

The Effect of Donor Atom and Ligand Size on the Molecular and Solid State Structure of Selected Tin (IV) Compounds*

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The arrangement of bonded and nonbonded atoms surrounding the central tin atom in several methyltin halide and pseudohalide compounds has been calculated using a stereochemical model that takes into account the spatial requirements of atoms. Inherent in the analytical procedure is a parameter which provides a measure of the validity of the calculations when applied to a particular compound. The technique calculates an optimum ligand arrangement based upon a balancing of nonbonded intramolecular interactions; the procedure is then completed by calculating the distances of the Sn...X intermolecular interactions that occur when the approach of the associating atom is restricted only by the van der Waals contacts of the ligands on the central tin atom. In general, the calculations reproduce or account for the structural features of the methyltin compounds of known structure. The calculations show that the $(\text{CH}_3)_3\text{SnX}$, $(\text{CH}_3)_2\text{SnX}_2$, and CH_3SnX_3 molecules have ligand arrangements that may accommodate 1, 2, or 3 strong intermolecular interactions, respectively. This agrees with the known tendency of $(\text{CH}_3)_3\text{SnX}$ compounds to possess five-coordination and $(\text{CH}_3)_2\text{SnX}_2$ compounds to exhibit six-coordination. The calculated strengths of the intermolecular interactions vary in the order $\text{Sn}\dots\text{F} > \text{Sn}\dots\text{Cl} > \text{Sn}\dots\text{Br} > \text{Sn}\dots\text{I}$. Also, the strength of a particular type of Sn...X intermolecular interaction in a series of $(\text{CH}_3)_n\text{SnX}_{4-n}$ compounds varies in the order $(\text{CH}_3)_3\text{SnX} > (\text{CH}_3)_2\text{SnX}_2 > \text{CH}_3\text{SnX}_3$. These calculations correlate with the observed variations in the discretely molecular or polymeric character of the solid states.

Introduction

The determination and description of the molecular geometry, coordination number, and degree of molecular association in the solid state of tetravalent tin compounds have been the subject of several studies (1-11). Such compounds are of fundamental interest since they are composed of four-coordinate molecules that exhibit varying degrees of molecular association in the solid state; in some cases, the molecular association is so great that these substances may be more appropriately described as having polymeric structures in which the central tin atoms possess five or six coordination. These compounds are also of interest because the

central tin atoms, which possess a variety of local atomic environments, are spectroscopically (Mössbauer and nmr) active. In particular, it is known that Mössbauer quadrupole splittings are dependent upon the coordination number and arrangement of ligands around a central tin atom. Hence, an understanding of the factors which govern the arrangement of ligands around the central tin atom is relevant to the determination of the detailed relationships existing between quadrupole splitting and molecular geometry.

It will be shown here that the arrangement of ligands around the central tin atom, as well as the location of nearest neighboring atoms of adjacent tin molecules, is a consequence of the sizes of the donor atoms and ligands. The observed solid state structures may be understood and, in most instances, reproduced with some accuracy by an analytical procedure that expresses atomic size in terms of intramolecular

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and intermolecular non bonded interactions. The procedure calculates a local atomic environment that includes both bonded donor atoms and those atoms of neighboring molecules that approach the central tin atom by distances which are less than the van der Waals separation. The number of these close neighboring atoms and their distance from the central tin atom will be related to the coordination number and degree of molecular association in the solid state. The compounds investigated in this study have been selected for both their varied solid state structural characteristics and their amenability to stereochemical analysis. The ligands of the selected compounds are neither bulky nor excessively long; thus, the nondonor ligand atoms do not interfere with the approach of neighboring molecules toward the central tin atom. Also, the ligands are monodentates and either possess or have approximate cylindrical symmetry along the central atom-donor atom bond axis. The technique has been applied to tin compounds with the chemical formula $(\text{CH}_3)_n\text{SnX}_{4-n}$ ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}, \text{SCN}$) (12); when possible, the results are compared with solid state structures that have been determined experimentally by X-ray diffraction (7-11).

