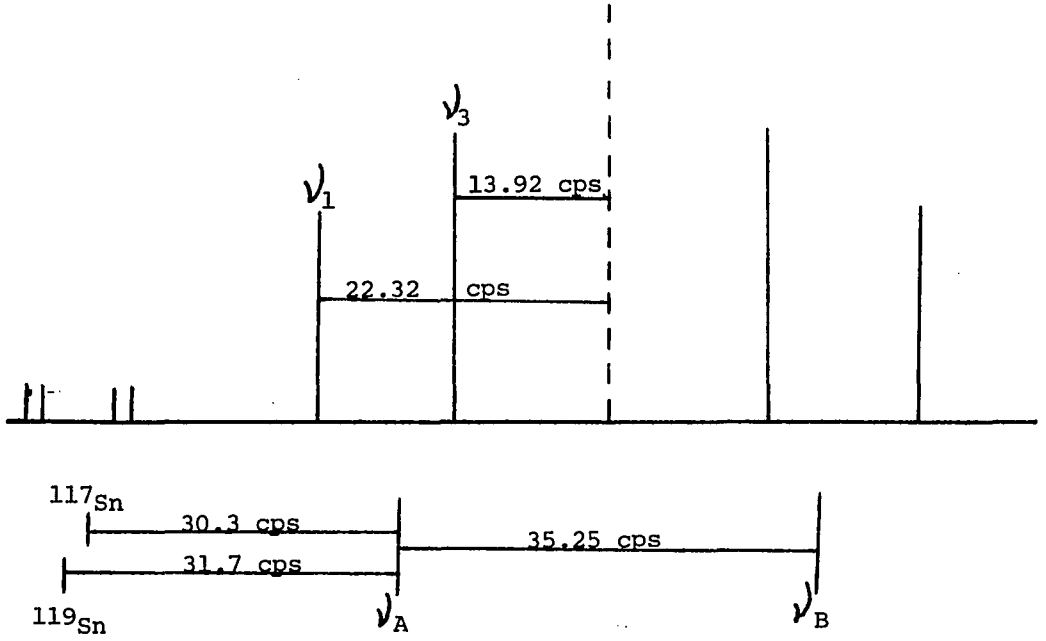
Figure III is a typical spectrum for the parasubstituted compounds studied in this work. The spectrum consists of two groups of peaks; the downfield protons are assigned as the ortho hydrogens, H_A, while the upfield group is assigned as the meta protons, H_B. A

pair of satellites is observed on the downfield side, assigned to the $^{117}Sn\text{-}H_A$ and $^{119}Sn\text{-}H_A$ coupling constants. It is also noted that the other half of the lines belonging to the coupling constants are hidden under the meta proton resonance.

If the chemical shift of the AA' nuclei can be obtained, then the tin H_A coupling constant, $J(^{119}Sn\text{-}C\text{-}C\text{-}H_A)$, may be calculated because the distance between the chemical shift of the AA' nuclei and the satellites is $\frac{1}{2} J(^{119}Sn\text{-}C\text{-}C\text{-}H_A)$.

The chemical shift of the AA' protons can be obtained without a detailed nmr analysis. One method is to find the center of the AA' multiplet and use this as the resonance frequency. However, the center of the multiplet is not always easy to assign since the outermost lines are sometimes of very weak intensity. Also the center of the multiplet is equal to the chemical shift only when the multiplet is perfectly symmetrical. The method employed in this study is to assign the most intense lines as lines 1 and 3. Having assigned lines 1 and 3, $\nu_o J$ can be calculated using equation 5. The resonance frequencies H_A and H_B can then be obtained since the distance $\nu_o J$ must be centered on the center of the spectrum. A sample calculation is shown in Figure V.

Figure V. Sample Calculation of $J(^{119}Sn\text{-}C\text{-}C\text{-}H_A)$ Coupling Constant for the Tris-parasubstitutedphenyltin Chloride Systems.



$N = \nu_1 - \nu_3 = 8.40$ cps

$[(\nu_o J)^2 + N^2]^{\frac{1}{2}} = \nu_1 + \nu_3 = 36.24$ cps

Therefore, $\nu_o J = 35.25$ cps

Hence $\frac{1}{2}\ J(^{117}Sn\text{-}C\text{-}C\text{-}H_A) = 30.3$ cps

$\frac{1}{2}\ J(^{119}Sn\text{-}C\text{-}C\text{-}H_A) = 31.7$ cps

Therefore, $J(^{117}Sn\text{-}C\text{-}C\text{-}H_A) = 60.6$ cps

$J(^{119}Sn\text{-}C\text{-}C\text{-}H_A) = 63.4$ cps.

The method described for calculating the Sn-H_A coupling constants is not applicable in the case of the unsubstituted compound, $(C_6H_5)_3SnCl$, since the equations employed do not hold for an AA'BB'C system. For the AA'BB'C system, the assumption was made that the center of the multiplet is equal to the chemical shift.

IV. Outline of The Experimental Approach

By means of infrared and nuclear magnetic resonance spectroscopy, the nature of the tin-phenyl bond as well as the possibility of $\underline{d}\pi$-$\underline{p}\pi$ bonding between the tin atom and the phenyl ring was investigated.

In addition to triphenyltin chloride, parasubstituted aryltin compounds, $(\underline{p}\text{-}XC_6H_4)_4Sn$, where X = Cl-, CH_3- and CH_3O-, and $(\underline{p}\text{-}XC_6H_4)_3SnCl$, where X = H-, CH_3-, and Cl-, were prepared and studied. Parasubstituted aryltins were employed primarily because the nmr spectra of para-disubstituted benzenes are easier to interpret than those of the monosubstituted benzenes. Theoretically, para-substituted benzenes give nmr spectra which contain 24 lines, while the spectra of monosubstituted benzenes contain 64 resonance absorptions. Also, as was discussed in Section III, the assignment of the resonance peaks, H_A and H_B, for para-substituted benzenes can be made with greater precision.

The substituents were chosen to provide a range of inductive effects, which varied from that of an electron donor-- the methyl group -- to electron acceptors -- chlorine and the methoxy group.

To identify specific effects due to $\underline{d}\pi$-$\underline{p}\pi$ bonding, the

influence of Lewis bases of various strengths on the observed spectra was also examined. It would be expected that the chemical shifts as well as the coupling constants would reflect changes due to $\underline{d}\pi$-$\underline{p}\pi$ bonding.

Since it is known that tetraaryltin compounds do not form addition complexes, the tetraaryltins were examined in inert solvents such as CCl_4 or $CDCl_3$ only. However, for the triaryltin chlorides, Lewis bases of various donor strengths in addition to inert solvents such as CCl_4 or $CDCl_3$ were used as solvents in order to correlate the chemical shift and the $J(^{119}Sn\text{-}C\text{-}C\text{-}H_A)$ coupling constants with the basicity of the Lewis base. The Lewis bases employed were acetone, diethyl ether, N,N-dimethylacetamide and dimethyl sulfoxide. These solvents give a range of basicity from acetone to DMSO, as reflected in the range of pK_{BH}^{+} values from -7.2 for acetone to +0.9 for DMSO. These solvents were also chosen on the basis of their ability to dissolve the tin compounds.

Since the method for the calculation of the $J(^{119}Sn\text{-}C\text{-}C\text{-}H_A)$ coupling constants using equations 4 and 5 requires the accurate assignment of the H_A resonance peak, detailed analyses of the nmr spectra by a computer method were carried out in order to verify the accuracy of the

proposed method of assignment as described in Section III. The detailed analyses were made using tris-parachlorophenyltin chloride dissolved in CCl_4, acetone and DMSO, respectively, and the experimental assignment of the H_A and H_B resonances were compared with that in the spectrum calculated by computer. Also, the computer-analyzed spectra yielded the coupling constants of the protons on the phenyl ring, and from these a correlation of the coupling constants with the basicity of the solvent could be obtained.

In the case of tris-paramethylphenyltin chloride, proton resonances of the phenyl ring were assigned with the aid of decoupling experiments. Irradiation of the methyl group eliminates any coupling of the methyl group with the H_B protons of the phenyl ring. Hence the H_B protons become sharper upon irradiation. A more detailed discussion on the decoupling experiments is given in the Experimental Section. It was assumed that the other parasubstituted compounds would have analogous spectra. Therefore, the assignments of these spectra were made according to the results obtained for the case of tris-paramethylphenyltin chloride.

Infrared studies were done to provide insight into the configurations of the compounds. There are three absorptions

of interest in the infrared spectra: the tin-chlorine stretching vibration, the symmetric tin-phenyl stretching mode and the asymmetric tin-phenyl stretching mode. The configuration of the adducts can be deduced from the presence or absence of the tin-phenyl symmetric vibration, while the tin-chlorine and tin-phenyl asymmetric modes will give an insight into the bonding of the tin compounds. An increase in the wavenumber of the tin-phenyl asymmetric mode would indicate an increase in s character of the tin hybrid in the tin-phenyl bond while a decrease in the tin-chlorine vibration would indicate a lowering of the tin-chlorine force constant as well as a decrease in s character of the tin-chlorine bond as compared to the uncomplexed form. Since the vibrations of interest absorb below 400 cm^{-1}, studies had to be carried out at long wavelengths.

In deducing molecular configurations, Raman spectra can be used to complement infrared studies. If the trigonal bipyramid configuration is assumed, then the tin-phenyl symmetric mode would be active in the Raman spectra but not in the infrared spectra. Also absorption frequencies at long wavelengths can be more readily observed in the Raman spectrum.

Raman spectra of tris-parachlorophenyltin chloride using benzene, acetone and DMAC solvents were obtained.

However, the Raman spectra obtained in this work could not be accurately interpreted. This is probably due to a combination of the low solubility of the compound in the pure Lewis bases as well as to faulty performance of the apparatus. The noise to signal ratio was excessively high and bands could not be assigned with certainty.

V. Experimental

Solvents.

Fisher Spectroanalyzed Grade benzene, chloroform, carbon tetrachloride, diethyl ether and acetone were used without further purification. Spectroquality Grade dimethyl sulfoxide (DMSO) and N,N-dimethylacetamide (DMAC) were obtained from Matheson, Coleman and Bell Co. and used without further purification. The solvents contained no impurities which could be detected in their nmr spectra. Except for acetone and diethyl ether, the solvents were stored over Linde 4A molecular sieve.

Reagents.

Triphenyltin chloride, obtained from the Metal and Thermit Co., was recrystallized twice from dried ligroin. M.p. 104.5° (Lit.[39] 106°).

Reagent grade parachlorobromobenzene, parabromotoluene, paramethoxybromobenzene, magnesium turnings and anhydrous tin(IV) chloride were used in the preparation of the tetraaryltin compounds and the tris-parasubstituted phenyltin chlorides. These starting materials were used without further purification.

Syntheses of Compounds.

Tetrakis-parachlorophenyltin, tetrakis-paramethylphenyltin and tetrakis-paramethoxyphenyltin were obtained by a Grignard procedure according to Krause and Weinberg.[40] The following is a typical procedure:

The Grignard solution was prepared in a three-necked flask from 36.5 g (1.5 moles) of magnesium and 187 g (1.5 moles) of parachlorobromobenzene in 400 ml of anhydrous ether. The reaction was initiated with iodine and lasted 2.5 hours. The mixture was then refluxed for another 30 minutes.

A solution of 21.3 ml (47.5 g; 0.182 moles; 70% of the theoretical amount) of tin(IV) chloride in 150 ml of dry benzene was added in the course of 30 minutes with stirring and cooling. The reaction mixture was refluxed for an additional hour. The mixture was then cooled and the excess Grignard reagent was decomposed by pouring the reaction mixture into 600 ml of a 10% HCl-ice-water mixture. The two layers were separated and the aqueous layer was extracted with ether. The combined ether layers were filtered and dried over molecular sieve overnight. Evaporation of the ether-benzene solution yielded crude tetrakis-parachlorophenyltin. Recrystallization from 150 ml of dry

benzene yielded 49 g of the pure compound. M.p. 195-196° (Lit.[1] 194.5-195°).

The melting points of the other tetraaryltins synthesized are as follows: Tetrakis-paramethylphenyltin 237.0-237.5° (Lit.[41] 238°); tetrakis-paramethoxyphenyltin 133-134° (Lit.[42] 134.8°).

Tris-parachlorophenyltin chloride and tris-paramethylphenyltin chloride were obtained by a disproportionation method. A typical procedure is the following:

A mixture of 8.57 g (15 mmoles) of tetrakis-parachlorophenyltin and 1.25 g (4.8 mmoles) of anhydrous tin(IV) chloride was heated at 205-215° for 3 hours and subsequently at 180-190° for another 3 hours. Recrystallization of the reaction product from 95% ethanol yielded 4.0 g of the pure tris-parachlorophenyltin chloride. M.p. 110-111° (Lit.[40] 110-111°). Anal: Calculated: C, 44.23; H, 2.47; Cl, 29.01%. Found: C, 44.33; H, 2.46; Cl, 28.83%.

The tris-paramethylphenyltin chloride was prepared from the tetrakis-paramethylphenyltin. M.p. 99.0° (Lit.[39] 97.5-98.0°). Anal: Calculated: C, 58.99; H, 4.95; Cl,8.29%. Found: C, 59.03; H, 5.18; Cl,7.96%.

Elemental Analyses.

The elemental analyses were done by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Infrared Spectra.

Infrared spectra in the 200-400 cm^{-1} region were obtained through the use of a Perkin-Elmer Model 225 spectrophotometer. Matched cesium iodide cells, with a path length of 0.1 mm, were used to obtain the solution spectra. In order to avoid absorption due to water vapor, the instrument was maintained under an atmosphere of dry nitrogen. The region of interest was expanded and the frequencies were measured to an accuracy of ± 0.5 cm^{-1}.

NMR Spectra.

The nmr spectra for the compounds studied, $(p\text{-}XC_6H_4)_{4-n}SnCl_n$ (where n = 0 or 1 and X = H-, Cl-, and CH_3O-), were measured on either the Varian Model A-60 or Model HA-100 spectrometer using CCl_4, $CDCl_3$, or one of the pure Lewis bases as solvent. The spectra were traced both ways using a sweep width of 500 cps and were found to be reproducible to ± 0.5 cps. The spectra were calibrated using TMS as an internal standard.

The $J(^{119}Sn\text{-}C\text{-}C\text{-}H_A)$ coupling constants were determined from spectra that were traced both ways using a sweep width

of 100 cps and were found to be reproducible to $\pm$0.2 cps. The expanded spectra were again calibrated using TMS as the internal standard.

The concentrations of samples for the nmr spectra are reported in Table III, and the integrated ratios for the nmr spectra of the methyl and methoxy compounds are listed in Table IV.

Interpretation of the NMR Spectra.

Depending on the solvent employed, the nmr spectra of the aryltin compounds studied contain one or two multiplets with two weak doublets on one or both sides of the observed multiplets.

Tris-parachlorophenyltin chloride in acetone yields two multiplets with a weak doublet on the downfield side, as illustrated in Figure III, while dissolution in CCl_4 yields two multiplets with weak doublets on either side, as shown in Figure VI. The only exception to this observation is the tetrakis-parachlorophenyltin compound when dissolved in CCl_4. In this case a singlet is observed with two sets of satellites on either side, as shown in Figure VII. A spectrum with a higher amplifier gain is shown in Figure VIII.

Table III. Concentrations of Samples in w/w for the NMR Spectra.

Compounds	Coordinating and Noncoordinating Solvents					
	CCl_4	$CDCl_3$	Acetone	Ether	DMSO	DMAC
$(C_6H_5)_3SnCl$	---	---	21%	---	13%	---
$(p\text{-}ClC_6H_4)_3SnCl$	24%	---	40%	20%	18%	16%
$(p\text{-}CH_3C_6H_4)_3SnCl$	24%	---	29%	20%	15%	28%
$(p\text{-}ClC_6H_4)_4Sn$	16%	---	---	---	---	---
$(p\text{-}CH_3C_6H_4)_4Sn$	17%	15%	---	---	---	---
$(p\text{-}CH_3OC_6H_4)_4Sn$	15%	---	---	---	---	---

Table IV. Integrated Ratio of Peak Heights of the Methyl and Methoxy Compounds.