Discussion

Calculations and Analytical Procedure

A stereochemical model, based upon the nonbonded intramolecular interactions existing

around a central atom, has previously been used to describe the arrangement of bonded donor atoms in mononuclear tin complexes (13). In this work, that same stereochemical model is used to determine the distorted tetrahedral arrangement for the four ligands that are related stoichiometrically to the central tin atom. Calculations are then made to determine the distance that an atom from a neighboring molecule may approach an adjacent tin atom that is surrounded by this distorted tetrahedral arrangement of ligands.

The arrangement of the four bonded ligands around the central atom is calculated using the steric angles listed in Table I. Also listed in Table I are the covalent radii and van der Waals radii that were used to calculate the steric angles, which are defined by the relationships, $\theta_A = 2 \arcsin R/S$, where, R = the van der Waals radius of donor atom A, and S = the sum of the covalent radii of the central atom and donor atom A (14). It is an assumption of the stereochemical model that the optimum ligand configuration balances the nonbonded intramolecular interactions by equalizing the overlap of van der Waals surfaces between adjacent donor atoms in the coordination sphere of the central atom. It is also assumed that this optimum ligand arrangement may be calculated by distributing the steric angles around the central atom such that the angular overlap (or separation) between these steric angles is equalized.

For the calculation of the optimum donor atom arrangements it is assumed that the

TABLE I
STERIC ANGLES, COVALENT RADII, AND VAN DER WAALS RADII USED IN THIS WORK

Element	Steric angle, θ_A deg	Covalent radius, Å ^a	van der Waals radius, Å
C	133 (methyl group)	0.77	2.0 (methyl group) ^b
N	81	0.75	1.4 ^c
F	80	0.72	1.35 ^b
Cl	97	0.99	1.8 ^b
Br	100	1.14	1.95 ^b
I	103	1.33	2.15 ^b
S		1.02	1.85 ^b
Sn		1.41	2.2 ^d

^a R. T. Sanderson, "Inorganic Chemistry," p. 74, Reinhold, New York (1967).

^b L. Pauling, "The Nature of the Chemical Bond," 3rd ed., p. 260, Cornell University Press, Ithaca (1960).

^c Ref. (13).

^d Ref. (8).

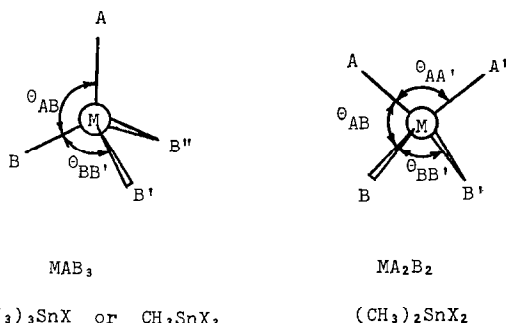


FIG. 1. Labeling schemes used to describe the $(\text{CH}_3)_3\text{SnX}$, $(\text{CH}_3)_2\text{SnX}_2$, and CH_3SnX_3 molecules.

$(\text{CH}_3)_3\text{SnX}$ and CH_3SnX_3 molecules possess C_{3v} symmetry, and that the $(\text{CH}_3)_2\text{SnX}_2$ molecules possess C_{2v} symmetry. The labeling schemes used to describe these molecular geometries are given in Fig. 1. The equations used to determine the molecular geometry of the $(\text{CH}_3)_3\text{SnX}$ and CH_3SnX_3 molecules are:

$$\theta_{AB} = \frac{\theta_A}{2} + \frac{\theta_B}{2} + \omega, \quad (1)$$

$$\theta_{BB'} = \frac{\theta_B}{2} + \frac{\theta_B}{2} + \omega = \theta_B + \omega, \quad (2)$$

where

θ_A = the steric angle of donor atom A measured in degrees.