Compounds.	Ratio C_6H_5/CH_3 Found (Calc.)
$(p\text{-}CH_3C_6H_4)_3SnCl$	1.34 (1.33)
$(p\text{-}CH_3C_6H_4)_4Sn$	1.32 (1.33)
$(p\text{-}CH_3OC_6H_4)_4Sn$	1.32 (1.33)

A spin decoupling experiment on tris-paramethylphenyltin chloride can be used as an aid in assigning the multiplets in the spectra. The methyl group on the phenyl ring can couple with the protons ortho to it, H_B, thereby causing broadening of this multiplet. Hence irradiation of the methyl group should decouple it from the ring and the ortho multiplet should become sharper in appearance. The decoupling experiments were done on a Varian Model HA-100 spectrometer using a third radio frequency field as the irradiating source. The spectra from the decoupling experiments are given in Figure IX. Both downfield, A, B, A' and B', and upfield, C, D, C' and D', sweeps have been carried out in the normal A', B', C' and D' and irradiated A, B, C and D modes. Comparisons should be made on the signals obtained in the same sweep direction. In other words, A and B should be compared with A' and B',

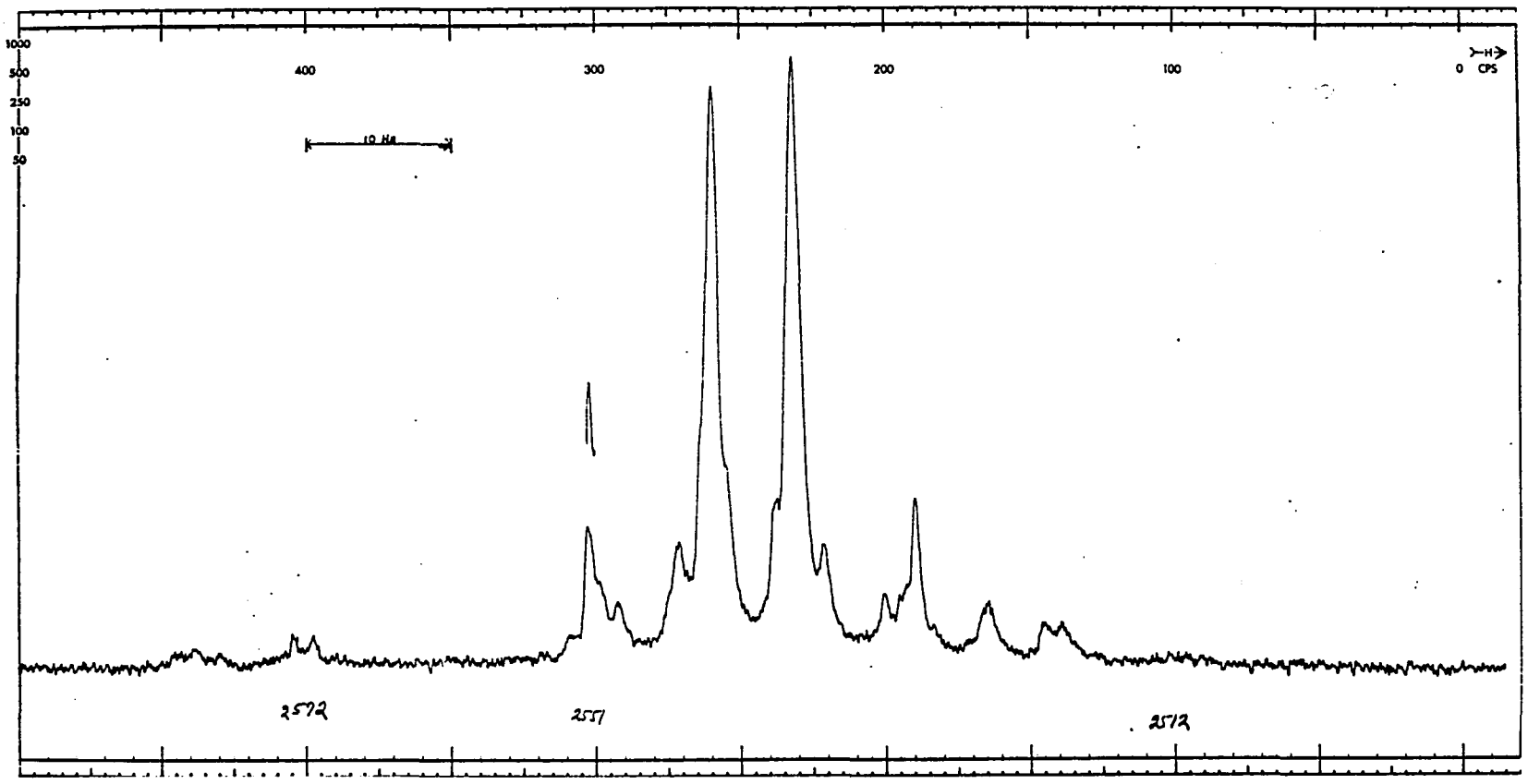


Figure VI. The ^{1}H Resonance Spectrum at 100 Mc sec^{-1} of Tris-parachlorophenyltin Chloride in Carbon Tetrachloride.

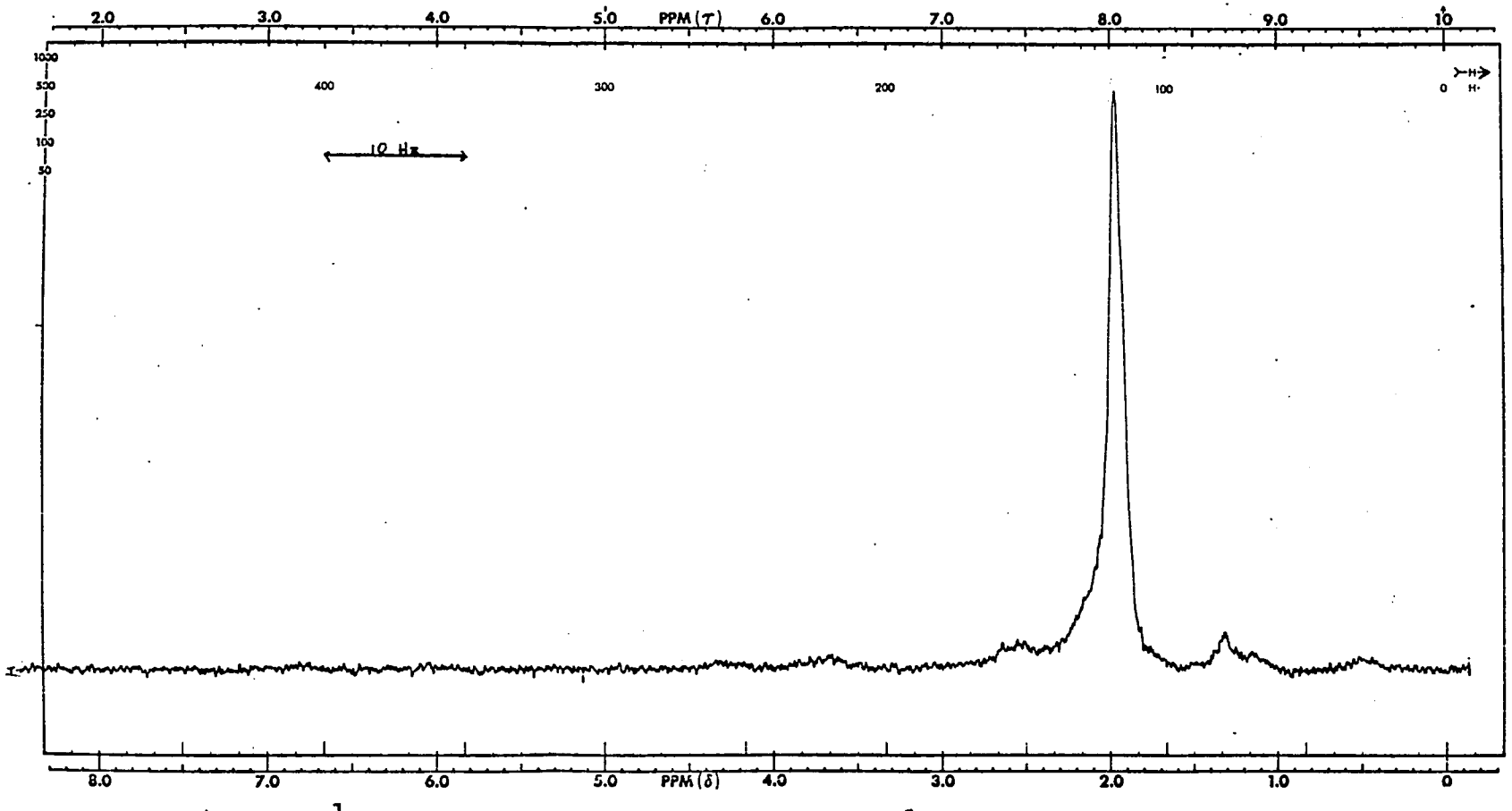


Figure VII. The ^{1}H Resonance Spectrum at 60 Mc sec^{-1} of Tetrakis-parachlorophenyltin in Carbon Tetrachloride at Moderate Amplifier Gain.

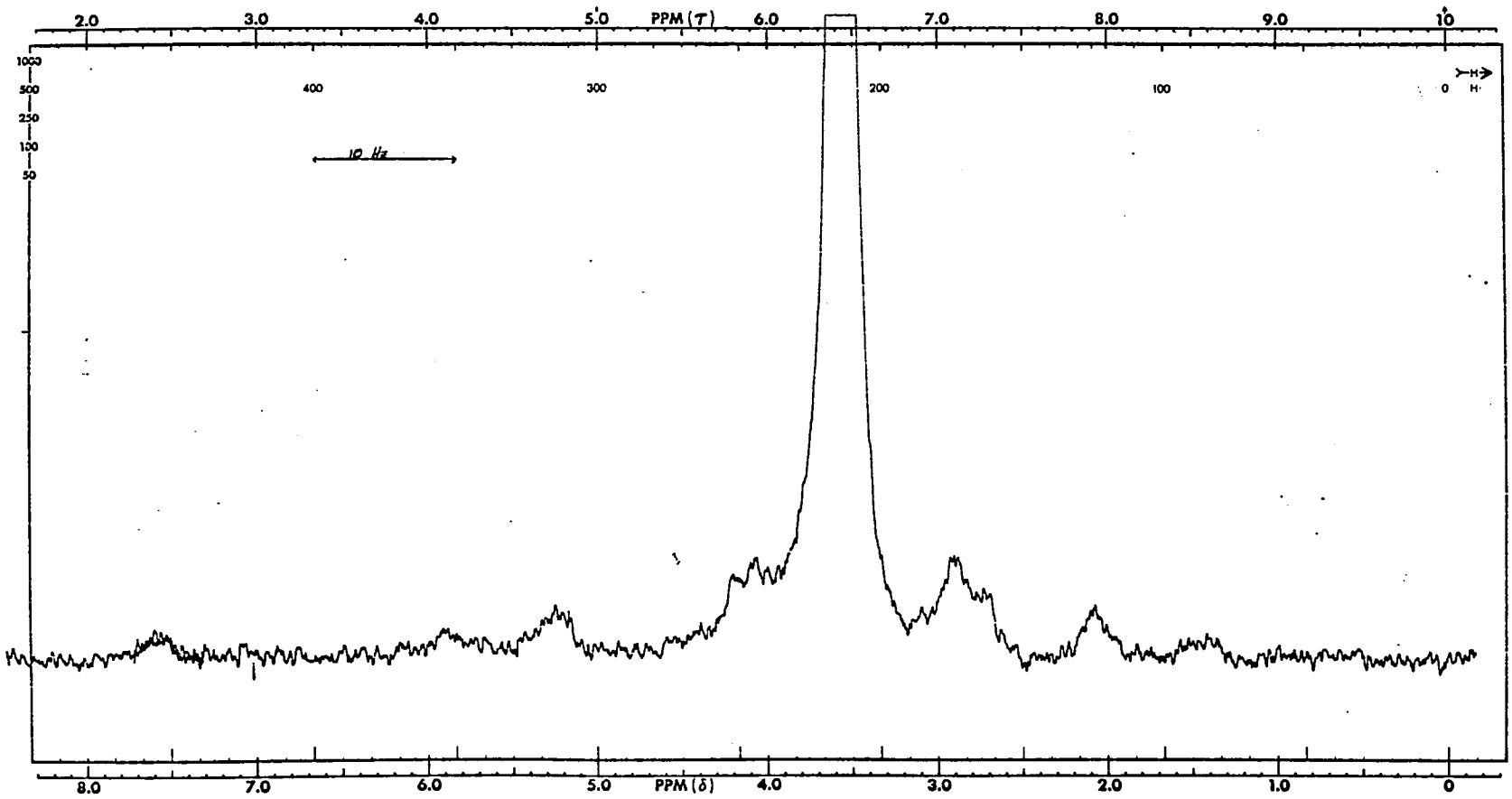


Figure VIII. The ^{1}H Resonance Spectrum at 60 Mc sec^{-1} of Tetrakis-parachlorophenyltin in Carbon Tetrachloride at High Amplifier Gain.

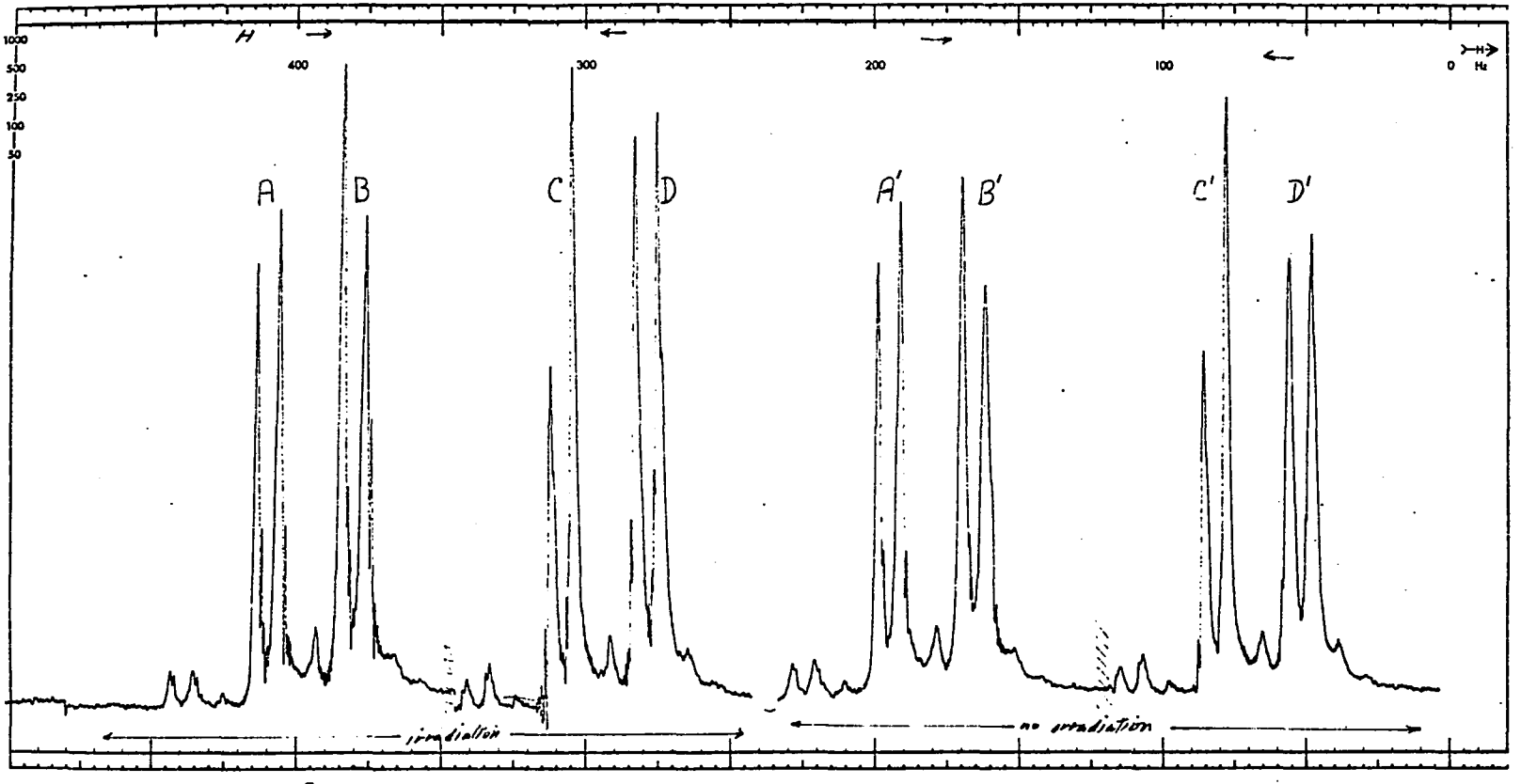


Figure IX. The ^{1}H Resonance Spectra at 100 Mc sec^{-1} of Tris-paramethyltin Chloride with and without Irradiation of the Methyl Group.

while C and D should be compared with C' and D' respectively. Figure IX confirms that B and D were observed to be sharper in comparison to B' and D'. Therefore, this multiplet occurring upfield, B or D, was assigned as the protons ortho to the methyl groups. For future reference, the upfield multiplet will be labeled as the H_B protons while the downfield multiplet will be designated as the H_A protons.

The weak doublets observed on the downfield side of the downfield multiplet are considered to be the satellites originating from the coupling of the ^{117}Sn and ^{119}Sn atoms with the H_A protons of the phenyl ring. In addition, the H_B protons can couple with the H_A protons, thereby giving two sets of doublets instead of one, as expected. This has been discussed in Section III.

The assignment of the weak doublets originating from the coupling of the tin atom with the H_A proton is confirmed by the nmr spectra of tris-parachlorophenyltin chloride. If the observed satellites result from coupling of the tin atom with the adjacent protons on the ring, H_A, then the magnitude of these satellites will be unaffected by changing the magnetic field strength. The expanded nmr spectra of tris-parachlorophenyltin chloride in CCl_4 show that the

separation of these satellites was the same whether the Model HA-100 or Model A-60 instrument was employed, as is shown in Figures VI and X, respectively. Therefore, the weak doublets can be unambiguously described as resulting from the coupling between the ^{117}Sn and ^{119}Sn with the H_A protons.