$\theta_{AA'}$ = the A-M-A' bond angle.

ω = the ligand angular overlap parameter. The numerical value is equal to the angular separation between adjacent steric angles measured in degrees. (A negative value of the parameter corresponds to an overlap of adjacent steric angles.)

$$\theta_{AB} = \theta_{AB'} = \theta_{AB''} \quad (3)$$

$$\theta_{BB'} = \theta_{B'B''} = \theta_{B''B} \quad (4)$$

$$\cos \theta_{BB'} = 1 - \frac{3}{2} \sin 2\theta_{AB} \quad (5)$$

Equations (3), (4), and (5) are independent of the stereochemical model and are solely a consequence of the assumed C_{3v} molecular symmetry. The equations used to determine the ligand arrangement of the $(\text{CH}_3)_2\text{SnX}_2$ molecules are:

$$\theta_{AA'} = \theta_A + \omega \quad (6)$$

$$\theta_{BB'} = \theta_B + \omega \quad (7)$$

$$\theta_{AB} = \frac{\theta_A}{2} + \frac{\theta_B}{2} + \omega \quad (8)$$

$$\theta_{AB} = \theta_{AB'} = \theta_{A'B} = \theta_{A'B'} \quad (9)$$

$$\cos \theta_{AB} = -\cos\left(\frac{\theta_{AA'}}{2}\right) \cos\left(\frac{\theta_{BB'}}{2}\right) \quad (10)$$

Solutions for specific molecules were obtained by making the appropriate substitutions into either

TABLE II

COMPARISON OF CALCULATED BOND ANGLES AROUND THE CENTRAL TIN ATOM IN $(\text{CH}_3)_n\text{SnX}_{4-n}$ COMPOUNDS WITH BOND ANGLES DETERMINED EXPERIMENTALLY

Compound	Determination method	Bond angles, deg			ω , deg	Ref.
		X-Sn-X	X-Sn-C	C-Sn-C		
$(\text{CH}_3)_2\text{SnCl}_2$	Exptl	93.0 ± 2	109 ± 4.5	123.5 ± 4.5	-6.5	a
	Calcd	90.5	108.5	126.5		
$(\text{CH}_3)_2\text{Sn}(\text{NCS})_2$	Exptl	84.1 ± 1.6	—	145.9 ± 1.4	+0.5	b
	Calcd	81.5	107.5	133.5		
$(\text{CH}_3)_2\text{SnF}_2$	Exptl	90	90	180	+0.9	c
	Calcd	81	107	134		
$(\text{CH}_3)_3\text{SnNCS}$	Exptl	—	95 ± 2	119 ± 2	-13.4	d
	Calcd	—	93.7	119.6		
$(\text{CH}_3)_3\text{SnF}$	Exptl	—	90^f	120^f	-13.3	e
	Calcd	—	93.2	119.7		

^a Ref. (7).

^b Ref. (8).

^c Ref. (9).

^d Ref. (10).

^e Ref. (11).

^f The structure was described as having five-coordinate tin atoms and planar $(\text{CH}_3)_3\text{Sn}$ groups.

Eq. (5) or (10) and solving for ω by approximation. The data resulting from these calculations and the experimentally determined bond angles are given in Table II.

Using the distorted tetrahedral configuration calculated above, a central tin atom ... neighboring atom distance may be computed for an intermolecular interaction in which the approach of the atom from the neighboring molecule is only limited by contacts with the van der Waals surfaces of the ligands bonded to the central tin

atom. This neighboring atom is positioned in such a way that its van der Waals surface is in simultaneous contact with the van der Waals surfaces of three donor atoms that comprise a tetrahedral face on the molecule that contains the central tin atom (15). This arrangement results in an incipient molecular packing scheme wherein the protrusions of one molecule fit into the depressions of an adjacent molecule (16). In assuming that the approach of an atom toward a central atom is limited only by the van der Waals

TABLE III

COMPARISON OF CALCULATED INTERMOLECULAR INTERACTION DISTANCES WITH EXPERIMENTALLY DETERMINED DISTANCES

Compound	Intermolecular interaction	Contact groups on tetrahedral face	Calcd Sn...X dist., Å	Obsd Sn...X dist., Å	R (Å) ^a	r (Å) ^b
(CH ₃) ₂ SnCl ₂	Sn...Cl	CH ₃ (2), Cl(1)	3.58	3.54 ± .05 ^c	4.0	2.40
		Cl(2), CH ₃ (1)	4.02			
(CH ₃) ₂ Sn(NCS) ₂	Sn...S	CH ₃ (2), N(1)	3.47	3.21 ± .01 ^d	4.05	2.43
		N(2), CH ₃ (1)	4.01			
(CH ₃) ₂ SnF ₂	Sn...F	CH ₃ (2), F(1)	2.78	2.12 ± .01 ^e	3.55	2.13
		F(2), CH ₃ (1)	3.29			
(CH ₃) ₃ SnNCS	Sn...S	CH ₃ (3)	3.30	3.13 ± .02 ^f	4.05	2.43
		CH ₃ (2), N(1)	4.08			
(CH ₃) ₃ SnF	Sn...F	CH ₃ (3)	2.67	~2.2-2.6 ^g	3.55	2.13
		CH ₃ (2), F(1)	4.05			

^a Sum of the van der Waals radii of the Sn and X atoms.

^b Sum of the covalent radii of the Sn and X atoms.

^c Ref. (7).

^d Ref. (8).

^e Ref. (9).

^f Ref. (10).

^g Ref. (11).

TABLE IV

CALCULATED INTRAMOLECULAR AND INTERMOLECULAR INTERACTION DATA FOR (CH₃)_nSnX_{4-n} COMPOUNDS

Compound	X-Sn-X (deg)	X-Sn-C (deg)	C-Sn-C (deg)	ω (deg)	Sn...X (Å)	Contact groups on tetrahedral face	v. d. Waals dist. (Å)	Covalent bond dist. (Å)
(CH ₃) ₃ SnCl	—	99	118	-15.6	3.54	CH ₃ (3)	4.0	2.40
(CH ₃) ₃ SnBr	—	100	117	-16.1	3.70	CH ₃ (3)	4.15	2.55
(CH ₃) ₃ SnI	—	101	116	-16.7	3.98	CH ₃ (3)	4.35	2.78
(CH ₃) ₂ SnBr ₂	92	109	125	-7.8	3.81	CH ₃ (2)Br(1)	4.15	2.55
(CH ₃) ₂ SnI ₂	94	109	124	-9.2	4.11	CH ₃ (2)I(1)	4.35	2.78
CH ₃ SnCl ₃	100	118	—	+2.9	3.60	CH ₃ (1)Cl(2)	4.0	2.40
CH ₃ SnBr ₃	101	117	—	+0.7	3.87	CH ₃ (1)Br(2)	4.15	2.55
CH ₃ SnI ₃	102	116	—	-1.5	4.23	CH ₃ (1)I(2)	4.35	2.78

interaction of three ligands, it is tacitly assumed that the central atom does not provide a physical barrier to the approaching atom. This condition will exist if both the central atom and neighboring atom are capable of intermolecular bonding. In this study, the central tin atoms and their neighboring atoms do display such attractive intermolecular interactions.