The ^{117}Sn and ^{119}Sn coupling constants were obtained in the following manner: (1) If both halves of the satellites were observed, then the ^{117}Sn and ^{119}Sn coupling constants were obtained by measuring the distance between the two satellites. (2) If only one-half of the satellites was observed, then the ^{117}Sn and ^{119}Sn coupling constants were calculated according to the procedure described in Section III.

Systems that fall into the first category are tetrakis-paramethoxyphenyltin in CCl_4, and tris-parachlorophenyltin chloride in $CDCl_3$ or ether. The systems that were observed to exhibit only one-half of the satellites are tetrakis-paramethylphenyltin chloride in acetone, DMAC or DMSO; tris-paramethylphenyltin chloride in CCl_4, acetone, ether, DMAC or DMSO; and triphenyltin chloride in CCl_4 or acetone. Coupling of the tin atoms with the H_B proton is also expected. However, the magnitude of this coupling is too small to be observed.

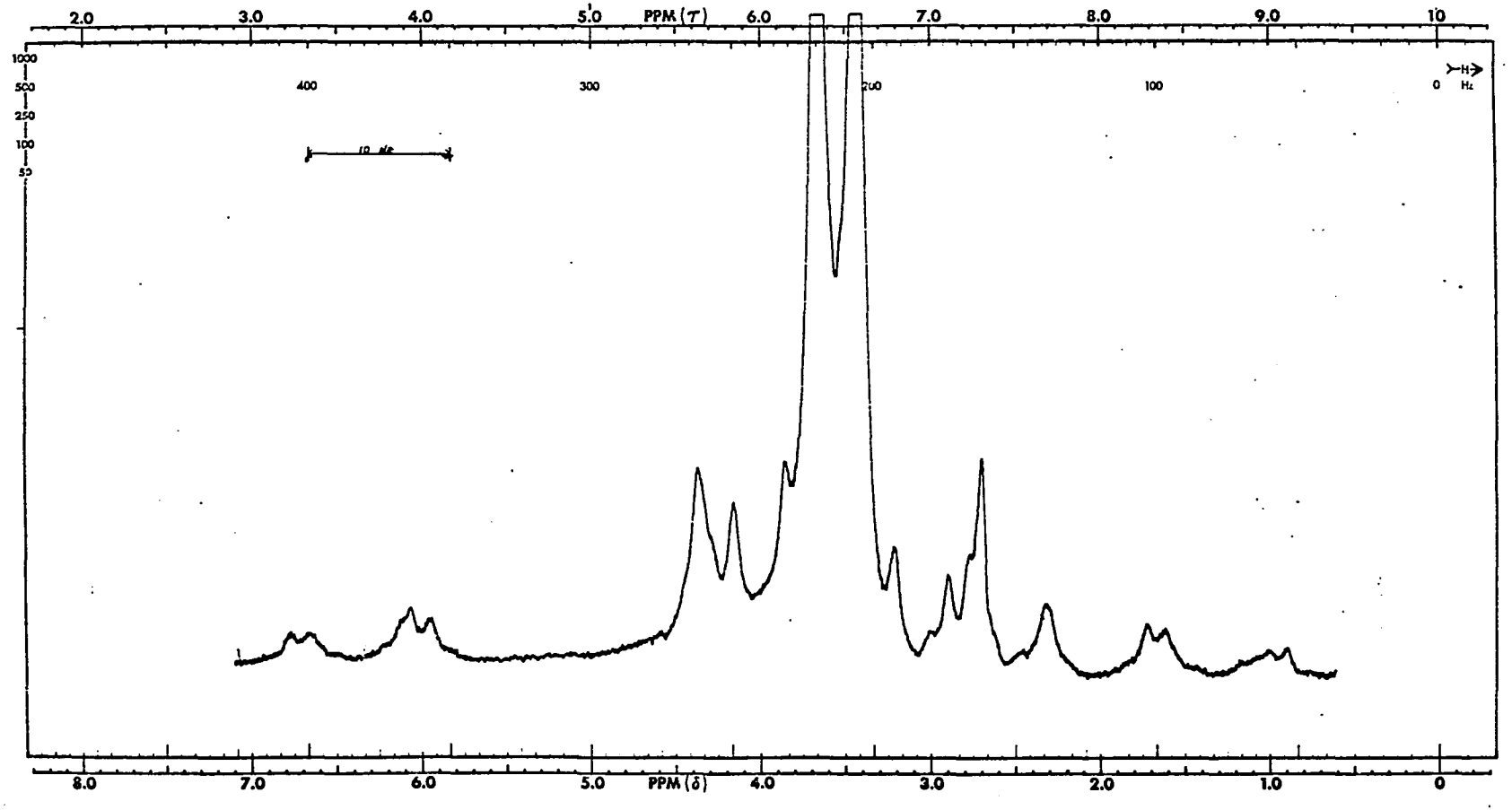


Figure X. The ^{1}H Resonance Spectrum at 60 Mc sec^{-1} of Tris-parachlorophenyltin Chloride in Carbon Tetrachloride.

VI. Results and Discussion

The results of this investigation provide further evidence that $\underline{d}\pi$-$\underline{p}\pi$ bonding exists between the empty $\underline{d}$ orbitals of the tin atom and the pi electrons of the phenyl ring in aryltin compounds. The data also indicate that while substitution on the tin atom has a large effect on the tin phenyl bond in aryltin compounds, Ar_nSnCl_{4-n}, where n = 3 or 4, substitution on the aromatic ring at the para position has little or no effect on the tin phenyl bond.

NMR Analyses.

It has already been established by means of decoupling experiments that the H_A protons are located downfield from the H_B protons. Detailed analyses as outlined in Section III were done on tris-parachlorophenyltin chloride using carbon tetrachloride, acetone and dimethyl sulfoxide as solvents in order to confirm that the method used for calculating the resonance peaks of the H_A and H_B protons was accurate since the accuracy of the $J(^{119}Sn\text{-}C\text{-}C\text{-}H_A)$ coupling constants depends on the accuracy of the assignment of the H_A protons. In addition, these analyses provide some evidence for $\underline{d}\pi$-$\underline{p}\pi$ bonding. Tabulated in Table V are the calculated values of the chemical shifts and coupling

Table V. Calculated and Observed Chemical Shifts and the Calculated Coupling Constants of Tris-parachlorophenyltin Chloride in CCl_4, Acetone and DMSO Solutions.

	CCl_4[a]	Acetone[a]	DMSO[b]
1	100.051 ± 0.032	99.801 ± 0.020	99.819 ± 0.025
2	100.051 ± 0.032	99.801 ± 0.020	99.819 + 0.025
3	111.302 ± 0.032	135.223 ± 0.020	120.923 ± 0.025
4	111.302 ± 0.032	135.223 ± 0.020	120.923 ± 0.025
$J_{1,2}$	0.464 ± 0.056	1.573 ± 0.035	1.627 ± 0.075
$J_{1,3}$	0.537 ± 0.036	0.426 ± 0.031	0.358 ± 0.035
$J_{1,4}$	7.996 ± 0.040	8.052 ± 0.030	8.036 ± 0.036
$J_{2,3}$	7.996 ± 0.040	8.052 ± 0.030	8.036 ± 0.036
$J_{2,4}$	0.537 ± 0.036	0.426 ± 0.031	0.358 ± 0.035
$J_{3,4}$	3.146 ± 0.041	2.345 ± 0.033	2.106 ± 0.070
$H_B - H_A$[c]	11.25	35.42	21.10
$H_B - H_A$[d]	11.25	35.42	20.87

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a Analysis done on 100 Hz instrument.

b Analysis done on 60 Hz instrument.

c Calculated values from nmr analyses.

d Observed values from nmr spectra.

constants for $(p\text{-}ClC_6H_4)_3SnCl$ in the three solvents. Also included is the difference of the chemical shifts of the H_A and H_B protons - those calculated from the nmr analyses as well as those observed from the nmr spectra. A comparison of the calculated and observed $H_B - H_A$ values indicates that the method of calculation is a valid way of determining the absorption peaks due to the H_A and H_B protons. The complete observed and calculated ^1H spectra of tris-parachlorophenyltin chloride using the three different solvents are given in Appendix B.

In the computed spectra of $(p\text{-}ClC_6H_4)_3SnCl$ tabulated in Table V, the H_A and H_B protons are labeled 1,2 and 3,4 respectively with proton 2 adjacent to proton 3 and proton 1 adjacent to proton 4. Examination of Table V reveals that in a solution of acetone or dimethyl sulfoxide the $J_{3,4}$ coupling constants decrease relative to those from a carbon tetrachloride solution. This indicates that as a result of coordination there is less electron interaction between the 3,4 positions. It is also seen that the $J_{1,2}$ coupling constants increase when a coordinating solvent is employed. Although the interpretation of coupling constants is not a simple procedure, the computed results may be interpreted as an indication of a shift of electrons toward the tin atom as the base strength increases, which is

consistent with the concept that $d\pi$-$p\pi$ bonding exists in these cases.

The chemical shifts and coupling constants without regard to sign for the tetraaryltin compounds in non-donating solvents are summarized in Table VI along with the Brown σ^+ values for the respective substituents.

In the compounds studied, the J_{AB} coupling constants range from 7.2 to 8.7 cps, which is within the values, 7.0 to 9.2 cps, characteristic of coupling constants for adjacent hydrogens in an aromatic ring. Except for the methoxy substituent, the J_{AB} values for various substituents are within experimental error of each other. The large coupling constant observed for the methoxy case can be explained by the fact that the methoxy group is a better electron donor than the other substituents.

With the exception of the fluoro compound, as the substituent X decreases in electron donating ability (a more positive σ^+ value) the differences of the chemical shifts, $H_B - H_A$, become smaller as would be expected.

Also the H_A and H_B values show that because of the resonance effect, the substituent X has a greater influence on the chemical shifts of the H_B protons than on those of the H_A protons. The trend shown in Table VI suggests that

Table VI. Chemical Shifts and Coupling Constants for Parasubstituted Tetraaryltin Compounds.

Substituent X	σ^+	H_B[a]	H_A[a]	$H_B - H_A$	J_{AB}[b]	$J(^{119}Sn\text{-}C\text{-}C\text{-}H_A)$[b]	$J(^{117}Sn\text{-}C\text{-}C\text{-}H_A)$[b]
CH_3O	-0.78	+0.45	-0.12	+0.57	8.7	46.1	44.2
CH_3	-0.31	+0.12	-0.16	+0.28	7.2	46.0	44.4
F[c]	-0.07	+0.16	-0.22	+0.37	7.63	----	----
H[c]	0.00	-0.16	-0.38	+0.22	----	----	----
Cl	+0.11	-0.11	-0.11	0.00	7.6	47.0	44.6

a The chemical shifts are measured relative to benzene in ppm. A negative value indicates a proton less shielded than benzene. The accuracy of the chemical shifts are within $\pm$0.01 ppm.

b The accuracy of the coupling constants is within $\pm$0.2 cps.

c Ref. 10.

a substituent having a Brown σ^+ value more positive than 0.11 would lead to a negative $H_B - H_A$ term which would indicate a switching of the resonance peaks of the H_A and H_B protons. Indeed, in bromobenzene and nitrobenzene, which have Brown σ^+ values of +0.15 and +0.79 respectively, the H_B protons are located downfield from the H_A protons.[43]

Also the $J(^{119}Sn\text{-}C\text{-}C\text{-}H_A)$ coupling constants for the compounds studied are independent of the substituent X, indicating that the substituent X on the aromatic ring in the para position has little or no influence on the tin phenyl bond.

Evidence of $\underline{d}\pi\text{-}\underline{p}\pi$ bonding in tetraaryltin compounds can be found in the comparison of the J_{AB} coupling constants as well as in the chemical shifts of the H_A protons of $(\underline{p}\text{-}ClC_6H_4)_4Sn$ and $(\underline{p}\text{-}CH_3C_6H_4)Sn$. The observed coupling constants are 7.6 and 7.2 cps respectively. Cox[44] has suggested that the short range coupling constants, J_{AB}, are particularly sensitive to changes in the bonding orbitals. However, these changes in σ orbitals may be either the result of inductive effects or the result of changes in the bond order of the pi electrons. Since the inductive effect of a chlorine atom outweighs its resonance effect, it is expected that the chlorine atom will withdraw electrons from

the phenyl ring. Therefore, the J_{AB} coupling constants for the chloro compound is expected to be smaller in comparison to its methyl analog due to the inductive effect. However, this was found not to be the case. A reasonable explanation of this observation would be to assume that the difference of the J_{AB} coupling constants for these compounds is a reflection of the difference in electron density of the pi orbitals.

A comparison of the chemical shifts of the H_A protons for $(\underline{p}\text{-}ClC_6H_4)_4Sn$ and $(\underline{p}\text{-}CH_3C_6H_4)_4Sn$ indicates that the methyl analog is less shielded (-0.16 ppm for CH_3- and -0.11 ppm for Cl-). Using the above criterion of inductive effects, it is expected that the reverse should be true. Thus, this is another indication that there is some $\underline{d}\pi\text{-}\underline{p}\pi$ bonding between the phenyl pi electron and the empty $\underline{d}$ orbitals of the tin atom.

The criterion of Wu and Bailey[32] can also be used as a test for $\underline{d}\pi\text{-}\underline{p}\pi$ bonding since it is observed that increasing negative values for chemical shifts of protons indicate decreasing pi electron densities in the aromatic ring as compared to benzene. Table VI reveals that all the H_A values are negative and the H_B values are negative with the exception of the cases where the substituents are

CH_3O-, F- and CH_3-. The use of the H_A chemical shift as a test for $\underline{d}\pi$-$\underline{p}\pi$ bonding is perhaps the better choice, since the H_B protons are affected to a greater extent by the substituent X. The positive values observed for the H_B protons for the CH_3O-, F- and CH_3- substituents can be rationalized by assuming that these substituents release more electron density at the adjacent position due to resonance and inductive effects than the withdrawal of pi electrons due to $\underline{d}\pi$-$\underline{p}\pi$ bonding.

In Table VII the chemical shifts and coupling constants of the Ar_4Sn and Ar_3SnCl compounds run in inert solvents are compared. Within experimental error, both the H_A and H_B protons are less shielded for the Ar_3SnCl compounds. Thus, the substitution of a chloro group for an aryl group tends to withdraw electrons from the phenyl ring toward the tin atom. It is also observed that both the J_{AB} and $J(^{119}Sn\text{-}C\text{-}C\text{-}H_A)$ coupling constants are larger for the Ar_3SnCl compounds. This indicates that there is more electron interaction between the adjacent protons on the phenyl ring as well as the tin atom and the H_A protons. Both of these results lead to the conclusion that there is more $\underline{d}\pi$-$\underline{p}\pi$ bonding in the Ar_3SnCl compounds than in the Ar_4Sn compounds. Therefore, while substitution of the phenyl

Table VII. A Comparison of Coupling Constants and Chemical Shifts between Ar_4Sn and Ar_3SnCl in an Inert Solvent.

	$(p\text{-}ClC_6H_4)_nSnCl_{4-n}$		$(C_6H_5)_nSnCl_{4-n}$		$(p\text{-}CH_3C_6H_4)_nSnCl_{4-n}$	
n	4	3	4	3	4	3
$J(^{119}Sn\text{-}C\text{-}C\text{-}H_A)^a$	47.0	61.6	----	61.7	46.0	61.5
J_{AB}^a	7.6	8.4	----	----	7.2	8.0
H_A^b	-0.11	-0.21	-0.38	-0.44	-0.16	-0.19
H_B^b	-0.11	-0.09	-0.16	-0.22	+0.12	+0.14

a The accuracy of the coupling constants is within $\pm$ 0.2 cps.

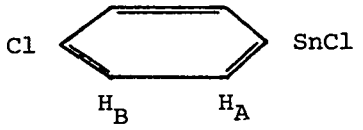
b The accuracy of the chemical shifts is within $\pm$ 0.01 ppm.

ring has little or no effect on the tin phenyl bond, substitution on the tin atom tends to enhance $d\pi$-$p\pi$ bonding.

In Tables VIII through X are listed the chemical shifts and coupling constants for the triaryltin chlorides in various solvents. The solvent carbon tetrachloride is noncoordinating and the others are listed in order of increasing donor strength. It should be noted that the base strengths of the solvents have no influence on the J_{AB} coupling constants. The values of these coupling constants are also within the characteristic values observed for any paradisubstituted benzene.

Tables VIII through X show that the H_A and H_B protons for the tris-parasubstituted phenyltin chlorides are more deshielded as the strength of the Lewis base increases. The donor molecule acts mainly as an electron donor, therefore, as the base strength increases, the H_A and H_B protons, especially the H_A protons, should be shielded rather than deshielded. The observed deshielding can be rationalized if it is assumed that $d\pi$-$p\pi$ bonding exists between the phenyl ring and the tin atom. Assuming $d\pi$-$p\pi$ bonding, then the removal of pi electron density from the phenyl ring toward the tin atom would tend to deshield the protons on the ring, especially the H_A protons.

Table VIII. Chemical Shifts and Coupling Constants for Tris-parachlorophenyltin Chloride.



Solvents	H_B[a]	ΔH_B[b]	H_A[a]	ΔH_A[b]	$H_B - H_A$	J_{AB}[c]	$J(^{119}Sn\text{-}C\text{-}C\text{-}H_A)$[c]	$J(^{117}Sn\text{-}C\text{-}C\text{-}H_A)$[c]
CCl_4	-0.09	-----	-0.21	-----	+0.12	8.4	61.6	59.0
Ether	-0.11	+0.02	-0.31	+0.10	+0.20	8.4	61.8	58.6
Acetone	-0.19	+0.10	-0.54	+0.33	+0.35	8.4	63.4	60.7
DMSO	-0.27	+0.18	-0.62	+0.41	+0.35	8.2	66.7	63.5
DMAC	-0.26	+0.17	-0.67	+0.46	+0.41	8.4	66.6	63.8

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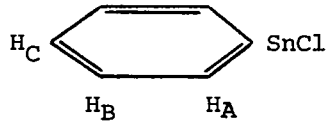
a The chemical shifts are measured relative to benzene in ppm. A negative value indicates a proton less shielded than benzene. The accuracy of the chemical shifts is within $\pm$0.01 ppm.

b ΔH_i is the chemical shift difference between CCl_4 and the Lewis base solvents.

c The accuracy of the coupling constants is within $\pm$0.2 cps.

Table IX. Chemical Shifts and Coupling Constants for Triphenyltin Chloride.



Solvents	$H_{B,C}$[a]	$\Delta H_{B,C}$[b]	H_A[a]	ΔH_A[b]	$H_{B,C} - H_A$	$J(^{119}Sn\text{-}C\text{-}C\text{-}H_A)$[c]	$J(^{117}Sn\text{-}C\text{-}C\text{-}H_A)$[c]
Neat[d]	-0.22	----	-0.44	----	+0.22	61.7	59.0
Acetone	-0.18	-0.04	-0.54	+0.10	+0.36	64.0	62.5
DMSO	-0.21	-0.01	-0.60	+0.16	+0.39	67.5	65.0

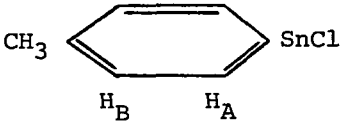
a The chemical shifts are measured relative to benzene in ppm. A negative value indicates a proton less shielded than benzene. The accuracy of the chemical shifts is within $\pm$0.01 ppm.

b ΔH_i is the chemical shift difference between CCl_4 and the Lewis base solvents.

c The accuracy of the coupling constants is within $\pm$0.2 cps.

d Ref. 20.

Table X. Chemical Shifts and Coupling Constants for Tris-paramethylphenyltin Chloride.



Solvents	H_B[a]	ΔH_B[b]	H_A[a]	ΔH_A[b]	$H_B - H_A$	J_{AB}[c]	$J(^{119}Sn\text{-}C\text{-}C\text{-}H_A)$[c]	$J(^{117}Sn\text{-}C\text{-}C\text{-}H_A)$[c]
CCl_4	+0.14	----	-0.19	----	+0.33	8.0	61.5	58.7
Ether	+0.07	+0.07	-0.30	+0.11	+0.37	8.0	60.5	57.9
Acetone	+0.01	+0.13	-0.36	+0.17	+0.37	8.0	62.2	59.6
DMSO	+0.03	+0.11	-0.45	+0.26	+0.48	8.0	66.4	63.4
DMAC	+0.04	+0.10	-0.53	+0.34	+0.57	8.0	66.0	63.2

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a The chemical shifts are measured relative to benzene in ppm. A negative value indicates a proton less shielded than benzene. The accuracy of the chemical shifts is within $\pm$0.01 ppm.

b ΔH_i is the chemical shift difference between CCl_4 and the Lewis base solvents.

c The accuracy of the coupling constants is within $\pm$0.2 cps.

The data in Tables VIII through X indicate that as the donor strength of the solvent increases, the H_A and H_B values become more negative. Again employing the criterion of Wu and Bailey,[32] the data can be interpreted as a delocalization of pi electrons toward the tin atom as the base strength increases. This type of delocalization would be maximized in a molecule having a trigonal bipyramidal structure with three coplanar phenyl rings.

Relative Acid Strengths.

Tables VIII through X reveal that the differences of the chemical shifts, $H_B - H_A$, increase as the strength of the Lewis base increases. However, it is noted that in the case of $(\underline{p}\text{-}CH_3C_6H_4)_3SnCl$ there is not a significant difference until dimethyl sulfoxide or N,N-dimethylacetamide were used as solvents. This difference was observable even when a weak donor such as acetone was used in the cases of $(C_6H_5)_3SnCl$ and $(\underline{p}\text{-}ClC_6H_4)_3SnCl$. The difference in the chemical shifts of the H_A and H_B protons indicates changes in the electron density at these positions. Thus, for a given base the magnitude of the difference between $H_B - H_A$ in the base as compared to the $H_B - H_A$ value in carbon tetrachloride can be used as a measure of the acid strength of the tin compound since a large difference indicates a

large change in electron density which in turn reflects the coordinating ability of the compounds. For example, the difference between $H_B - H_A$ in dimethyl sulfoxide as compared to the $H_B - H_A$ values in carbon tetrachloride is 0.23, 0.17 and 0.15 ppm for $(\underline{p}\text{-}ClC_6H_4)_3SnCl$, $(C_6H_5)_3SnCl$ and $(\underline{p}\text{-}CH_3C_6H_4)_3SnCl$ respectively. Using the criterion of $H_B - H_A$ as a measure of acid strength then the order of acidity for the compounds studied would be the following:

$$(\underline{p}\text{-}ClC_6H_4)_3SnCl > (C_6H_5)_3SnCl > (\underline{p}\text{-}CH_3C_6H_4)_3SnCl.$$

A similar order of acid strength was observed for the coordination of 1,2-diamino-4-nitrobenzene with aryltin trichlorides.[45]

Relative Donor Preference.

In Table XI are listed the dipole moments of the solvents and their relative basicities in aqueous solution, as indicated by their pK_{BH}^+ values.

Table XI. Basicity and Dipole Moments of the Lewis Bases.[46]

Lewis Base	pK_{BH}^+	Dipole Moment
Acetone	-7.2	2.8
Diethyl Ether	-3.6	1.1
N,N-dimethylacetamide	+0.1	3.8
Dimethyl Sulfoxide	+0.9	3.9

There seems to be a correlation between the polarity as well as the basicity of the solvent with the $J(^{119}Sn\text{-}C\text{-}C\text{-}H_A)$ coupling constants for the tris-parasubstituted phenyltin chlorides listed in Tables VIII through X. Within experimental error, the $J(^{119}Sn\text{-}C\text{-}C\text{-}H_A)$ coupling constants are also observed to increase as the basicity increases in all cases with the exception of diethyl ether. The data indicate that although ether is a more basic solvent, $pK_{BH^+} = -3.6$, than acetone, $pK_{BH^+} = -7.2$, acetone is a better complexing agent. However, it must be recognized that the pK_{BH^+} values for the bases were obtained in aqueous media and may not be applicable to the neat compounds. Therefore, any correlation of the basicities observed here with those observed in aqueous solution can only be tentative. In addition, the more bulky nature of Lewis acids such as tris-parasubstituted phenyltin chlorides, introduces the possibility of steric hindrance to complex formation. Therefore, a reasonable explanation is that the diethyl ether molecule is prevented from coordination due to steric hindrance. This is in agreement with the results of Fratiello who showed by construction of molecular models that the BF_3·acetone complex encounters much less steric hindrance than the BF_3·diethyl ether

complex.[46] Thus the coordination of tris-parasubstituted phenyltin chlorides is dependent on the basicity, polarity and steric effects of the complexing agent and the order of ligand preference for the tris-parasubstituted phenyltin chlorides studied in this work is

$$(CH_3CH_2)_2O < (CH_3)_2CO < (CH_3)_2SO \approx CH_3CON(CH_3)_2.$$

A similar order was observed for the cases of the trimethyltin chlorides.[5]

The data of Tables VIII through X also indicate that the change in the $J(^{119}Sn\text{-}C\text{-}C\text{-}H_A)$ coupling constants is smaller when going from a nondonating solvent such as carbon tetrachloride to a strong Lewis base such as dimethyl sulfoxide when compared to the $J(^{119}Sn\text{-}CH_3)$ coupling constants in the trimethyltin chloride adducts. The change is 11.6 cps in the latter case while the maximum change is only 5.8 cps in the compounds studied. The per cent s character is expected to be the same in both types of addition compounds, however, the data indicate that there is not a linear correlation between the long range coupling constants, $J(^{119}Sn\text{-}C\text{-}C\text{-}H_A)$, and the per cent s character as was observed in the alkyl case. The long range coupling constants in the aryltins are a measure of the spin-spin interaction of tin and hydrogen atoms which are four atoms

apart. Therefore, it is not surprising that these long range coupling constants cannot be used to measure the amount of s character in the tin carbon bond.

In some organometallic systems, long range coupling constants have been observed to be larger than the short range coupling constants. For example, for a series of molecules with the general formula $(CH_3CH_2)_nX$, where X = ^{31}P, ^{205}Tl, ^{19}F, ^{119}Sn, ^{199}Hg and ^{207}Pb, the $J(CH_3\text{-}X)$ coupling constants are larger than the $J(CH_2\text{-}X)$ coupling constants.[47] In order to account for this anomaly, it has been suggested that occupied d orbitals involved in chemical bonding between the atom X and the alkyl group cause large variations in both the magnitude and sign of the Fermi contact contribution to the spin coupling constants.[47] Extending this line of reasoning, the long range coupling constants should increase as more d electrons are involved in the bonding. This study has indicated that $d\pi\text{-}p\pi$ bonding exists between the empty d orbitals on the tin atom and the pi electrons of the phenyl ring. Therefore, as more pi electrons are donated into the d orbitals of the tin atom, the long range coupling constants, $J(^{119}Sn\text{-}C\text{-}C\text{-}H_A)$, should increase due to delocalization of the phenyl electrons. Examination of Tables VIII through X confirms that as the

strength of the Lewis base increases, the coupling constants also increase. Thus, the results indicate that the long range coupling constants can be used to determine qualitatively the extent of $d\pi$-$p\pi$ interaction. Verdonck has also suggested that the long range coupling constants in $(C_6H_5)_4SnCl_{4-n}$ depend on the pi electron interaction.[20]

Results of Infrared Studies.

The proposed configuration for the compounds and adducts can be substantiated by infrared studies. The infrared vibrations that are of interest are listed in Table XII and shown in Figures XI through XIII. The band at 340 cm^{-1} is assigned to the tin-chlorine stretching mode while the bands at 240 and 270 cm^{-1} are assigned as the tin-phenyl symmetric and tin-phenyl asymmetric modes respectively. These assignments are in agreement with those of Poller,[15] Tanaka[16] and Smith.[48]

Due to the mass effect of the substituent X, the tin-phenyl asymmetric modes for the parasubstituted compounds would be expected to absorb at a lower frequency than that of the unsubstituted molecule. By means of a simple calculation, assuming that the force constant for the tin-phenyl bond does not change, it is predicted that in the spectrum of tris-paramethylphenyltin chloride, the methyl-phenyl

Table XII. Selected Infrared Vibrations for $(p\text{-}XC_6H_4)_3SnCl$.

	ν_{Sn-Cl} (cm^{-1})	$\nu_{Sn-C_6H_5}$ (Asym) (cm^{-1})	$\nu_{Sn-C_6H_5}$ (Sym) (cm^{-1})
		$(C_6H_5)_3SnCl$	
Solvents			
Benzene	340 (s)	271 (vs)	240 (m)
Acetone (0.0289M)	340 (s)	271 (vs)	240 (m)
Acetone (0.201M)	340 (s)	271 (vs)	240 (m)
DMSO (0.209M)	324 (s)	273 (vs)	-------
DMSO (1.05M)	324 (s)	276 (vs)	-------
		$(p\text{-}ClC_6H_4)_3SnCl$	
Benzene	346 (vs)	226 (vs)	<200
DMSO	342 (s)	231 (vs)	-------
		$(p\text{-}CH_3C_6H_4)_3SnCl$	
Benzene	339 (vs)	248 (vs)	<200
DMSO	336 (vs)	248 (vs)	-------

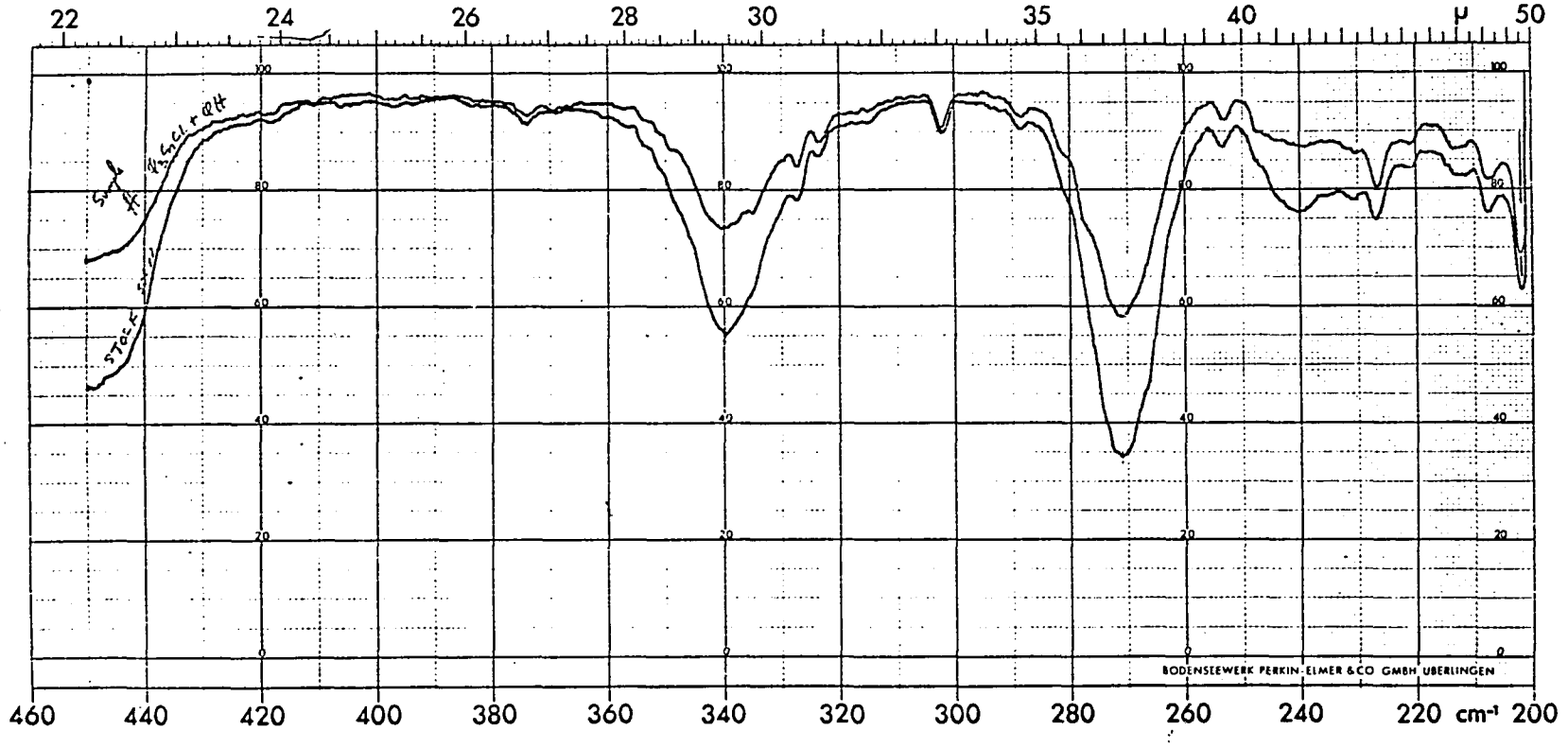


Figure XI. Infrared Spectra of Triphenyltin Chloride in Benzene at Two Concentrations.