The assumed molecular symmetries require that the $(\text{CH}_3)_3\text{SnX}$ molecules possess three similar tetrahedral faces that have two CH_3 contact points and one X contact point, designated $\text{CH}_3(2)\text{X}(1)$, and one tetrahedral face that has three CH_3 contact points, $\text{CH}_3(3)$; the $(\text{CH}_3)_2\text{SnX}_2$ molecules possess two similar $\text{CH}_3(2)\text{X}(1)$ faces and two similar $\text{X}(2)\text{CH}_3(1)$ faces; the CH_3SnX_3 molecules have three $\text{X}(2)\text{CH}_3(1)$ faces and one $\text{X}(3)$ face. The central atom ... neighboring atom distances that correspond to a neighboring van der Waals sphere simultaneously touching these three contact points have been computed for each of the tetrahedral faces. These intermolecular distances are compared with experimental values in Table III. Calculations have also been made on several analogous tin compounds whose structures have not been determined experimentally. The results of these calculations are given in Table IV.

Interpretation of Results

The data in Table II show that the calculated bond angles, with the exception of those calculated for $(\text{CH}_3)_2\text{SnF}_2$, are in agreement with the experimental bond angles. Further, it can be seen that the overall agreement is correlated with the ligand angular overlap parameter, ω . If ω has a negative value, the van der Waals surfaces of adjacent ligands overlap when the central atom-donor atom bond lengths are equal to their respective normal covalent bond lengths. This overlap assures that nonbonded intramolecular interactions will be competitive with electronic effects of the ligands and central atom in governing the ligand geometry around the central atom. A comparison of the calculated and observed $\text{Sn}\dots\text{X}$ intermolecular distances in Table III reveals that the calculated distances are invariably greater than the observed values. This result is expected since the calculation assumes that the intermolecular distances may be computed from ordinary van der Waals interactions and that the computed optimum four-coordinate

geometry is not altered by molecular association. The calculations do show, however, that $\text{Sn}\dots\text{X}$ intermolecular interactions must exist that are stronger than ordinary van der Waals interactions. Strong $\text{Sn}\dots\text{X}$ interactions produce deformations from the computed geometry which allow for the close approach of the associating atom; however, the extent and direction of this effect is predictable. Hence, the calculated $\text{Sn}\dots\text{X}$ distance represents an upper limit for the actual $\text{Sn}\dots\text{X}$ distance. The success of these calculations in reproducing observed solid state structures is therefore correlated with both the magnitude of the ligand angular overlap parameter, ω , and the value of the calculated $\text{Sn}\dots\text{X}$ intermolecular distance. If the angular overlap is large ($-\omega$), then the nonbonded intramolecular interactions are large and the calculated four-coordinate arrangement of ligands is resistant to deformation by intermolecular interactions. On the other hand, if a short $\text{Sn}\dots\text{X}$ distance is calculated, then the initial four-coordinate configuration is subjected to strong intermolecular interactions. Thus, when ω is positive and the $\text{Sn}\dots\text{X}$ distance is short, the tetrahedral approximation may be inappropriate, and the central atom environment might better be described by a coordination number greater than four. In this regard, the values of ω and the $\text{Sn}\dots\text{X}$ distance provide an internal measure of the validity of the calculations.

An examination of Table III shows that, depending upon the particular tetrahedral face, substantial differences may exist in the calculated $\text{Sn}\dots\text{X}$ distances. This aspect of the calculation is considered to be of some significance, since it may be assumed that the solid state packing scheme which maximizes the number of close contacts, also corresponds to the packing arrangement which is energetically preferred. Therefore, the number of tetrahedral faces that allow short $\text{Sn}\dots\text{X}$ distances is construed to be important in establishing the solid state molecular packing scheme. The compounds investigated experimentally in this study exhibit polymeric or molecular packing schemes that incorporate all of the calculated close $\text{Sn}\dots\text{X}$ contacts into their solid state structure. Thus, the $(\text{CH}_3)_3\text{SnX}$ molecules, which have just one face that allows a close intermolecular contact, $\text{CH}_3(3)$, exhibit a central atom environment that varies between 4- and 5-coordination, depending upon the extent of the $\text{Sn}\dots\text{X}$ interaction. The $(\text{CH}_3)_2\text{SnX}_2$ molecules have two similar faces, $\text{CH}_3(2)\text{X}(1)$, with close $\text{Sn}\dots\text{X}$ contacts; thus, these molecules

display geometries that vary between 4- and 6-coordination (17). The CH_3SnX_3 compounds have three tetrahedral faces, $\text{CH}_3(1)\text{X}(2)$, where short $\text{Sn}\dots\text{X}$ approaches may occur. Whether the solid state structures of these compounds employ a packing scheme that utilizes all three close approaches is not known, since the crystal structure of a CH_3SnX_3 compound has not yet been reported.