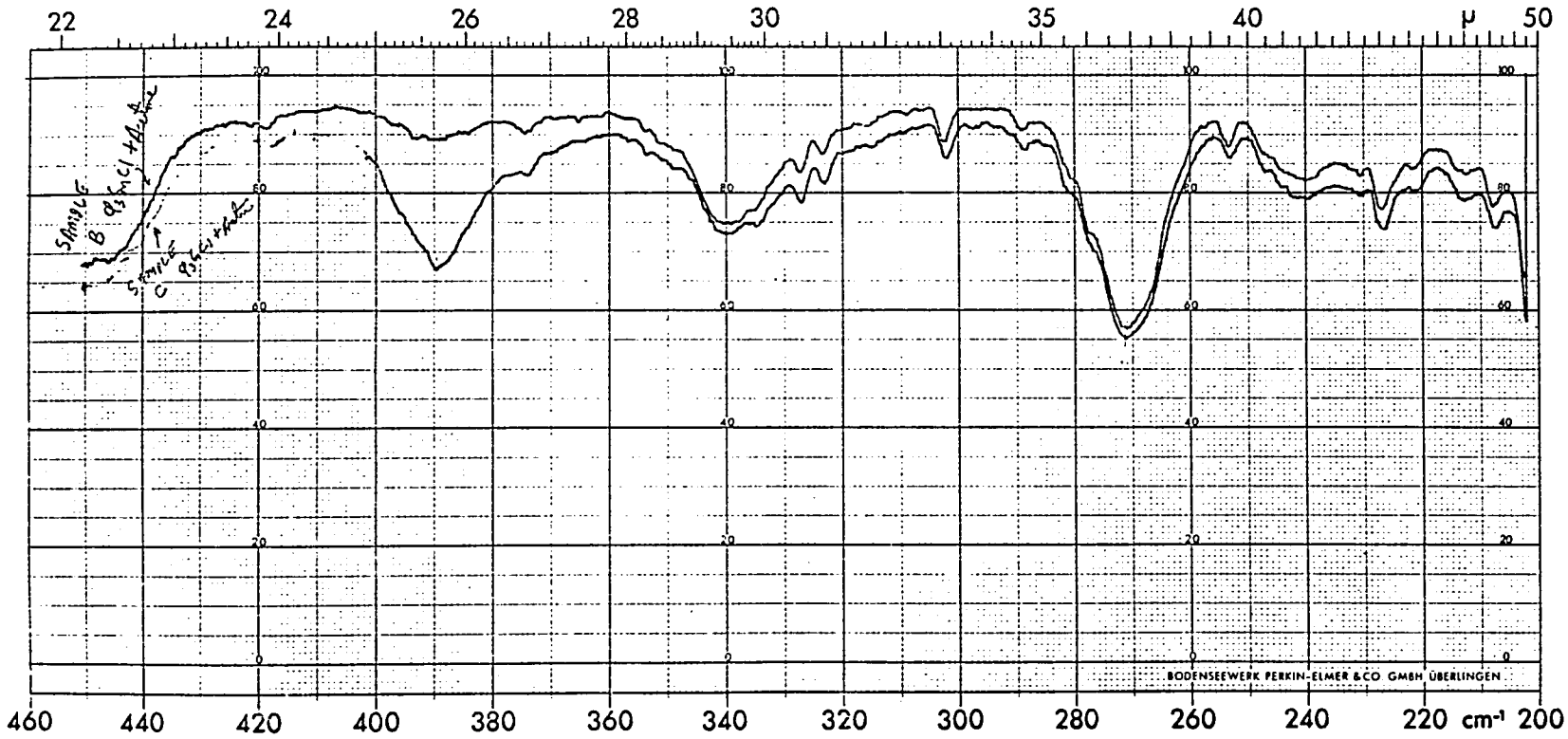


Figure XII. Infrared Spectra of Triphenyltin Chloride in Acetone at Two Concentrations.

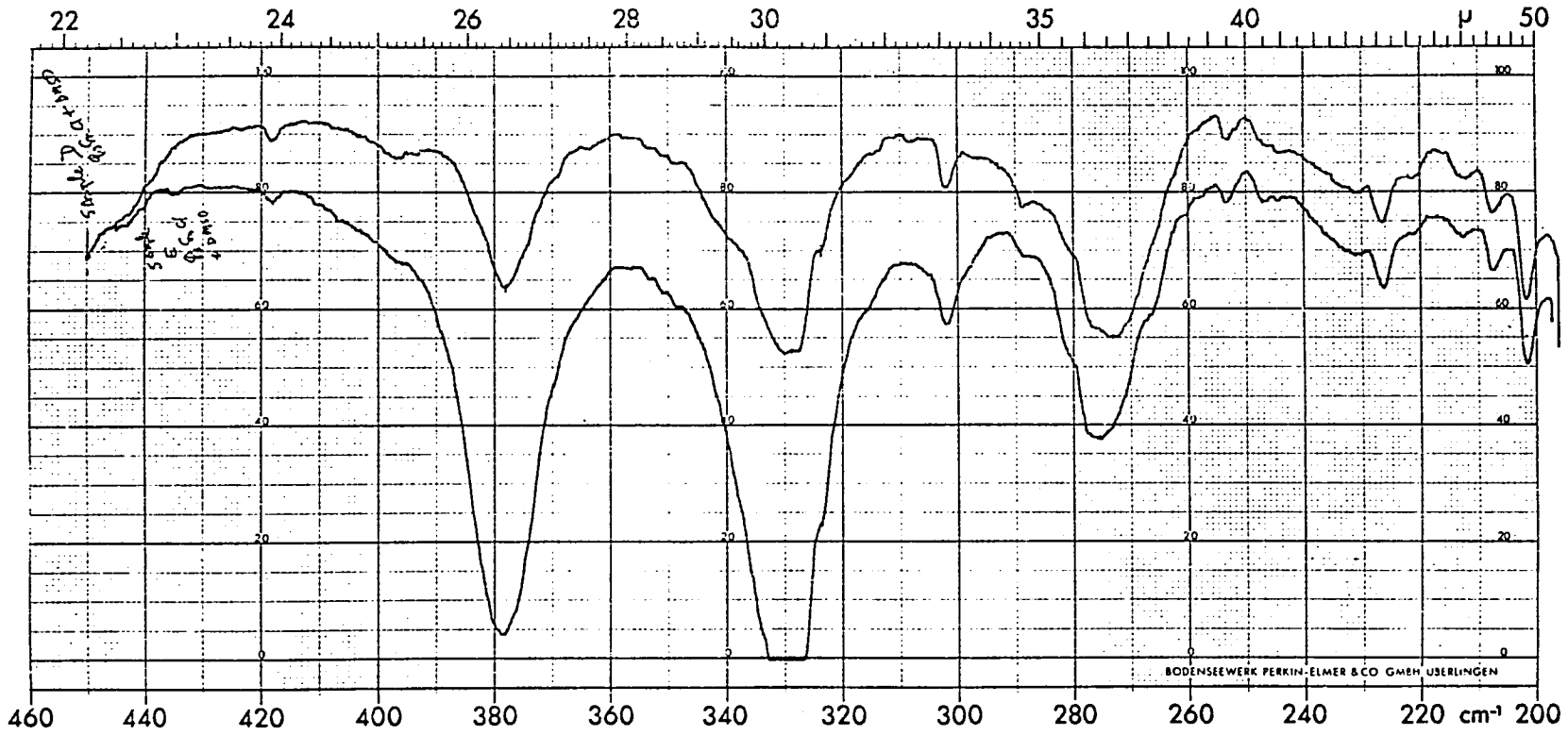


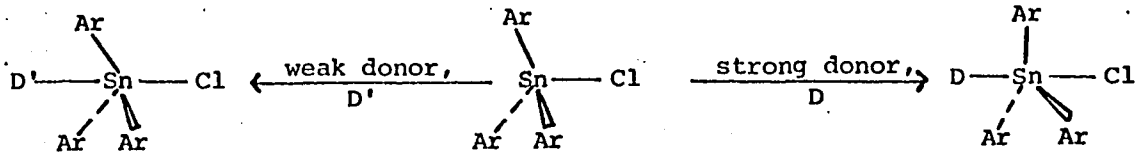
Figure XIII. Infrared Spectra of Triphenyltin Chloride in Dimethyl Sulfoxide at Two Concentrations.

asymmetric mode would occur at 257 cm^{-1} while the tin-phenyl asymmetric mode for tris-parachlorophenyltin chloride would occur at 240 cm^{-1}. Hence, in the spectra of $(\underline{p}\text{-}ClC_6H_4)_3SnCl$ and $(\underline{p}\text{-}CH_3C_6H_4)_3SnCl$, the peaks at 225 and 248 cm^{-1} were assigned as due to the chloro-phenyl tin and methyl-phenyl tin asymmetric vibrations, respectively. The tin-phenyl symmetric modes for these two compounds were not observed and are assumed to occur at frequencies below 200 cm^{-1}.

Examination of the data listed for the adducts of $(C_6H_5)_3SnCl$ in Table XII reveals that the tin-phenyl asymmetric vibrations are shifted to higher wavenumbers as the basicity of the Lewis base increases, while the tin-phenyl symmetric mode is absent when dimethyl sulfoxide is employed as the solvent. On the other hand, both the symmetric and asymmetric modes are observed when acetone is used as the solvent. These results indicate that the three phenyl rings in the addition compound, $(C_6H_5)_3SnCl\cdot DMSO$ are coplanar, while in $(C_6H_5)_3SnCl\cdot$acetone, they are not coplanar.

The infrared data then substantiate the model of coordination of the triaryltin chlorides as was suggested by the results of nmr studies. The coordination may be

illustrated as follows:



It has been shown that the amount of s character in a given bond is related to the stretching frequency of that bond in that an increase in the stretching frequency vibration would indicate an increase in s character.[28] Table XII and Figures XI through XIII show that the asymmetric stretching mode increases with increasing base strength, therefore, it is concluded that the tin-phenyl bonds in the addition compounds contain a greater per cent s character than the uncomplexed molecules.

Thus adduct formation must be viewed in terms of valence bond theory as follows: the tin atom is very nearly sp^2 hybridized with the three phenyl groups in the trigonal plane, while the axial bonds contain orbitals composed of p_z and d_z2 orbitals. If this proposed model of bonding is correct then the frequency of the tin-chlorine stretching vibration is expected to decrease upon adduct formation. Examination of Table XII and Figures XI through XIII reveals that the band due to the tin-chlorine stretch does decrease upon adduct formation, giving further support for the proposed model of coordination. This proposed model

of bonding is also in agreement with the conclusions drawn about the coordination of trimethyltin chloride.[5]

Infrared data also provide an insight into the possibility of $d\pi$-$p\pi$ bonding between the tin atom and the phenyl ring. Gordy[49] has proposed an empirical formula for calculating the bond order from force constant values. The parameters used in his formula, together with the data used to calculate the tin phenyl bond orders, are listed in Table XIII. The bond order for the tin phenyl bond is calculated, employing Gordy's rule, as 1.1 when $(C_6H_5)_3SnCl$ is dissolved in benzene or acetone, while the bond order increases to 1.3 when dimethyl sulfoxide is employed as the solvent. It is noted that the bond order depends on the electronegativity of both the phenyl and the tin groups, the bond length of the tin phenyl bond, and the force constant of the tin phenyl bond. The electronegativity of the phenyl ring and the bond length of the tin phenyl bond are both constant. Therefore, the observed increase in the bond order is due to either the change in the force constant or the change in the effective electronegativity of the tin atom due to its coordination with the solvent molecule. However, since the bond order is the same whether benzene or acetone is used as the solvent, the increase in the bond order must be due to an increase in the force constant and

Table XIII. Parameters Used in the Calculation of the Bond Order[49] in $(C_6H_5)_3SnCl \cdot D$.

$$N = (K - b)/a(X_A \cdot X_B/d^2)^{0.75} \qquad (16)$$

where K = force constant in dynes/cm X 10^{-5}

d = bond length of the phenyl bond in Å

N = bond order of the tin phenyl bond

X_A = electronegativity of phenyl group

X_B = electronegativity of the tin atom

a = 1.67

b = 0.30

Solvents	ν (cm^{-1})	K[a]	X_A[50]	X_B[51]	d[51]	N
Benzene	271	2.02	2.5	1.7	2.18	1.12
Acetone	271	2.02	2.5	1.7	2.18	1.12
DMSO	276	2.09	2.5	1.7	2.18	1.34

a The calculation of the force constants from the observed frequencies is given in Appendix D.

not an increase in the effective electronegativity of the tin atom. These results indicate that, as expected, there is more double bond character in the tin phenyl bond when a strong Lewis base is used as the solvent. However, it must be recognized that the observed change in the bond order is close to the experimental error, therefore, this conclusion must be viewed as tentative.

The results of this investigation have given further support for the postulate of $\underline{d}\pi$-$\underline{p}\pi$ bonding between the tin atom and the pi electrons of the phenyl ring in aryltin compounds. By studying the addition compounds, $(\underline{p}\text{-}XC_6H_4)_3SnCl\cdot D$, using Lewis bases of various strengths as ligands, it was possible to estimate the extent of $\underline{d}\pi$-$\underline{p}\pi$ bonding. The data indicate that as the strength of the Lewis base increases the degree of $\underline{d}\pi$-$\underline{p}\pi$ bonding also increases. It has also been shown that the configurations of the addition compounds, in solution, for both the trimethyltin chloride and $(\underline{p}\text{-}XC_6H_4)_3SnCl$ systems are the same despite differences in the approaches used to investigate the two systems. The data also indicate that while substitution on the tin atom has a large effect on the tin phenyl bond, substitution on the aromatic ring at the para position has little or no effect on the tin phenyl bond in aryltin compounds.

The results obtained suggest that the Brown σ^+ values for parasubstituted benzenes can be used to determine the relative positions of the chemical shifts of the H_A and H_B protons. Hence, use of σ^+ values can be helpful in assigning the chemical shifts of new parasubstituted aryltin compounds.

The infrared studies show that the tin phenyl bond is stabilized by $\underline{d}\pi$-$\underline{p}\pi$ bonding in solvents that have donating ability. Therefore, the tendency for cleavage of the phenyl group from the tin atom in donating solvents is expected to be lessened.

Finally, it has been found that coordination of triaryltin chlorides by donor molecules involves configurational rearrangements of the molecules, as the base strength of the donor increases, from a distorted tetrahedron to that of a trigonal bipyramidal structure with three coplanar phenyl groups. The observation of only two resonance peaks in the nmr, one due to the H_A protons and the other peak assigned to the H_B protons, discounts the possibility of "propeller" or perpendicular models for the three phenyl rings within the nmr time scale.

Proposals for Further Studies.

An extension of this work would be to undertake

similar studies on $(p\text{-}XC_6H_4)_2SnCl_2$ and $(p\text{-}XC_6H_4)SnCl_3$ because both of these series of compounds have the tendency to form 1:2 addition compounds. In these cases, it would be interesting to determine the structural configurations as well as to determine whether there is more or less $d\pi$- $p\pi$ bonding in these adducts as compared to the triaryltin chloride adducts.

The compounds used in this investigation could also be studied using uv spectroscopy, since delocalization of the phenyl ring electrons would cause λ_{max} of the benzene ring to increase. It is expected that $d\pi$-$p\pi$interaction would decrease as the number of phenyl rings decreases because delocalization of the pi electrons is maximized in the triaryltin case. If this prediction were found to be true, it would confirm the results obtained in this work.

A Mössbauer study on the triaryltin halide adducts would also give insight into the bonding of the tin atom in these addition compounds. The isomer shift obtained in Mössbauer spectroscopy is a function of the s electron density at the tin nucleus. Duncan[52] has suggested that, in general, the more negative the isomer shift the more pi bonding is involved in a complex. Therefore, for solutions of Ar_3SnCl in Lewis bases, the isomer shifts should become

more negative as the base strengths of the solvents increase, indicating a greater amount of $d\pi$-$p\pi$ bonding between the tin atom and the phenyl ring.

It would also be interesting to vary the halogen and determine what effect it would have on the tin phenyl bond and also to see if there are any changes in the apparent bond order for the $(C_6H_5)_3SnX \cdot DMSO$ adduct. The structural configurations of these adducts should also be investigated. Tanaka has found that the configuration of adducts depends on the nature of the halogen.[16]

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APPENDICES

Appendix A

The following is a listing of the LAOCOON III program used in this work:

```
      C     LAOCOON III 4 SPINS AA'BB' SYSTEMS ONLY.
0001        IMPLICIT REAL*8(A-H,O-Z)
0002        DIMENSION IL(25),F(25),ISO(4),W(4),A(4,4),IA(7,6),IB(7,6),
           1 NO(5),LL(5),NP(16),B(25),DC(25,7),X(6,6),D(16,6),VA(6,6),BV(7)
           2VB(6,6),CORR(7),E(16),FNO(6),NAME(15),NKTL(2),FZ(16,4)
0003        COMMON F,W,A,FZ,B,DC,X,D,VA,BV,CORR,E,VB,NOS,NN,NL,NI,IL,ISO,IA
           1IB,NO,LL,NP
0004     8005 NNO=0
      C      READ IN DATA
0005     8010 READ(5,7000)NC,NN,NAME
0006        IF(NC)8042,8042,8050
0007     9999 WRITE(6,4958)
0008     8042 CALL EXIT
0009     8050 READ(5,7002)FR1,FR2,AMIN
0010        READ (5,7001)(ISO(I),I=1,4)
0011        READ(5,7002)(W(I),I=1,4)
0012        NNM=NN-1
0013        DO 8340 J=1,NNM
0014            CALL SETCLK(10)
0015        JP=J+1
0016        READ(5,7002)(A(J,K),K=JP,NN)
0017        DO8339K=JP,NN
0018        IF(ISO(J)-ISO(K))8335,8337,8335
0019     8335 A(K,J)=0.
0020        GO TO 8339
0021     8337 A(K,J)=0.5*A(J,K)
0022     8339 CONTINUE
0023     8340 CONTINUE
      C      CALCULATE SPIN FUNCTIONS IF NOT ALREADY DONE
0024        IF(NN-NNO)9351,160,9351
0025     9351 NNO=NN
0026        NO(1)=1
0027        LL(1)=1
0028        DO8357J=1,NN
0029        JP=J+1
0030        JD=NN+1-J
0031        NO(JP)=(NO(J)*JD)/J
0032     8357 LL(JP)=LL(J)+NO(J)
0033        NNP=NN+1
0034        MAX=2**NN
0035        MAXM=MAX-1
0036        NP(1)=0
0037        DO8371J=1,MAXM
0038        ISUM=1
0039        DO8368M=1,NN
0040        MEX2=2**M
0041        IZ=(2*J)/MEX2-2*(J/MEX2)
0042     8368 ISUM=ISUM+IZ
0043        K=LL(ISUM)
0044        NP(K)=J
0045     8371 LL(ISUM)=LL(ISUM)+1
0046        DO8373J=2,NNP
0047     8373 LL(J)=LL(J)-NC(J)
0048        DO8379K=1,MAX
```

```
0049                N=NP(K)
0050                DO8379M=1,NN
0051                MEX2=2**M
0052                FZ(K,M)=2*(N/MEX2)-(2*N)/MEX2
0053             8379 FZ(K,M)=FZ(K,M)+0.5
                 C       READ IN ITERATIONS,LINES TO BE MATCHED AND PARAMETERS, IF ANY
0054              160 READ(5,7001)NI,(NKTL(K),K=1,2)
0055                  IF(NI)24,24,3
0056                3 NL=0
0057              118 NL=NL+1
0058                  READ(5,1001)IL(NL),F(NL)
0059                  IF(IL(NL))120,120,118
0060              120 NL=NL-1
0061                  NOS=0
0062              146 NOS=NOS+1
0063                  READ(5,1053)(IA(NOS,K),IB(NOS,K),K=1,6)
0064                  IF(IA(NOS,1))150,150,146
0065              150 NOS=NOS-1
                 C       ORDER LINES TO BE MATCHED BY ORIGIN
0066                  NLM=NL-1
0067                  DO 22 J=1,NLM
0068                  JP=J+1
0069                  ILSM=IL(J)
0070                  NOTE=0
0071                  DO 14 K=JP,NL
0072                  IF(IL(K)-ILSM) 12,14,14
0073               12 ILSM=IL(K)
0074                  NOTE=K
0075               14 CONTINUE
0076                  IF(NOTE) 16,22,16
0077               16 FS=F(J)
0078                  IS=IL(J)
0079                  F(J)=F(NOTE)
0080                  IL(J)=ILSM
0081                  F(NOTE)=FS
0082                  IL(NOTE)=IS
0083               22 CONTINUE
0084               24 KT1=8
0085                  KT2=9
0086                  KT1KT2=KT1*KT2
                 C       OUTPUT INITIAL DATA
0087                  WRITE(6,1002)NC,NAME,NN,FR1,FR2,AMIN
0088                  DO 1535 K=1,NN
0089                  WRITE(6,1003)ISO(K),K,W(K)
0090            1535 CONTINUE
0091                  NNM=NN-1
0092                  DO 1536 J=1,NNM
0093                  JP=J+1
0094                  DO 1536 K=JP,NN
0095                  WRITE(6,1004)J,K,A(J,K)
0096            1536 CONTINUE
0097                  IF(NI)61,61,2250
0098            2250 WRITE(6,1057)
0099                  DO 2330 J=1,NOS
```

```
DOS FORTRAN IV 360N-FO-479 3-3          MAINPGM              DATE    12/23/70      TIME

0100                WRITE(6,1058)J
0101                DO 2320 K=1,6
0102                IF(IA(J,K))9999,2330,2280
0103             2280 IF(IB(J,K)) 9999,2290,2310
0104             2290 WRITE(6,1062)IA(J,K)
0105                GO TO 2320
0106             2310 WRITE(6,1063)IA(J,K),IB(J,K)
0107             2320 CONTINUE
0108             2330 CONTINUE
                C       ENTER ITERATIVE LOOP
0109               61 ER1=10000.0
0110                ITER=0
0111              400 REWIND KT1
0112                REWIND KT2
0113                NA=1
0114              403 MOA=NO(NA)
                C       COMPUTE ELEMENTS OF HAMILTONIAN MATRIX
0115                DO 1432 J=1, MOA
0116                DO 432 K=J,MOA
0117                JL=LL(NA)+J-1
0118                KL=LL(NA)+K-1
0119                IF(J-K)408,425,408
0120              408 KINV=0
0121                DO 418 M=1,NN
0122                P=FZ(JL,M)*FZ(KL,M)
0123                IF(P)412,418,418
0124              412 KINV=KINV+1
0125                IF(KINV-1)418,414,416
0126              414 MA=M
0127                GO TO 418
0128              416 IF(KINV-2)418,417,422
0129              417 MB=M
0130              418 CONTINUE
0131                X(J,K)=A(MB,MA)
0132                X(K,J)=X(J,K)
0133                GO TO 432
0134              422 X(J,K)=0.
0135                X(K,J)=0.
0136                GO TO 432
0137              425 X(J,J)=0.
0138                DO427 M=1,NN
0139              427 X(J,J)=X(J,J)+FZ(JL,M)*W(M)
0140                DO 431 M=1,NNM
0141                MP=M+1
0142                DO 431 N=MP,NN
0143              431 X(J,J)=X(J,J)+FZ(JL,M)*FZ(JL,N)*A(M,N)
0144              432 CONTINUE
0145             1432 CONTINUE
0146                IF(ITER)8042,1500,500
0147             1500 KNTRL=0
0148                GO TO 512
                C       ROUGH DIAGONALIZATION
0149              500 READ (KT2)((VB(J,K),J=1,MOA),K=1,MOA)
0150                DO 505 JA1=1,MOA
```

```
0151              DO 505 JA2=1,MOA
0152              VA(JA1,JA2)=0.
0153              DO 505 JX1=1,MOA
0154            505 VA(JA1,JA2)=VA(JA1,JA2)+X(JA1,JX1)*VB(JX1,JA2)
0155              DO 510 JX1=1,MOA
0156              DO 510 JX2=1,MOA
0157              X(JX1,JX2)=0.
0158              DO 510 JA1=1,MOA
0159            510 X(JX1,JX2)=X(JX1,JX2)+VB(JA1,JX1)*VA(JA1,JX2)
                C         FINISH DIAGONALIZATION
0160              KNTRL=1
0161            512 CALL MATRIX(X,VB,MOA,KNTRL)
                C         STORE ENERGIES AND EIGENVECTORS
0162              DO 515 J=1,MOA
0163              JL=J+LL(NA)-1
0164            515 E(JL)=X(J,J)
0165              WRITE(KT1)((VB(J,K),J=1,MOA),K=1,MOA)
0166              IF(NI) 516,516,1515
0167           1515 CALL DIFFER (MOA,NA)
0168            516 NA=NA+1
0169              IF(NA-NN-1) 403,403,1518
0170           1518 IF(NI) 602,602,518
                C       LEAST SQUARES ROUTINES
0171            518 CALL CONDIT
0172              CALL ERROR9(NEXIT,ER1,ITER)
0173              CALL NORMAL
0174              IF(NEXIT) 9999,523,526
0175            526 CALL INVERT(VA,NOS)
0176              DO 530 NSA=1,NOS
0177              CORR(NSA)=0.
0178              DO 530 NSB=1,NOS
0179            530 CORR(NSA)=CORR(NSA)+VA(NSA,NSB)*BV(NSB)
                C       APPLY COMPUTED CORRECTIONS
0180              CALL CORREC
0181              KT1=KT2
0182              KT2 = KT1KT2/KT2
0183              ITER=ITER+1
0184              GO TO 400
                C       END OF LOOP. OUTPUT REFINED PARAMETERS
0185            523 KNTRL=0
0186              WRITE(6,1012)NC
0187              DO 538 K=1,NN
0188              WRITE(6,1003)ISO(K),K,W(K)
0189            538 CONTINUE
0190              DO 543 K=1,NNM
0191              KP=K+1
0192              DO 543 L=KP,NN
0193              WRITE(6,1004)K,L,A(K,L)
0194            543 CONTINUE
0195              WRITE(6,1005)
                C       BEGIN ERROR ANALYSIS
0196              CALL MATRIX(VA,VB,NOS,KNTRL)
0197              FNL=NL
0198              FNS=NOS
```

```
0199              DEV=(ER1*ER1*FNL)/(FNL-FNS)
0200              DO 642 NS=1,NCS
0201              ER2=DSQRT(DEV/VA(NS,NS))
0202              WRITE(6,1006)(VB(K,NS),K=1,NOS)
0203              WRITE(6,1007)ER2
0204              DO 1642 J=1,NCS
0205           1642 CORR(J)=CORR(J)+(VB(J,NS)*ER2)**2
0206            642 CONTINUE
0207              DO701NS=1,NOS
0208            701 CORR(NS)=0.6745*DSQRT(CORR(NS))
0209              WRITE(6,7003)(NS,CORR(NS),NS=1,NOS)
                C       CALCULATE INTENSITIES AND OUTPUT LINES
0210              LM=1
0211              IZ=1
0212            602 LINZ=0
0213              LCT=0
0214              NOTA=1
0215              WRITE(6,1009)NC
0216              REWIND KT1
0217              READ(KT1) VB(1,1)
0218              NA=0
0219            605 NA=NA+1
0220              NB=NA+1
0221              MCA=NO(NA)
0222              MOB=NO(NB)
0223              DO2624 JB=1,MOB
0224              DO 1610 JA=1,MOA
0225           1610 VA(JA,JB)=0.
0226              NPB=JB+LL(NB)-1
0227              DO 624 JA=1,MCA
0228              NPA=JA+LL(NA)-1
0229              NDIF=NP(NPB)-NP(NPA)
0230              DO 617 M=1,NN
0231              MEX2=(2**M)/2
0232              IF(NDIF-MEX2) 617,622,617
0233            617 CONTINUE
0234              GO TO 624
0235            622 DO 623 JC=1,MOA
0236            623 VA(JC,JB)=VA(JC,JB)+VB(JA,JC)
0237            624 CONTINUE
0238           2624 CONTINUE
0239              READ(KT1)((VB(J,K),J=1,MOB),K=1,MOB)
0240              DO 4671 KA=1,MOA
0241              DO 671 KB=1,MCB
0242              LINZ=LINZ+1
0243              S=0.
0244              DO 665 KD=1,MCB
0245            665 S=S+VA(KA,KD)*VB(KD,KB)
0246              S=S*S
0247              KAL=KA+LL(NA)-1
0248              KBL=KB+LL(NB)-1
0249              FR=E(KAL)-E(KBL)
0250              IF(NI)1669,1669,1668
0251           1668 IF(LINZ-IL(LM)) 1669,669,1669
```

```
0252          1669 IF(S-AMIN) 671,2669,2669
0253          2669 IF(FR-FR1) 671,4669,4669
0254          4669 IF(FR2-FR) 671,1670,1670
0255          1670 WRITE(6,1016)LINZ,FR,S
0256               LCT = LCT+1
0257               IF(LCT-300) 3670,3670,3671
0258          3670 DC(LCT,1)=LINZ
0259               DC(LCT,2)=0.
0260               DC(LCT,3)=FR
0261               DC(LCT,4)=S
0262               GO TO 671
0263          3671 NOTA=0
0264               GO TO 671
0265           669 WRITE (6,999)LINZ,F(LM),FR,S,B(LM)
0266               LCT = LCT+1
0267               IF(LCT-300) 3669,3669,670
0268          3669 DC(LCT,1)=LINZ
0269               DC(LCT,2)=F(LM)
0270               DC(LCT,3)=FR
0271               DC(LCT,4)=S
0272               DC(LCT,5)=B(LM)
0273           670 LM=LM+1
0274           671 CONTINUE
0275          4671 CONTINUE
0276               IF(NN-NA)930,930,605
              C         ORDER LINES IN STORAGE
0277           930 LCT= MINO (LCT,300)
0278               LCTM=LCT-1
0279               DO 948 J=1,LCTM
0280               NOTE=0
0281           932 FSM=DC(J,3)
0282               JP=J+1
0283               DO 937 K=JP,LCT
0284               IF(FSM-DC(K,3)) 937,937,935
0285           935 FSM=DC(K,3)
0286               NOTE=K
0287           937 CONTINUE
0288               IF(NOTE) 9999,948,939
0289           939 DO 940 KT=1,5
0290           940 FNO(KT)=DC(J,KT)
0291               DO 942 KT=1,5
0292           942 DC(J,KT)=DC(NOTE,KT)
0293               DO 944 KT=1,5
0294           944 DC(NOTE,KT)=FNO(KT)
0295           948 CONTINUE
0296               IF(NKTL(1))1950,1950,949
              C       OUTPUT ORDERED LINES
0297           949 WRITE(7,1000)NC
0298          1950 WRITE(6,4105)NC
0299           950 DO 955 L=1,LCT
0300               IDC = DC(L,1)+0.5
0301               IF(NKTL(1))960,960,965
0302           965 WRITE(7,7002)DC(L,3),DC(L,4)
0303           960 IF(NI)952,952,951
```

```
0304          951 IF(DC(L,2)) 954,952,954
0305          952 WRITE(6,1016)IDC,DC(L,3),DC(L,4)
0306          953 GO TO 955
0307          954 WRITE(6,999) IDC,(DC(L,J),J=2,5)
0308          955 CONTINUE
0309          956 IF(NOTA)673,957,673
0310          957 WRITE(6,4957)
0311          673 WRITE(6,1011)NC
             C      GO ON TO NEXT PROBLEM
0312          675 GO TO 8010
0313          999 FORMAT(1H ,19X,I4,F11.3,F12.3,F9.3,F9.3)
0314         1000 FORMAT(I3)
0315         1001 FORMAT(I4,F20.0)
0316         1002 FORMAT(1H1,20X,18HLAOCOON III        //21X,4HCASE,I4,15A4///21X,
                 13HNN=,I2,17H  FREQUENCY RANGE,2F10.3,20H  MINIMUM INTENSITY ,
                 2F7.5///21X,16HINPUT PARAMETERS//)
0317         1003 FORMAT(1H ,20X,I1,9X,2HW(I1,2H)=F9.3)
0318         1004 FORMAT(1H ,30X,2HA(I1,1H,I1,2H)=F9.3)
0319         1005 FORMAT(1H0,19X,37HERROR VECTORS AND STANDARD ERRORS      )
0320         1006 FORMAT(1H ,20X,12F8.4)
0321         1007 FORMAT(1H ,30X,15HSTANDARD ERROR=F8.3)
0322         1009 FORMAT(1H1,19X,8HCASE NO I4//20X,43HLINE   EXP FREQ   CALC FREQ
                 1INTEN   ERROR //)
0323         1010 FORMAT(1H ,19X,I4,F11.3,F12.3,F9.3,F12.3)
0324         1011 FORMAT(1H0,20X,12HEND OF CASE I3)
0325         1012 FORMAT(1H1,20X,16HBEST VALUES CASE I4//)
0326         1015 FORMAT(10F12.4)
0327         1016 FORMAT(1H ,19X,I4,F23.3,F9.3)
0328         1053 FORMAT(6(I1,I1,2X))
0329         1057 FORMAT(1H0,24X,14HPARAMETER SETS)
0330         1062 FORMAT(1H ,24X,2HW(I1,1H))
0331         1063 FORMAT(1H ,24X,2HA(I1,1H,I1,1H))
0332         1058 FORMAT(1H ,I21)
0333         4105 FORMAT(1H1,20X,19HORDERED LINES CASE I4/// 21X,4HLINE,3X,
                 18HEXP FREQ,3X,9HCALC FREQ,3X,5HINTEN,3X,5HERROR///)
0334         4957 FORMAT(1H0,20X,15HDC STORAGE FULL)
0335         4958 FORMAT(1H ,25X,16H IMPOSSIBLE DATA)
0336         7000 FORMAT(2I3,15A4)
0337         7001 FORMAT(4I1)
0338         7002 FORMAT(7F10.3)
0339         7003 FORMAT(1H0,19X,33HPROBABLE ERRORS OF PARAMETER SETS //(1H ,20X,
                 1I2,F10.3))
0340              END
```