In examining the results of the individual compounds, it may be seen that the calculated bond angles and intermolecular distances of $(\text{CH}_3)_2\text{SnCl}_2$ agree with the observed values within experimental error (18). This agreement is expected since the calculated distorted tetrahedral geometry possesses substantial intramolecular interactions (the angular overlap of the steric angles, $\omega = -6.5^\circ$), and is subjected to only comparatively moderate $\text{Sn}\dots\text{Cl}$ intermolecular interactions. The calculated $\text{Sn}\dots\text{Cl}$ distances, 3.58 Å, at the two $\text{CH}_3(2)\text{Cl}(1)$ tetrahedral faces indicate that the central tin atom environment may also be viewed as a highly distorted octahedron. The value of the $\text{Cl}-\text{Sn}\dots\text{Cl}$ angle, which lies in the mirror plane that bisects the $\text{CH}_3(2)\text{Cl}(1)$ tetrahedral face, is calculated to be 71° ; this angle and the other calculated data completely determine the local environment of the central atom. Visualizing the central atom environment as a distorted octahedron is simplified if it is realized that the two bonded Cl atoms, the two associated Cl atoms, and the $\text{Cl}-\text{Sn}\dots\text{Cl}$ angle, all lie in an equatorial plane.

The quantitative agreement of the calculated bond angles and intermolecular distances with the experimental values (8) for $(\text{CH}_3)_2\text{Sn}(\text{NCS})_2$ is only fair; this lesser agreement may be foreshadowed by the lack of ligand overlap in the calculated four-coordinate configuration. The value of ω is $+0.5^\circ$, thus, the calculated tetrahedral ligand arrangement is susceptible to deformation. The calculated and observed $\text{C}-\text{Sn}-\text{C}$ bond angles (133.5° and 145.9° , respectively) differ by 12.4° ; this difference results from an increase in the $\text{C}-\text{Sn}-\text{C}$ angle to accommodate two strongly associated sulfur atoms in the coordination sphere. The calculated $\text{Sn}\dots\text{S}$ intermolecular distances at the two $\text{CH}_3(2)\text{N}(1)$ faces are 3.47 Å. The shorter observed $\text{Sn}\dots\text{S}$ distance of 3.21 Å may be readily rationalized, since the rather substantial intermolecular attractive forces not only affect the calculated tetrahedral configuration, but change the ligand geometry so that a yet shorter $\text{Sn}\dots\text{S}$ approach is possible. The

calculated results, however, do adequately describe the solid state features of $(\text{CH}_3)_2\text{Sn}(\text{NCS})_2$ and correctly predict the number and location of the close intermolecular contacts. The calculated $\text{N}-\text{Sn}\dots\text{S}$ angle is 66° . This additional information completely specifies the central tin atom environment.