OS FORTRAN IV 360N-FO-479 3-3 MATRIX DATE 12/23/70 TIME

```
0001                SUBROUTINE MATRIX(X,E,N,KNTRL)
0002              IMPLICIT REAL*8(A-H,O-Z)
0003              DIMENSION X(6,6),E(6,6)
0004              NSQP=3*N*N/2
0005              ITER=0
0006              NMI=N-1
0007              IF(NMI)87,2,3
0008            2 E(1,1)=1.
0009              GO TO 87
0010            3 IF(KNTRL) 7,9,7
          C       ENTER E MATRIX
0011            9 DO11I=1,N
0012              DO10J=1,N
0013           10 E(I,J)=0.0
0014           11 CONTINUE
0015              DO12K=1,N
0016           12 E(K,K)=1.
          C       FIND LARGEST OFF-DIAGONAL ELEMENT
0017            7 ITER=ITER+1
0018           21 BIGX=0.0
0019           22 DO25J=2,N
0020              JM1=J-1
0021              DO25I=1,JM1
0022              IF(BIGX-DABS(X(I,J)))23,25,25
0023           23 BIGX=DABS(X(I,J))
0024              K=I
0025              L=J
0026           25 CONTINUE
0027              IF (BIGX-0.00001) 76,76,27
          C       COMPUTE ROTATION
0028           27 TS=X(K,L)*X(K,L)
0029           28 DEL=X(K,K)-X(L,L)
0030              R=DSQRT(DABS(DEL*DEL+4.*TS))
0031              A=DSQRT(DABS((R+DEL)/(2.*R)))
0032              IF(.707-A)30,30,29
0033           29 B=-A
0034              A=DSQRT(1.-B*B)
0035              GO TO 32
0036           30 B=-DSQRT(1.-A*A)
0037           32 IF(DEL/X(K,L))33,60,60
0038           33 B=-B
          C       ENTER ROTATION IN EIGENVECTOR MATRIX
0039           60 DO65J=1,N
0040              F1=E(J,K)
0041              E(J,K) = A*F1-B*E(J,L)
0042           75 E(J,L) = B*F1+A*E(J,L)
          C         ORTHOGONAL ROTATION OF MATRIX
0043              IF(K-J)61,65,61
0044           61 IF(L-J)62,65,62
0045           62 X(K,J)=A*X(J,K)-B*X(J,L)
0046              X(L,J)=B*X(J,K)+A*X(J,L)
0047           67 X(J,K)=X(K,J)
0048              X(J,L)=X(L,J)
0049           65 CONTINUE
```

```
0050              D=X(K,K)+X(L,L)
0051              X(K,K)=A*A*X(K,K)+B*B*X(L,L)-2.*A*B*X(K,L)
0052              X(L,L)=D-X(K,K)
0053              X(L,K)=0.0
0054              X(K,L)=0.0
0055              IF(ITER-NSQP)7,90,90
0056           90 WRITE(6,91)
0057           91 FORMAT(26H TOUGH MATRIX  SKIPPED OUT)
0058           87 RETURN
0059           76 BIGR=0.00004
0060              DO86 I=1,NMI
0061              IPI=I+1
0062              DO86J=IPI,N
0063              IF(X(I,J))77,86,77
0064           77 DEL=X(I,I)-X(J,J)
0065              IF(DEL) 79,86,79
0066           79 ROT=DABS(X(I,J)/DEL)
0067              IF(ROT-BIGR)86,86,78
0068           78 BIGR=ROT
0069              K=I
0070              L=J
0071           86 CCNTINUE
0072              IF(BIGR-0.00005) 87,87,88
0073           88 WRITE(6,89)
0074           89 FORMAT(1H,30X,10HDEGENERACY)
0075              GO TO 27
0076              END
```

```
0001              SUBROUTINE INVERT(A,N)
0002             IMPLICIT REAL*8(A-H,O-Z)
0003             DIMENSION A(6,6),B(6),C(6),LZ(6)
0004             DO 10 J=1,N
0005          10 LZ(J)=J
0006             DO 20 I=1,N
0007             K=I
0008             Y=A(I,I)
0009             L=I-1
0010             LP=I+1
0011             IF(N-LP)14,11,11
0012          11 DO 13 J=LP,N
0013             W=A(I,J)
0014             IF(DABS(W)-DABS(Y))13,13,12
0015          12 K=J
0016             Y=W
0017          13 CONTINUE
0018          14 DO15J=1,N
0019             C(J)=A(J,K)
0020             A(J,K)=A(J,I)
0021             A(J,I)=-C(J)/Y
0022             A(I,J)=A(I,J)/Y
0023          15 B(J)=A(I,J)
0024             A(I,I)=1.0/Y
0025             J=LZ(I)
0026             LZ(I)=LZ(K)
0027             LZ(K)=J
0028             DO19K=1,N
0029             IF(I-K)16,19,16
0030          16 DO18J=1,N
0031             IF(I-J)17,18,17
0032          17 A(K,J)=A(K,J)-B(J)*C(K)
0033          18 CONTINUE
0034          19 CONTINUE
0035          20 CONTINUE
0036             DO200I=1,N
0037             IF(I-LZ(I))100,200,100
0038         100 K=I+1
0039             DO500J=K,N
0040             IF(I-LZ(J))500,600,500
0041         600 M=LZ(I)
0042             LZ(I)=LZ(J)
0043             LZ(J)=M
0044             DO700L=1,N
0045             C(L)=A(I,L)
0046             A(I,L)=A(J,L)
0047         700 A(J,L)=C(L)
0048         500 CONTINUE
0049         200 CONTINUE
0050             RETURN
0051             END
```

DOS FORTRAN IV 360N-FO-479 3-3 CORREC DATE 12/23/70 TIME

```
0001                  SUBROUTINE CORREC
0002                  IMPLICIT REAL*8(A-H,O-Z)
0003                  DIMENSION IL(25),F(25),ISO(4),W(4),A(4,4),IA(7,6),IB(7,6),
                     1 NO(5),LL(5),NP(16),B(25),DC(25,7),X(6,6),D(16,6),VA(6,6),BV(7),
                     2VB(6,6),CORR(7),E(16),FNO(6),NAME(15),NKTL(2),FZ(16,4)
0004                  COMMON F,W,A,FZ,B,DC,X,D,VA,BV,CORR,E,VB,NOS,NN,NL,NI,IL,ISO,IA,
                     1IB,NO,LL,NP
0005               300 DO 310 NS=1,NOS
0006               301 DO 309 K=1,6
0007               302 IF(IA(NS,K)) 303,310,303
0008               303 IAS=IA(NS,K)
0009              1303 IF(IB(NS,K)) 304,308,304
0010               304 IBS=IB(NS,K)
0011              1304 A(IAS,IBS)=A(IAS,IBS)+CORR(NS)
0012               305 IF(ISO(IAS)-ISO(IBS)) 309,306,309
0013               306 A(IBS,IAS)=A(IAS,IBS)/2.
0014               307 GO TO 309
0015               308 W(IAS)=W(IAS)+CORR(NS)
0016               309 CONTINUE
0017               310 CORR(NS)=0.0
0018               311 RETURN
0019                   END
```

)OS FORTRAN IV 360N-FO-479 3-3 DIFFER DATE 12/23/70 TIME

```
0001                SUBROUTINE DIFFER(MOA,NA)
0002               IMPLICIT REAL*8(A-H,O-Z)
0003               DIMENSION IL(25),F(25),ISO(4),W(4),A(4,4),IA(7,6),IB(7,6),
                  1 NO(5),LL(5),NP(16),B(25),DC(25,7),X(6,6),D(16,6),VA(6,6),BV(7),
                  2VB(6,6),CORR(7),E(16),FNO(6),NAME(15),NKTL(2),FZ(16,4)
0004               COMMON F,W,A,FZ,B,DC,X,D,VA,BV,CORR,E,VB,NOS,NN,NL,NI,IL,ISO,IA,
                  1IB,NO,LL,NP
0005              31 DO 58 J=1,MOA
0006              32 JL=J+LL(NA)-1
0007              33 DO 58 NS=1,NOS
0008              34 D(JL,NS)=0.
0009              35 DO 57 NPS=1,6
0010              36 IF(IA(NS,NPS)) 9999,58,37
0011              37 IAS=IA(NS,NPS)
0012              38 IF(IB(NS,NPS)) 9999,39,43
0013              39 DO 41 K=1,MOA
0014              40 KL=K+LL(NA)-1
0015              41 D(JL,NS)=D(JL,NS)+VB(K,J)*VB(K,J)*FZ(KL,IAS)
0016              42 GO TO 57
0017              43 IBS=IB(NS,NPS)
0018              44 DO 46 K=1,MOA
0019              45 KL=K+LL(NA)-1
0020              46 D(JL,NS)=D(JL,NS)+VB(K,J)*VB(K,J)*FZ(KL,IAS)*FZ(KL,IBS)
0021              47 IF(ISO(IAS)-ISO(IBS)) 57,48,57
0022              48 MOAM=MOA-1
0023             148 IF(MOAM)57,57,54
0024              54 IDIF=(2**IBS-2**IAS)/2
0025              49 DO157 JA=1,MCAM
0026              50 JAL=JA+LL(NA)-1
0027              51 JAP=JA+1
0028              52 DO157 KA=JAP,MOA
0029              53 KAL=KA+LL(NA)-1
0030              55 IF(NP(KAL)-NP(JAL)-IDIF)157,66,157
0031              66 SS=0.
0032              67 DO68KM=1,NN
0033              68 SS=SS+(FZ(KAL,KM)-FZ(JAL,KM))**2
0034              69 NTST=SS+0.1
0035              70 IF(NTST-2)157,56,157
0036              56 D(JL,NS)=D(JL,NS)+VB(JA,J)*VB(KA,J)
0037             157 CONTINUE
0038              57 CONTINUE
0039              58 CONTINUE
0040              59 RETURN
0041            9999 STOP
0042                 END
```

```
OS FORTRAN IV 360N-FO-479 3-3          ERROR9              DATE    12/23/70      TIME

0001                  SUBROUTINE ERROR9(NEXIT,ER1,ITER)
0002                  IMPLICIT REAL*8(A-H,O-Z)
0003                  DIMENSION IL(25),F(25),ISO(4),W(4),A(4,4),IA(7,6),IB(7,6),
                     1 NO(5),LL(5),NP(16),B(25),DC(25,7),X(6,6),D(16,6),VA(6,6),BV(7),
                     2VB(6,6),CORR(7),E(16),FNO(6),NAME(15),NKTL(2),FZ(16,4)
0004                  COMMON F,W,A,FZ,B,DC,X,D,VA,BV,CORR,E,VB,NOS,NN,NL,NI,IL,ISO,IA,
                     1IB,NO,LL,NP
0005                1 ER2=0.0
0006                2 FNL=NL
0007                3 DO 4 K=1,NL
0008                4 ER2=ER2+B(K)*B(K)
0009                5 ER2=DSQRT(ER2/FNL)
0010                6 WRITE(6,3000)ITER,ER2
0011                7 IF((ER1-ER2)/ER1-0.01) 8,8,10
0012                8 NEXIT=0
0013               18 ER1=ER2
0014                9 RETURN
0015               10 IF(ITER-NI) 110,8,8
0016              110 ER1=ER2
0017               11 NEXIT=1
0018               12 RETURN
0019             3000 FORMAT(1H ,20X,9HITERATIONI3,16H  R M S ERROR = F8.3)
0020                  END
```

```
OS FORTRAN IV 360N-FO-479 3-3          NORMAL              DATE   12/23/70      TIME

0001                    SUBROUTINE NORMAL
0002                  IMPLICIT REAL*8(A-H,O-Z)
0003                  DIMENSION IL(25),F(25),ISO(4),W(4),A(4,4),IA(7,6),IB(7,6),
                     1 NO(5),LL(5),NP(16),B(25),DC(25,7),X(6,6),D(16,6),VA(6,6),BV(7),
                     2VB(6,6),CORR(7),E(16),FNO(6),NAME(15),NKTL(2),FZ(16,4)
0004                  COMMON F,W,A,FZ,B,DC,X,D,VA,BV,CORR,E,VB,NOS,NN,NL,NI,IL,ISO,IA,
                     1IB,NO,LL,NP
0005               207 DO 210 NS1=1,NOS
0006               202 DO 206 NS2=NS1,NOS
0007               203 VA(NS1,NS2)=0.
0008               204 DO 205 LEQ=1,NL
0009               205 VA(NS1,NS2)=VA(NS1,NS2)+DC(LEQ,NS1)*DC(LEQ,NS2)
0010               206 VA(NS2,NS1)=VA(NS1,NS2)
0011               208 BV(NS1)=0.
0012               209 DO 210 LEQ=1,NL
0013               210 BV(NS1)=BV(NS1)+DC(LEQ,NS1)*B(LEQ)
0014               211 RETURN
0015                    END
```

```
0001                SUBROUTINE CONDIT
0002               IMPLICIT REAL*8(A-H,O-Z)
0003               DIMENSION IL(25),F(25),ISO(4),W(4),A(4,4),IA(7,6),IB(7,6),
                  1 NO(5),LL(5),NP(16),B(25),DC(25,7),X(6,6),D(16,6),VA(6,6),BV(7),
                  2VB(6,6),CORR(7),E(16),FNO(6),NAME(15),NKTL(2),FZ(16,4)
0004               COMMON F,W,A,FZ,B,DC,X,D,VA,BV,CORR,E,VB,NOS,NN,NL,NI,IL,ISO,IA,
                  1IB,NO,LL,NP
0005             99 LUL=0
0006            100 NA=0
0007            101 K=1
0008            102 NA=NA+1
0009            103 NB=NA+1
0010            104 IF(NA-NN) 105,105,120
0011            105 LLL=LUL+1
0012            106 MOA=NO(NA)
0013            107 MOB=NO(NB)
0014            108 LUL=LUL+MOA*MOB
0015            109 IF(LUL-IL(K)) 102,110,110
0016            110 IDX=IL(K)-LLL
0017            111 JA=(IDX/MOB)+1
0018            112 JB=IDX-(JA-1)*MOB +1
0019            113 JAL=JA+LL(NA)-1
0020            114 JBL=JB+LL(NB)-1
0021            115 B(K)=F(K)+E(JBL)-E(JAL)
0022            116 DO 117 NS=1,NCS
0023            117 DC(K,NS)=D(JAL,NS)-D(JBL,NS)
0024            118 K=K+1
0025            119 IF(K-NL) 109,109,120
0026            120 RETURN
0027                END
```

```
LAOCOON III

CASE   1 FINAL CCL4 ANALYSIS 100 HZ

NN= 4  FREQUENCY RANGE     65.000    175.000  MINIMUM INTENSITY 0.02500

INPUT PARAMETERS

1          W(1)=  100.000
1          W(2)=  100.000
1          W(3)=  111.250
1          W(4)=  111.250
           A(1,2)=    0.368
           A(1,3)=   -0.050
           A(1,4)=    8.450
           A(2,3)=    8.450
           A(2,4)=   -0.050
           A(3,4)=    2.632

     PARAMETER SETS
1
     W(1)
     W(2)
2
     W(3)
     W(4)
3
     A(1,2)
4
     A(1,3)
     A(2,4)
5
     A(1,4)
     A(2,3)
6
     A(3,4)
ITERATION  0  R M S ERROR =     0.476
ITERATION  1  R M S ERROR =     0.070
ITERATION  2  R M S ERROR =     0.068
ITERATION  3  R M S ERROR =     0.068
```

108

BEST VALUES CASE 1

1	W(1)=	100.051
1	W(2)=	100.051
1	W(3)=	111.302
1	W(4)=	111.302
	A(1,2)=	0.464
	A(1,3)=	0.537
	A(1,4)=	7.996
	A(2,3)=	7.996
	A(2,4)=	0.537
	A(3,4)=	3.146

ERROR VECTORS AND STANDARD ERRORS

0.4770	-0.4770	0.0187	-0.0560	-0.7079	-0.2010
STANDARD ERROR=	0.028				
0.7071	0.7071	0.0000	0.0000	0.0000	0.0000
STANDARD ERROR=	0.031				
0.2741	-0.2741	0.7613	-0.3297	0.3956	0.0706
STANDARD ERROR=	0.100				
-0.0954	0.0954	0.5185	0.8262	-0.1721	-0.0282
STANDARD ERROR=	0.034				
0.3390	-0.3390	-0.3226	0.3796	0.5510	-0.4673
STANDARD ERROR=	0.072				
0.2708	-0.2708	-0.2170	0.2481	0.0961	0.8576
STANDARD ERROR=	0.058				

PROBABLE ERRORS OF PARAMETER SETS

1	0.032
2	0.032
3	0.056
4	0.036
5	0.040
6	0.041

109

CASE NO 1

LINE	EXP FREQ	CALC FREQ	INTEN	ERROR
1	102.820	102.882	3.209	-0.062
3	116.920	117.003	0.791	-0.083
5		103.244	3.727	
7	110.620	110.654	1.255	-0.034
9	118.220	118.149	0.226	0.071
12	117.520	117.541	0.258	-0.021
14		109.615	1.742	
19	96.620	96.533	0.733	0.087
21		104.029	1.270	
22	116.920	116.922	0.786	-0.002
24		101.738	1.742	
26	93.820	93.811	0.258	0.009
29		108.109	3.727	
34		96.033	0.637	
36	107.420	107.393	1.363	0.027
37	100.620	100.699	1.255	-0.079
39	114.920	114.820	0.733	0.100
42	104.020	103.959	1.363	0.061
44		115.320	0.637	
45	93.320	93.203	0.226	0.117
47		107.324	1.270	
51	94.320	94.431	0.786	-0.111
53	108.420	108.470	3.209	-0.050
55	94.320	94.350	0.791	-0.030