The solid state structure of $(\text{CH}_3)_2\text{SnF}_2$ is polymeric (9). The central tin atom has an octahedral configuration with trans methyl groups and four equatorial fluorine atoms. These fluorine atoms are bridged to other tin atoms, resulting in a polymeric planar network of tin and fluorine atoms. This structure cannot be constructed by the packing of tetrahedral molecules; however, the tetrahedrally-based calculations of this work do show that the observed structure is not unexpected. The calculated $\text{Sn}\dots\text{F}$ distances of 2.78 Å reveal very strong intermolecular interactions. It must be kept in mind that these values are obtained for a tetrahedral configuration in which the van der Waals surfaces of adjacent ligands were not in contact ($\omega = +0.9^\circ$); if these ligands are bent away from the approaching fluorine atoms so that the van der Waals surfaces of the ligands are in contact, an ever shorter and stronger $\text{Sn}\dots\text{F}$ interaction results. If the ligands are allowed to overlap by amounts typically found in real molecules, the two "nonbonded" fluorine atoms may approach the central tin atom close enough to reach the normal covalent bond distance and produce the observed polymeric structure. Thus, the high thermal stability and polymeric solid state of $(\text{CH}_3)_2\text{SnF}_2$ need not be considered as anomalous properties, but rather, a predictable consequence of the small size and small steric requirements of both the bonded and nonbonded fluorine atom.

The calculated bond angles in $(\text{CH}_3)_3\text{SnNCS}$ are in agreement with experiment (10). The one short calculated $\text{Sn}\dots\text{S}$ distance, 3.30 Å, agrees with the somewhat shorter observed $\text{Sn}\dots\text{S}$ distance of 3.13 Å, and suggests that the solid state should be intermediate between a discretely molecular solid and a polymeric solid. Both the calculated and observed $\text{C}-\text{Sn}-\text{N}$ bond angles (93.7° and $95^\circ \pm 2^\circ$, respectively) support the idea that the local environment of the central tin atom is intermediate between four- and five-coordination. It is significant that the methyl groups of the $(\text{CH}_3)_3\text{Sn}$ moiety are bent away from the bonded nitrogen atom rather than the sulfur atom. If $(\text{CH}_3)_3\text{SnNCS}$ were essentially five-coordinate in the solid state, the methyl groups

would be expected to bend away from the sterically larger bonded sulfur atom; thus, the observed molecular geometry clearly suggests that some molecular identity is preserved in the solid state. This view is consistent with the large ω value (-13.4°), which reflects a strong tendency for the $(\text{CH}_3)_3\text{SnNCS}$ molecule to maintain some four-coordinate character.

The crystal structure determination of $(\text{CH}_3)_3\text{SnF}$ was too ambiguous and inaccurate to provide detailed numerical results (11). The structure may be described as polymeric with five-coordinate tin atoms linked by bridging fluorine atoms. The central tin atom has three methyl groups in the equatorial plane, one short 2.1 Å Sn-F bond, and one longer ~ 2.2 -2.6 Å Sn-F bond. By comparison, the calculated values for the C-Sn-F and C-Sn-C bond angles in $(\text{CH}_3)_3\text{SnF}$ are 93.2° and 119.7° , respectively. The calculated Sn...F distance is 2.67 Å, which corresponds to a very strong intermolecular interaction. Whether the large ω value causes a further distortion of the tetrahedral geometry or whether the strong intramolecular interactions effectively deter such deformation is essentially inconsequential, since the calculated four-coordinate configuration, with one very short Sn...F distance at the $\text{CH}_3(3)$ face, already displays a geometry that appears to be five-coordinate. Thus, in either case, the geometry is best described as trigonal bipyramidal. Perhaps it is of theoretical interest that the two experimental Sn-F distances are of different lengths, since this allows for the possibility that some four-coordinate character still persists in $(\text{CH}_3)_3\text{SnF}$.

In Table IV, structural trends may be observed in the calculated results for several methyltin halide compounds. Using the normal van der Waals separations and covalent bond distances listed in Table IV as measures of the extreme distances to be expected for Sn...X intermolecular interactions, the calculated Sn...X distances for a particular $(\text{CH}_3)_n\text{SnX}_{n-4}$ compound indicate that the strength of the Sn...X interactions should vary in the order, Sn...F > Sn...Cl > Sn...Br > Sn...I. Also, when considering the strength of a particular type of Sn...X interaction, the calculated distances show that the strength of the individual interactions in $(\text{CH}_3)_n\text{SnX}_{4-n}$ compounds vary in the order, $(\text{CH}_3)_3\text{SnX} > (\text{CH}_3)_2\text{SnX}_2 > \text{CH}_3\text{SnX}_3$. These trends, together with the fact that the $(\text{CH}_3)_3\text{SnX}$, $(\text{CH}_3)_2\text{SnX}_2$, and CH_3SnX_3 molecular geometries allow 1, 2, and 3 close intermolecular approaches, respectively account for the major

features of the local environments of the central atoms.