ORDERED LINES CASE 1

LINE	EXP FREQ	CALC FREQ	INTEN	ERROR	RELATIVE INTENSITIES CALC	OBS[a]	ERROR
45	93.320	93.203	0.226	0.117	0.026	0.067	-0.041
26	93.820	93.811	0.258	0.009	0.029	0.119	-0.090
55	94.320	94.350	0.791	-0.030	0.182	0.263	-0.081
51		94.431	0.786	-0.111			
34		96.033	0.637				
19	96.620	96.533	0.733	0.087	0.116	0.119	-0.003
37	100.620	100.699	1.255	-0.079	0.145	0.191	-0.046
24		101.738	1.742				
1	102.820	102.882	3.209	-0.062	1.000	1.000	0.000
5		103.244	3.727				
42	104.020	103.959	1.363	0.061			
21		104.029	1.270		0.303	0.321	-0.018
47		107.324	1.270				
36	107.420	107.393	1.363	0.027	0.303	0.282	0.021
29		108.109	3.727				
53	108.420	108.470	3.209	-0.050	1.000	0.952	0.048
14		109.615	1.742				
7	110.620	110.654	1.255	-0.034	0.145	0.211	-0.066
39	114.920	114.820	0.733	0.100			
44		115.320	0.637		0.116	0.110	0.006
22	116.920	116.922	0.786	-0.002			
3	116.920	117.003	0.791	-0.083	0.182	0.268	-0.086
12	117.520	117.541	0.258	-0.021	0.029	0.086	-0.057
9	118.220	118.149	0.226	0.071	0.026	0.056	-0.030

END OF CASE 1

a Normalised to same intensity as calculated values.

```
LAOCOON III

CASE   2  FINAL ACETONE ANALYSIS 100 HZ

NN= 4  FREQUENCY RANGE     65.000    175.000  MINIMUM INTENSITY 0.02500

INPUT PARAMETERS

1          W(1)=  100.000
1          W(2)=  100.000
1          W(3)=  135.253
1          W(4)=  135.253
           A(1,2)=    1.560
           A(1,3)=   -0.500
           A(1,4)=    7.900
           A(2,3)=    7.900
           A(2,4)=   -0.500
           A(3,4)=    2.320

     PARAMETER SETS
1
     W(1)
     W(2)
2
     W(3)
     W(4)
3
     A(1,2)
4
     A(1,3)
     A(2,4)
5
     A(1,4)
     A(2,3)
6
     A(3,4)
ITERATION  0  R M S ERROR =     0.469
ITERATION  1  R M S ERROR =     0.073
ITERATION  2  R M S ERROR =     0.073
```

112

BEST VALUES CASE 2

1	W(1)=	99.801
1	W(2)=	99.801
1	W(3)=	135.223
1	W(4)=	135.223
	A(1,2)=	1.573
	A(1,3)=	0.426
	A(1,4)=	8.052
	A(2,3)=	8.052
	A(2,4)=	0.426
	A(3,4)=	2.345

ERROR VECTORS AND STANDARD ERRORS

0.7510	0.6597	-0.0119	0.0117	-0.0218	0.0054
STANDARD ERROR=	0.028				
-0.6182	0.7114	0.1117	0.1833	0.2442	-0.0776
STANDARD ERROR=	0.027				
0.1653	-0.1769	0.6675	0.4800	0.1078	-0.5038
STANDARD ERROR=	0.060				
0.1461	-0.1600	-0.4312	0.4791	0.7192	0.1431
STANDARD ERROR=	0.051				
0.0708	-0.0434	0.4704	-0.5926	0.6076	0.2270
STANDARD ERROR=	0.034				
-0.0071	-0.0057	0.3670	0.3939	-0.2049	0.8174
STANDARD ERROR=	0.044				

PROBABLE ERRORS OF PARAMETER SETS

1	0.020
2	0.020
3	0.035
4	0.031
5	0.030
6	0.033

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CASE NO 2

LINE	EXP FREQ	CALC FREQ	INTEN	ERROR
1		103.540	2.466	
3	139.940	139.962	1.534	-0.022
5	103.740	103.661	2.497	0.079
7	133.420	133.423	1.583	-0.003
9	141.780	141.878	0.385	-0.098
12		139.838	0.696	
14	132.180	132.173	1.304	0.007
19	96.980	97.001	1.231	-0.021
21	105.520	105.455	0.764	0.065
22	139.940	139.905	1.539	0.035
24	102.820	102.851	1.304	-0.031
26		95.186	0.696	
29		131.362	2.497	
34	95.780	95.940	0.884	-0.160
36	131.540	131.419	1.116	0.121
37	101.580	101.601	1.583	-0.021
39	137.980	138.023	1.231	-0.043
42	103.740	103.604	1.116	0.136
44	138.980	139.084	0.884	-0.104
45	93.080	93.146	0.385	-0.066
47	129.620	129.569	0.764	0.051
51	95.100	95.119	1.539	-0.019
53	131.540	131.484	2.466	0.056
55	95.100	95.061	1.534	0.039

```
LAOCOON III

CASE    3  FINAL DMSO ANALYSIS 60 HZ

NN= 4  FREQUENCY RANGE     65.000    175.000  MINIMUM INTENSITY 0.02500

INPUT PARAMETERS

1          W(1)=   100.000
1          W(2)=   100.000
1          W(3)=   120.873
1          W(4)=   120.873
           A(1,2)=     0.555
           A(1,3)=     0.245
           A(1,4)=     8.645
           A(2,3)=     8.645
           A(2,4)=     0.245
           A(3,4)=     3.067

    PARAMETER SETS
1
    W(1)
    W(2)
2
    W(3)
    W(4)
3
    A(1,2)
4
    A(1,3)
    A(2,4)
5
    A(1,4)
    A(2,3)
6
    A(3,4)
ITERATION  0  R M S ERROR =     0.308
ITERATION  1  R M S ERROR =     0.100
ITERATION  2  R M S ERROR =     0.080
ITERATION  3  R M S ERROR =     0.080
```

BEST VALUES CASE 3

1	W(1)=	99.819
1	W(2)=	99.819
1	W(3)=	120.923
1	W(4)=	120.923
	A(1,2)=	1.627
	A(1,3)=	0.358
	A(1,4)=	8.036
	A(2,3)=	8.036
	A(2,4)=	0.358
	A(3,4)=	2.106

ERROR VECTORS AND STANDARD ERRORS

0.5886	-0.5886	-0.1552	0.0380	-0.5300	0.0265
STANDARD ERROR= 0.031					
0.7071	0.7071	-0.0000	-0.0000	0.0000	0.0000
STANDARD ERROR= 0.033					
0.1766	-0.1766	0.5140	0.4166	0.3035	0.6386
STANDARD ERROR= 0.048					
-0.1525	0.1525	-0.3607	0.8824	-0.1757	-0.1175
STANDARD ERROR= 0.044					
0.3125	-0.3125	-0.2620	0.1003	0.7586	-0.3879
STANDARD ERROR= 0.058					
-0.0383	0.0383	-0.7162	-0.1904	0.1436	0.6537
STANDARD ERROR= 0.149					

PROBABLE ERRORS OF PARAMETER SETS

1	0.025
2	0.025
3	0.075
4	0.035
5	0.036
6	0.070

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CASE NO 3

LINE	EXP FREQ	CALC FREQ	INTEN	ERROR
1	103.380	103.212	2.739	0.168
3	125.880	125.924	1.261	-0.044
5	103.380	103.402	2.842	-0.022
7	119.480	119.392	1.571	0.088
9	127.480	127.631	0.326	-0.151
12		125.671	0.607	
14		117.979	1.393	
19	96.680	96.680	1.045	-0.000
21	104.980	104.919	0.958	0.061
22	125.880	125.898	1.258	-0.018
24		102.764	1.393	
26		95.071	0.607	
29	117.480	117.340	2.842	0.140
34	95.480	95.521	0.710	-0.041
36		117.528	1.290	
37	101.380	101.350	1.571	0.030
39	124.080	124.062	1.045	0.018
42		103.214	1.290	
44	125.180	125.221	0.710	-0.041
45	92.980	93.111	0.326	-0.131
47	115.880	115.823	0.958	0.057
51	94.800	94.844	1.258	-0.044
53	117.480	117.530	2.739	-0.050
55	94.800	94.818	1.261	-0.018

ORDERED LINES CASE 3

LINE	EXP FREQ	CALC FREQ	INTEN	ERROR	RELATIVE INTENSITIES CALC	OBS[a]	ERROR
45	92.980	93.111	0.326	-0.131	0.039	0.101	-0.062
55	94.800	94.818	1.261	-0.018			
51	94.800	94.844	1.258	-0.044	0.378	0.516	-0.138
26		95.071	0.607				
34	95.480	95.521	0.710	-0.041	0.086	0.240	-0.154
19	96.680	96.680	1.045	-0.000	0.126	0.186	-0.060
37	101.380	101.350	1.571	0.030	0.190	0.271	-0.081
24		102.764	1.393				
1	103.380	103.212	2.739	0.168	1.000	1.000	0.000
42		103.214	1.290				
5	103.380	103.402	2.842	-0.022			
21	104.980	104.919	0.958	0.061	0.116	0.209	-0.093
47	115.880	115.823	0.958	0.057	0.116	0.202	-0.086
29	117.480	117.340	2.842	0.140			
36		117.528	1.290				
53	117.480	117.530	2.739	-0.050	1.000	0.837	0.163
14		117.979	1.393				
7	119.480	119.392	1.571	0.088	0.190	0.233	-0.043
39	124.080	124.062	1.045	0.018	0.126	0.163	-0.037
44	125.180	125.221	0.710	-0.041	0.086	0.225	-0.139
12		125.671	0.607				
22	125.880	125.898	1.258	-0.018	0.378	0.465	-0.087
3	125.880	125.924	1.261	-0.044			
9	127.480	127.631	0.326	-0.151	0.039	0.070	-0.031

END OF CASE 3

a Normalised to same intensity as calculated values.

Appendix C

The following is a listing of the computer program used to calculate the trial chemical shifts and coupling constants using equations 4 through 8 together with a sample calculation:

```
DOS FORTRAN IV 360N-FC-479 3-3          MAINPGM          DATE   08/27/70      TIME

      C     CALCULATION OF COUPLING CONSTANT FROM K L M N VALUES AABB SYS
      C     PHENYL RING NUMBERED AS FOLLOWING          2    1
      C
      C                                                3    4
0001        DIMENSION TITLE (35)
0002      1 FORMAT (6F10.3)
0003      4 FORMAT (20X, 5H V1 =F7.2,5X4HDEL=F7.2,5X5HJ12 =F7.2)
0004      5 FORMAT (20X, 5H V3 =F7.2,5X4HK  =F7.2,5X5HJ13 =F7.2)
0005      6 FORMAT (20X, 5H V6 =F7.2,5X4HM  =F7.2,5X5HJ14 =F7.2)
0006      7 FORMAT (20X, 5H V8 =F7.2,5X4HN  =F7.2,5X5HJ23 =F7.2)
0007      8 FORMAT (20X, 5H V9 =F7.2,5X4HL  =F7.2,5X5HJ24 =F7.2)
0008      9 FORMAT(20X, 5H V11=F7.2,21X5HJ34 =F7.2//)
0009     11 FORMAT (4F10.3)
0010     16 FORMAT (2F10.3)
0011     17 FORMAT (F10.3)
0012     18 FORMAT (2H00)
0013     33 FORMAT (1H1)
0014     42 FORMAT (50HODEL IS A SQUARE ROOT OF A NEGATIVE NUMBER. IT IS
           17HEXACTLY F7.2//)
0015     43 FORMAT (53HOL IS A SQ. ROOT OF A NEGATIVE NUMBER. IT IS EXACTL
           1F6.2//)
0016    101 FORMAT (I3, 1X, 35A1, 2(F10.3))
0017    102 FORMAT (2I3,1X 35A1,2HK=F6.2,2X2HN=F6.2,2X2HL=F6.2,2X2HM=F6.2)
0018    103 FORMAT (3F10.3)
0019    104 FORMAT (21X, 35A1///)
0020    105 FORMAT (4I1)
0021            CALL SETCLK(1)
0022        PRINT 33
0023     70 READ 101, IPNU, TITLE, FR1, FR2
0024        IF (IPNU) 106,106,107
0025    106 CALL EXIT
0026    107 READ 1, V1, V3, V6, V8, V9, V11
0027        READ 11, XK, XN, XL, XM
0028        IF (XN) 30,31,30
0029     31 XN = V1-V3
0030     30 IF (XK) 21,20,21
0031     20 XK = (V3-V8) + (V1-V3) + (V3-V6)
0032     21 Y = (V1+V3)**2 -(XN**2)
0033        IF (Y) 35,35,27
0034     27 DEL = SQRT (Y)
0035        IF (XM) 22,23,22
0036     23 XM =.5*((V9+V11)**2-(V9-V11)**2-DEL**2)/DEL
0037     22 IF (XL) 24,25,24
0038     25 W = (V9-V11)**2 - (XM**2)
0039        IF (W) 36,36,37
0040     37 XL = SQRT (W)
0041     24 XJ12  = .5*(XK+XM)
0042        XJ23 = .5*(XL+XN)
0043        XJ24  = .5*(XL-XN)
0044        XJ34  = .5*(XK-XM)
0045        XJ13 = XJ24
0046        XJ14= XJ23
0047     46 PRINT 104, TITLE
0048        PRINT 4, V1, DEL, XJ12
```

DCS FORTRAN IV 360N-FC-479 3-3 MAINPGM DATE 08/27/70 TIME

```
0049            PRINT 5, V3, XK, XJ13
0050            PRINT 6, V6, XM, XJ14
0051            PRINT 7, V8, XN, XJ23
0052            PRINT 8, V9, XL, XJ24
0053            PRINT 9, V11, XJ34
0054         45 ISPIN = 4
0055            Z = 100.00
0056            XDEL = 100.00+DEL
0057            AMIN = 0.025
0058            ISOID =1
0059            PUNCH 102, IPNU, ISPIN, TITLE, XK, XN, XL, XM
0060            PUNCH 103, FR1, FR2, AMIN
0061            PUNCH 105, (ISOID, I=1,4)
0062            PUNCH 11, Z, Z, XDEL, XDEL
0063            PUNCH 103, XJ12, XJ13, XJ14
0064            PUNCH 16, XJ23, XJ24
0065            PUNCH 17, XJ34
0066            PUNCH 18
0067            GO TO 10
0068         35 PRINT 104, TITLE
0069            PRINT 42, Y
0070            GO TO 10
0071         36 PRINT 104, TITLE
0072            PRINT 43, W
0073         10 CONTINUE
0074            GO TO 70
0075            END
```

TRIS-P-CL-PHENYLTIN CL + ACETONE

V1 =	22.32	DEL=	35.25	J12 =	1.56
V3 =	13.92	K =	3.88	J13 =	-0.50
V6 =	20.36	M =	-0.76	J14 =	7.90
V8 =	12.00	N =	8.40	J23 =	7.90
V9 =	21.36	L =	7.40	J24 =	-0.50
V11=	13.92			J34 =	2.32

Appendix D

Calculation of the Force Constant from the Tin Phenyl Asymmetric Stretching Frequencies in $(C_6H_5)_3SnCl \cdot D$.

$$K = 4c^2\pi^2\nu^2\mu$$

where K = force constant

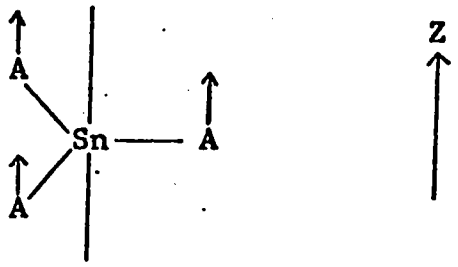
μ = reduced mass

ν = asymmetric stretching frequency.

Solvents	μ(g)	ν(cm^{-1})	K X 10^{-5}
Benzene	7.76 X 10^{-23}	271	2.02
Acetone	7.76 X 10^{-23}	271	2.02
DMSO	7.76 X 10^{-23}	276	2.09

Appendix E

Hybridization Scheme for $\underline{d}\pi$-$\underline{p}\pi$ Bonding.



A represents phenyl groups which are coplanar with the tin atom. The three vectors represent pi orbitals on the phenyl ring in the $Ar_3SnCl \cdot D$ molecule which belong to the group C_{3v}.

The three vectors are used to form the following basis for a representation, $\Gamma_{(\perp)}$, of the group C_{3v}

C_{3v}	E	$2C_3$	$3\sigma_v$
$\Gamma_{(\perp)}$	3	0	1

which reduces to $\Gamma_{(\perp)} = A_1 + E$.

Thus, in order for the tin atom to form pi bonds to each of the phenyl groups, it must use three hybrid orbitals built of one atomic orbital transforming as A_1 and/or a degenerate pair of atomic orbitals transforming as E. Reference to the C_{3v} character table shows that the $\underline{s}$, $\underline{p}$, or $\underline{d}$ orbitals meeting these requirements are:

A_1 : $\underline{s}$, $\underline{p}_z$

E : ($\underline{p}_x$, $\underline{p}_y$), ($\underline{d}_{x^2-y^2}$, $\underline{d}_{xy}$), ($\underline{d}_{xz}$, $\underline{d}_{yz}$)

Therefore, a set of three equivalent hybrid orbitals constructed from these is the only possible set for forming pi bonding. However, the $\underline{s}$ and $\underline{p}_z$ orbitals are used for σ bonding and the three phenyl rings are known to be coplanar from the nmr spectra thereby eliminating the use of the $\underline{p}_x$, $\underline{p}_y$, $\underline{d}_{x^2-y^2}$, and $\underline{d}_{xy}$ as possible pi bonding orbitals. Therefore the $\underline{d}_{xz}$ and $\underline{d}_{yz}$ orbitals can form two pi bonds among the three groups, equivalent to 2/3 pi bond each.