It is a point of interest that while the $(\text{CH}_3)_3\text{SnX}$ and CH_3SnX_3 molecules have identical molecular symmetries, their ligand arrangements require very different symmetries for the Sn...X interactions and optimum solid state packing schemes. Calculations of Mössbauer quadrupole splittings (19) based upon the structural parameters presented in this work, support this view.

Conclusion

The calculations presented here may be used to produce a model for the arrangement of ligands surrounding a central tin atom in associated organotin compounds. The model is limited in that the calculated arrangement includes only the disposition of the few adjacent ligands from neighboring tin atoms in addition to the ligands that are directly bonded to a central tin atom. The calculations are also restricted to compounds with small symmetrical ligands. More important than the applicability of the model to associated tin compounds is the observation that a stereochemical model based upon atomic size effects can provide detailed results pertaining to molecular geometry and the tendency for a central atom to participate in solid-state intermolecular association.

It should be noted that the same conclusions might be reached by assigning effective van der Waals radii to the ligands. A method for computing the van der Waals radii of bonded atoms has been suggested in an earlier work (13). This stereochemical model has no inherent advantage other than its being designed to take into account the sizes of atoms and ligands and the attendant space-filling requirements. Any success with the model lies in its application to molecular systems wherein size effects are indeed the dominant structural factor.

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12. The solid state structures of the dimethyl and trimethyl tin cyanides have been determined experimentally and the local atomic environments of the central tin atoms conform to the calculations. While these methyltin cyanides do possess interesting overall solid state structures, the stereochemical calculations presented here do not lead to *complete* three-dimensional solid state representations. The methyltin cyanide compounds have been omitted from the manuscript, since it is felt that their inclusion would provide no further insight.
13. R. F. ZAHROBSKY, *J. Amer. Chem. Soc.* **93**, 3313 (1971).
14. An adjustment to the value of a steric angle may be made for a bulky ligand. Details of the criteria and procedure for adjustment are given in the work cited in Ref. (13).
15. The methyl group ligand is simply assigned a van der Waals radius of 2.0 Å. It is also assumed that for the NCS ligand, only the nitrogen atom presents a barrier to the approach of a neighboring atom toward the central tin atom.
16. This treatment is consistent with the close packing model of molecular crystals. For further details, consult A. I. KITAIGORODSKII, "Organic Chemical Crystallography," Consultants Bureau Enterprises, Inc., New York, N.Y., 1961.
17. The symmetry of the packing scheme excludes any intermediate geometries that resemble five-coordination.
18. A. G. DAVIES et al. [Ref. (7)] and D. A. BERTA [Ref. (6)] both report X-ray crystal structure determinations of $(\text{CH}_3)_2\text{SnCl}_2$. The cell constants of the two works are in agreement; however, they report different space groups and very significant differences in the detailed molecular structure. There is difficulty reconciling both structure determinations as being correct. It is possible, but highly fortuitous, that polymorphic forms of a substance would exist in different space groups and still exhibit identical cell constants. It is simpler to assume that one of the structures was "solved" in the wrong space group. In this regard, the A. G. Davies structure determination and the results of the calculations presented here are in very good agreement. While this agreement does not constitute a scientific proof, it may be taken as evidence that the structure determination of A. G. Davies et al. is correct.
19. Private communication with Dr. N. W. G. DEBYE.